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CHEMISTRY AND BIOLOGY OF WATER, AIR AND SOIL

Environmental Aspects

Edited by
J. Tölgyessy

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CONTENTS

1 Introduction

The essential mission of mankind can be defined as the many-sided material and cultural development of each human being and the society as a whole. A healthy development can be fully achieved only in a good quality environment, and thus environmental protection has become one of the primary targets of society.

The need to pay increased attention to water sources, purity of air and soil can be encountered in all long-term forecasts. Man pollutes the environment by his activity; primarily he pollutes its fundamental components, water, soil and air, and thus he unfavourably affects the cycle of chemical substances and causes serious damage to living organisms. It is, therefore, urgently necessary to seek solutions which would contribute to a general improvement of this rather negative and continuing situation.

Water, air and soil protection is a universal problem for the continued existence of mankind, and the management of this problem requires cooperation between all countries and nations.

The outcomes of studies in the chemical and biological sciences have made positive contributions to the problems of reduction and disposal of gaseous, liquid and solid wastes, and thus these sciences participate significantly in the improvement of water, air and soil quality.

The aim of this book is to provide a comprehensive view of the chemistry and biology of water, air and soil, particularly those aspects connected with the protection of the environment.

The first part presents fundamental information on the chemistry and biology of water in its natural state, as well as on changes caused by water pollution due to industry, traffic, agriculture and urbanization. The composition of natural, service and wastewaters is described, as well as the processes taking place in them and influencing the forms of the occurrence of particular substances, their distribution and circulation. The effects of different inorganic and organic substances on the properties of natural, service and wastewaters are studied. The sections dealing with the principles of the ecology of aquatic organisms, water microbiology, aquatic plants and animal kingdom are of special significance. Along with chemical and biological changes, considerable attention is paid to the toxicological aspects. This first part of the book studies the methods of chemical and biological water analyses, and water treatment.

The second part of the book deals with atmospheric problems, particularly the basic composition of atmosphere and its pollution caused by different sources (especially industry and traffic), methods of restriction and reduction of emissions, and air analysis. This part also includes important information on the biology of air, particularly the microbiological and palynological aspects.

The third part of the book deals with soil. Attention is focused on the characteristics of soil and soil components, natural and anthropogenous soil processes, the chemistry, biology and microbiology of soil, and on its analysis with particular reference to fertility and contamination with harmful matters.

The book is intended for all who are engaged in the sphere of environmental protection, for chemists, biologists, physicians, pharmacists, farmers, veterinarians, for university students, and also for the more extensive (and growing) circle of all those who are interested in the problems of environmental protection.

2 Water, air and soil — fundamental sources of the biosphere

Life on our planet dates back to some three thousand million years ago. A number of millennia have elapsed since a thinking being — man — developed from a single-cell organism. He collected forest fruits, roots and hunted animals. Later, he invested the first primitive tools which could be used for wood cutting, land cultivation and cereal growing; he used these simple techniques to modify nature. He built villages, towns, destroyed the original natural environment and created his own artificial environment (Fig. 2.1) [1].

For a long time the natural sources seemed to be infinite in comparison with relatively negligible possibilities he possessed for using them up. The main role of man at this stage, as far as the interaction between man and nature was concerned, was the prospecting for sources and the search for their most efficient separation from the natural environment.

Within a relatively short period of time, particularly in the last 40 to 50 years, man and his economic activity have become a powerful force determining to a remarkable extend the circulation of the components of the biosphere and its general dynamics.

2.1 Biosphere

The biosphere is a relatively very thin layer (compared with the radius of the planet) forming a boundary between the atmosphere, hydrosphere and lithosphere. Here, living organisms live, develop and reproduce. From both the interaction of organisms and effect of the environment surrounding them, communities of organisms are formed — *geobiocenoses*, complex ecological systems. The upper biosphere zone is the atmosphere up to 12,000 to 14,000 m. In water, life can be found to a depth of approximately 10,000 m; in soil, life has been recorded up to a depth of 20 to 30 m (specialized systems involving plant roots in dry deserts). In Fig. 2.2 the

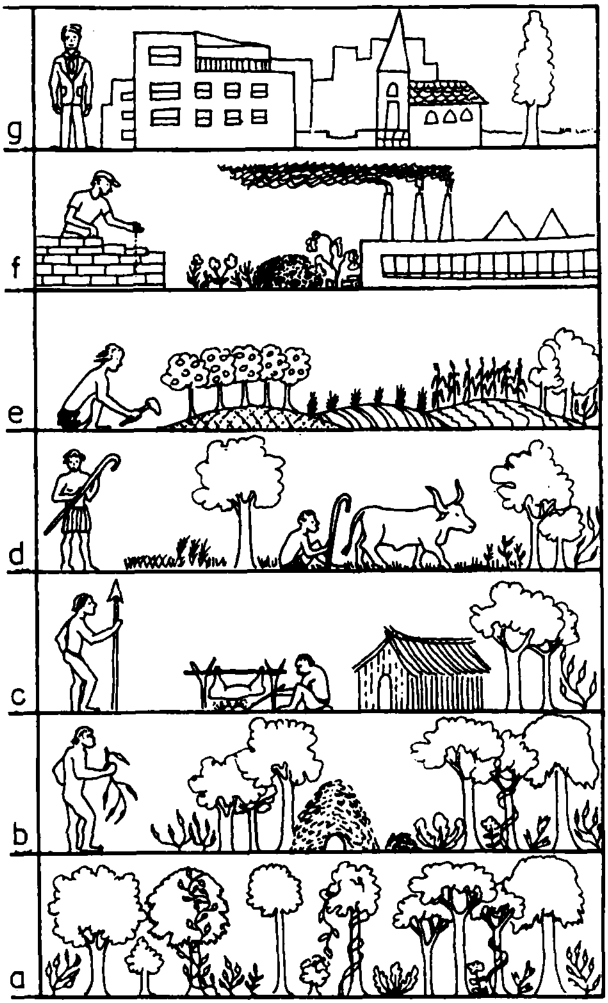


Fig. 2.1. Effect of man's activity on nature. a — untouched, natural forest ecosystem, b — forest fruit collection, c — hunting, d — man the shepherd, e — soil cultivation, f — industry, g — urbanization

vertical distribution of living organisms is illustrated [2]; it is evident that the central hundred metres of the section include most of the living matter on our planet.

One part of the biosphere is the region directly influenced by the activity of man, the sphere of human society, *social sphere* or *anthroposphere*. In Russian literature one encounters .the term *noosphere*, the sphere of man-transformed biosphere.

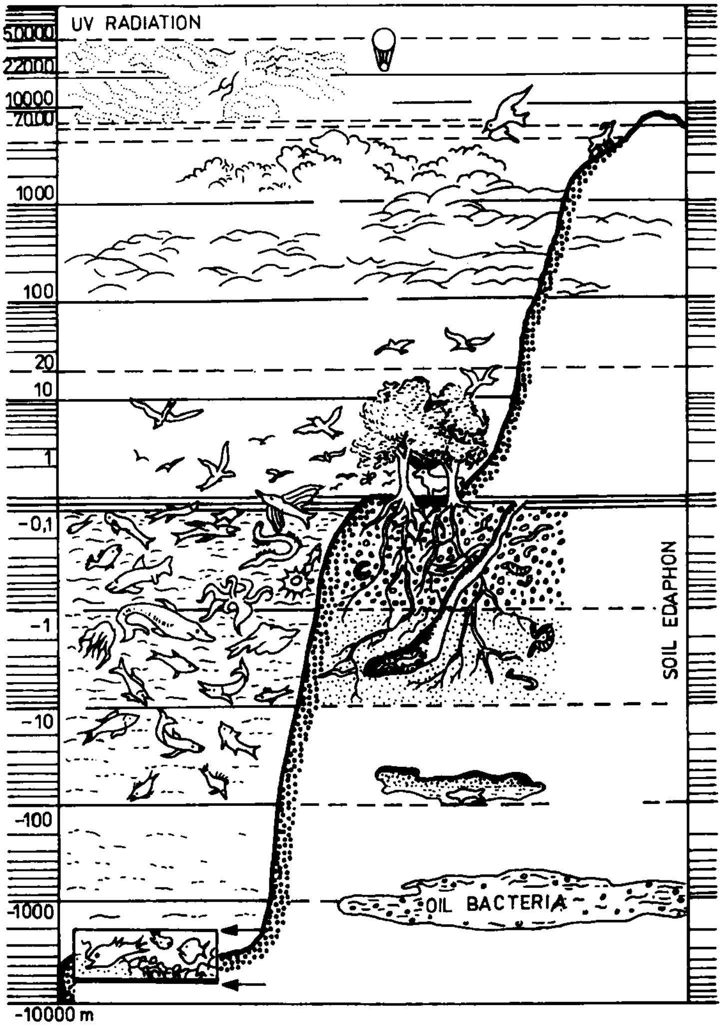
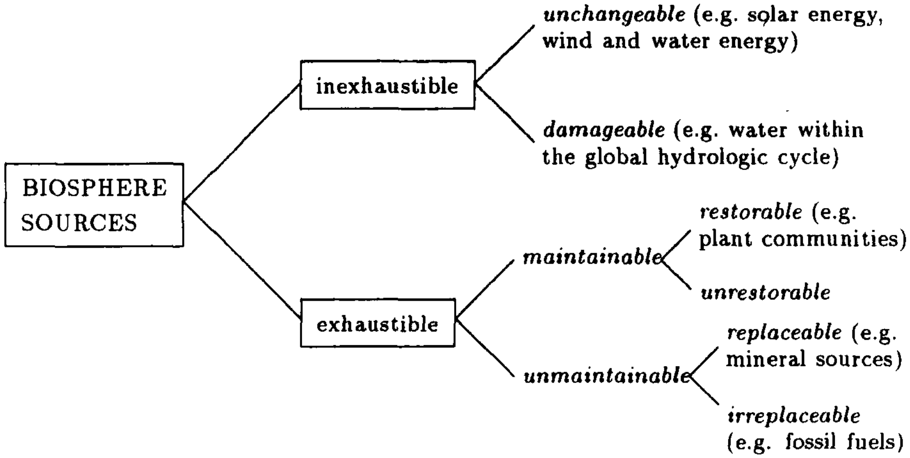


Fig. 2.2. Expansion of life in the biosphere

Life has intensively biologized the earth's crust, air and waters for the 2.5 to 3 billion years of its existence. The soil layer and overland biocenoses are closely linked with air by the continuous exchanges of matter in solid, liquid and gaseous phases, and the world ocean and atmospheric cover of the Earth are mutually connected through the circulation of energy, gases, fallout and evaporation. Overland ecosystems and the ecosystems of the world ocean are mutually conditioned by water flows and air migration — generation, transfer and fall of atmospheric precipitations and aerosols, as well as by mutual exchange of an immense quantity of living and decayed material [3].

2.1.1 Sources of the biosphere

The life of man and the whole of human society depends on the sources of the biosphere needed for the satisfaction of his needs. These sources include the essential components of the biosphere, such as water, air, soil, plants, animals, raw materials and solar radiation. In detail they can be classified as follows:



The inexhaustible sources of the biosphere cannot be exhausted by man even when they are continuously used, however, they can be damaged and deteriorated; waters, air and soil which are the subject of this book are such sources. The exhaustible sources of the biosphere can be used up or permanently deteriorated by man.

Apart from the atmosphere, the biosphere sources vary in their extent and nature in individual countries and each country can employ them with sovereignty within its boundaries. However, there are factors affecting sources which are of international importance (e.g. the purity of rivers flowing through several countries), or of worldwide global importance (e.g. the purity of the water in oceans, and the purity of air).

The rapid increase in the population of the Earth and the many-sided economic activity of current human society cause significant quantitative and qualitative changes in the biogeochemical cycles of the elements in the biosphere. These threaten the very functions of the biosphere and the vital conditions for the activity and existence of man himself. The scope of the

Table 2.1. Biochemical and technochemical factors in the biosphere [4]

Land biomass	3×10^{12}–1×10^{13} t
Land photosynthesis (annual)	10^{10}–10^{11} t
Annual turnover of ash matters in organic land materials	10^{8}–10^{9} t (incl. nitrogen up to 10^{10} t)
Annual amounts of	
(a) dissolved solids in rivers	3×10^{9} t
(b) dispersed solids in rivers	1.6×10^{10} t
Annual production of industrial fertilizers	3×10^{8} t
Industrial fall-out	0.25×10^{9} t annually
Solid waste, refuse	20×10^{9} t annually
Ore mining	5×10^{9} t annually
Industrial and municipal wastewaters	Up to 55×10^{11} m^3 annually

affects of man on the biosphere and its components is evident from the data in Table 2.1 [4].

The most important interferences with the components of the biosphere are the changes of the chemical composition of air, particularly reduction of oxygen and increase in the amount of carbon dioxide and air pollution with solid materials which result in changes in the quantity of solar radiation falling on the earth's surface, thermal pollution of the atmosphere, changes in the water cycle in nature, and pollution of the hydrosphere and soil, etc.

It seems that man is still not fully aware of the fact that the biosphere and its components has acquired a new influence, namely a modern society with an immense energetic, industrial, transport and agricultural potential, and with a highly developed scientific and intellectual capacity. This influence has entered the biosphere without restraint and has become a powerful source of changes, producing unforeseen chaotic, and frequently negative impacts and deviations from normal processes.

2.1.2 Biogeochemical cycles

The most important biogenic elements (carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus) take part in the so-called biochemical cycle which is more or less a circular (actually helical) pathway of elements in the biosphere and ecosystem from non-living to living organisms. The cycles are not always regular, they frequently have stagnating points, where, for instance, a higher quantity of organic compounds can accumulate, and many elements are stagnant for a certain period of time.

Each cycle has 2 basic parts as follows:

- a non-biological, i.e. a fundamental (geological) reservoir of matter changing very slowly (air, water, earth's crust),
- biological, i.e. an exchange (circulating part) in which a comparatively rapid movement of elements takes place.

Some important biogenic elements, such as phosphorus,calcium and magnesium, have their own characteristic sedimentation cycle. In this type of cycle, elements from biological systems are continuously lost due to erosion and excessive use in economic activities (e.g. phosphorus in the form of industrial fertilizers, detergents, etc.) and they are finally stored in the sea.

The return of such elements into the earth's biological systems is rather complex and depends on processes such as, for example, erosion. The sedimentation cycles are less perfect than others (e.g. the cycles of carbon or nitrogen) and, therefore, they are more easily disturbed by man; for example, he accelerates the losses of phosphorus to such an extent that this element may become a decisive factor in the functioning of the biosphere in the future.

We already have some idea of the circulation of the majority of chemical elements which are necessary for the life on our planet [5, 6].

2.1.3 Effect of man on biogeochemical cycles

Man is a factor of great importance in biogeochemical cycles. He affects particular cycles by removal of elements (plant production, mowing, wood cutting and forest burning, etc.), accumulation of elements (fertilization), change in the hydrological cycle by draining and irrigation, and application of new elements into the biosphere.

In the ecosystems, for example, in a forest without any activity of man, an almost closed circulation of biogenic elements exists. In fact, the production of organic matter depends on the quantity of nutrients originally present in water and parent rock (mineral), on moisture and climatic conditions balancing the equilibrium. However, man takes wood from forests, and together with it also a number of chemical elements present in it.

If man's activity is well-considered and based on scientific knowledge of the material balance, the circulation of elements is only slightly disturbed. The missing elements are substituted by erosive destruction of the mineral rock base and growth of roots into deeper layers. Alternatively, the material balance of nutrients is impaired, which is shown by a decrease in production and change in the species composition in favour of less demanding species. In the case of intensive large-scale production of agricultural crops the nutrient losses are so high that agricultural production without additional fertilization would be sufficient for approximately only half of the population.

By his activity, man also pollutes the environment chemically, influencing thus the circulation of chemical substances and seriously threatening living organisms. It has been proved by various measurements that as much as 30% of industrial fertilizers is eluted from water and appears in the cycle of surface and groundwaters. Pesticides are accumulated in organisms and cause, for example, a decrease in their reproductive capacity. Pollution of the biosphere results in impoverishment, reduction of diversity and stability of ecosystems, it decreases their self-control capabilities, the ecological equilibrium is impaired not only at the level of the particular ecosystems, but also at the level of the countryside, as damage to the material circulation and energy flow in the biosphere takes place [3, 7].

2.2 Air

Air forms a gaseous envelope around the Earth. Its physical and chemical properties change markedly with the height above the earth's surface; pressure and density of the atmosphere exponentially decrease and the atmosphere gradually passes into the sparse interplanetary gases. The temperature does not change evenly; the atmosphere layers have different temperatures depending on how they absorb solar radiation.

Although the atmosphere consists mainly of gaseous components, it also has a solid component (microscopic particles forming an atmospheric aerosol) and a liquid one (rain, fog). The atmosphere as a whole is in a dynamic equilibrium with its surroundings, with the earth's surface, hydrosphere, biosphere and cosmic space.

Air has some special properties by which it differs from other natural substance. It is omnipresent, its occurrence is not linked to certain places, it is not necessary to transport it and its use is not limited by any state boundaries. Pure air, free from dust or contaminants of gaseous origin, is an unattainable ideal which does not occur in nature.

The atmosphere is an essential component of the biosphere without which the existence of the present form of life on the Earth would be impossible. The oxygen in air is vital for the vast majority of living organisms, and carbon dioxide present in air is required for the plant growth.

Man influences the atmosphere intensively, many-sidedly and mostly negatively. Air is the most threatened component of the natural environments at present and its pollution is rapidly increasing [8–13].

2.3 Water

Water form the earth's hydrosphere which includes oceans, lakes, rivers, glaciers and groundwater. The majority of the hydrosphere (96.5%) is formed by seas and oceans. Slightly less than 1% of the world hydrosphere is natural (fresh) water which can be potentially utilized. The major part of this water is under the surface of land in the form of soil moisture, or undersurface ice and groundwater, frequently in large reservoirs formed by porous water-saturated rocks. About one tenth of the total quantity of fresh water is in lakes and rivers, and only a very small fraction is present in the atmosphere.

Water is the most wide-spread substance on the earth. It is perhaps the most essential part of the biosphere and along with soil it is of primary importance for the nutrition of mankind. It is the essential component of biomass, and the main means of nutrient transport, their uptake and excretion. As for the plants, not only its total quantity per year is important, but also its occurrence and distribution in the vegetative period with respect to their growth phases. Water is the life environment for a large number of animals. Each animal species has adapted to a certain water composition. Man (like an animal) dies in a few minutes without oxygen, within a few days without water, and within several weeks without food.

Water as one of the basic sources of the biosphere has a number of functions concerned with human society, such as transformation of energy potential and transport. The properties of a particular sample of water reflect its environmental chemistry, including anthropogenic changes [14–19].

The importance of water for man and his environment has been clearly defined in 12 items of the *European Charter on Water* declared by the *European Council* on May 6, 1948 in Strasbourg:

(1) There is no life without water. Water is precious and vital for man.

(2) Reserves of fresh water are not inexhaustible. Therefore, they must be preserved, protected and improved to the fullest possible extent.

(3) Water pollution is dangerous to man and other living organisms dependent on water.

(4) Water quality must satisfy the requirements for different kinds of use, it must satisfy particularly the standards concerning human health.

(5) After discharge of used water into rivers, the water quality must not prevent its further use for public and private purposes.

(6) For the preservation of water sources, the plant kingdom, particularly forest, is of great importance.

(7) Water sources must be preserved.

(8) Authorized organizations must plan proper water management.

(9) Water protection calls for intensification of scientific research, education of professionals and information of the public.

(10) Water is a common property whose value must be recognized by everybody. The duty of an individual is to use water purposefully and economically.

(11) Water sources management should be implemented within the framework of natural river basins and not within the framework of political and administrative boundaries.

(12) Water does not know any boundaries; as a common resource, it requires international cooperation.

2.4 Soil

Soil is the uppermost part of the earth's crust (lithosphere), modified by the effects of soil-forming processes. It is both an agricultural necessity and part of the natural environment. The soil properties are determined by the character and structure of the parent rock, effects of climatic factors, particularly of water, wind and heat, effects of microorganisms, as well as by the activity of man.

An important property of soil is its fertility. Fertility is the ability of soil to provide the plants with such conditions during their vegetative period that will ensure their growth, development and yields. The soil fertility depends on both the properties of the soil itself (natural fertility) and the activity of man in cultivating the soil (artificial fertility).

Soil as a component of the environment has a particular character determined first of all by the fact that it is indestructible, but its quality can be considerably worsened by industrial activity. Soil can be repeatedly employed in different spheres of production, social and other activities, although such use is usually linked with a long period of time. A specific property of soil is that areas of it cannot readily be re-located.

The total land area on the Earth is given, it cannot be increased, and, therefore, given an ever-increasing number of inhabitants its proper management and treatment become ever more urgent. This concerns particularly the agricultural land, and therefore the following items should be observed in the future:

- protection of agricultural land against development for other purposes (housing, recreational and industrial construction),
- the achievement of set qualitative standards for agricultural land.

The protection and improvement of soil are among the essential problems involving the protection of the environment. Healthy soil is the basis of large-scale agricultural production. Agricultural and forest soils are threatened to a great extent by degradation and reduction of nutrients. Soil is degraded by gaseous, liquid and soil pollutants. A very serious world-wide problem is the problem of solid wastes, which also cause considerable soil degradation [20–23].

The so-called *European Charter on Soil* was declared by the *European Council* in 1972:

(1) Soil is one of the most valuable of man's properties. It enables the life of plants, animals and humans on the Earth.

(2) Soil is a limited resource which is easily destroyed.

(3) The industrial society employs soil for agriculture as well as for industrial and other purposes. The policy of regional planning must combine considerations of the soil properties, and the present and future needs of the society.

(4) Agriculturalists and foresters must apply methods which protect the soil quality.

(5) Soil must be protected against erosion.

(6) Soil must be protected against pollution.

(7) Development of urbanization must be planned so that the neighbouring areas are exposed to the minimum possible damage.

(8) During the planning of engineering projects the effects on the soil must be evaluated so that the price includes provision for adequate protective measures.

(9) A list of soil sources is a prerequisite for any planning.

(10) To ensure the extensive use and protection of soil, further research and interdisciplinary cooperation are required.

(11) Attention at all professional levels as well as ever-increasing attention of the general public should be paid to soil protection.

(12) Governments and State authorities must carefully plan and nurture their soil sources.

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3 The chemistry of water

3.1 Composition and structure of pure water

Water is a chemical compound whose molecules each contain two hydrogen atoms and one oxygen atom. Since natural hydrogen and oxygen consist of several isotopes, water consequently consists of more than one type of molecule. The quantitative ratio of molecules of different isotope composition is determined by the ratio of the individual isotopes in the individual elements. The existence of three hydrogen isotopes (light hydrogen ^{1}H, heavy hydrogen — deuterium ^{2}H, or alternatively D, tritium ^{3}H or T) and 6 oxygen isotopes (^{14}O, ^{15}O, ^{16}O, ^{17}O, ^{18}O, ^{19}O) allows altogether 36 possibilities for the structure of a water molecule, 9 of which contain only stable nuclides. The water molecules formed by stable nuclides are present in natural water in the concentrations as follows (mol.%): $^{1}H_2{}^{16}O$ — 99.73; $^{1}H_2{}^{17}O$ — 0.04; $^{1}H_2{}^{18}O$ — 0.20; $^{1}HD^{16}O$ — 0.03; $^{1}HD^{17}O$ — 1.2×10^{-15}; $^{1}HD^{18}O$ — 5.7×10^{-5}; $D_2{}^{16}O$ — 2.3×10^{-6}; $D_2{}^{17}O$ — 0.9×10^{-9} and $D_2{}^{18}O$ — 4.4×10^{-9}.

Differences in the isotope composition of molecules are apparent from different saturated vapour pressure, temperature and heat of phase conversion, heat capacity, and in the thermal dependence of thermodynamic quantities, etc. Some physical constants of $^{1}H_2{}^{16}O$ and $D_2{}^{16}O$ are shown in Table 3.1 [1].

The chemical properties of deuterium oxide do not differ greatly from the chemical properties of $H_2{}^{16}O$. However, its reactivity is generally lower, and the reactions are usually slower; similarly to $H_2{}^{16}O$, it reacts with a number of compounds. For example, the reaction with respective anhydrides gives a "heavy" sulphuric acid (D_2SO_4) and phosphoric acid (D_3PO_4). From the chemical viewpoint the differences in the solubility of isotope compounds are of great importance. The solubility of some inorganic compounds in pure and heavy waters are shown in Table 3.2 [2].

Table 3.1. Physical constants of H_2O and D_2O [1]

Water	Mailing point (°C)	Boiling point (°C)	Density ($kg\ m^{-3}$)	Temperature of maximum density (°C)	Latent heat of melting ($kJ\ kg^{-1}$)	Latent heat of boiling ($kJ\ kg^{-1}$)	Specific heat heat capacity ($kJ\ kg^{-1}\ K^{-1}$)
$^{1}H_2{}^{16}O$	0 (101.325 kPa)	100 (101.325 kPa)	998.203 (20°C)	3.98	333.5	2259	4.1819 (20°C)
$D_2{}^{16}O$	3.82 (101.325 kPa)	101.42 (101.325 kPa)	1105.34 (20°C)	11.185	332.4	2072	4.27 (20°C)

Table 3.2. Solubilities of some inorganic compounds in H_2O and D_2O [2]

Compound	Temperature (°C)	Solubility $\left[\frac{\text{mol of dissolv. species}}{\text{mol of solvent}}\right]$		Δ	$\frac{\Delta}{L_{H_2O}}100$
		L_{H_2O}	L_{D_2O}		
KCl	0	6.81	5.69	1.12	16.4
	25	8.65	7.80	0.85	8.8
	100	13.54	13.06	0.48	3.5
	180	18.44	18.12	0.32	1.7
CdI_2	25	4.34	3.21	1.13	26.0
NaBr	5	3.25	2.87	0.38	11.9
$K[Ag(CN)_2]$	5	1.290	0.974	0.316	24.5
$K_2Cr_2O_7$	5	0.358	0.236	0.122	33.5
	25	0.955	0.712	0.243	26.6
	35	1.372	1.067	0.305	23.0
$KClO_3$	5	0.585	0.512	0.073	12.4
$Hg(CN)_2$	5	0.537	0.424	0.113	21.0
$PbCl_2$	25	0.071	0.045	0.026	36.0

Similarly, differences in the solubility of organic compounds can be observed.

In natural waters of different origin the deuterium content evidently differs (within a range from 0.0133 to 0.0185%). This plays a certain role in the study of water genesis. Due to the different pressure values of saturated vapours of H_2O and D_2O precipitation waters are enriched by light hydrogen and oxygen isotopes. In the groundwaters the D_2O content increases with increasing depth. An increased amount of heavy water has been found in some lakes, in the Dead Sea and in great depths of oceans.

Two atoms of hydrogen and one atom of oxygen in a water molecule are bonded by a simple polar covalent bond $H \rightarrow \overline{\underline{O}} \leftarrow H$. A water molecule has a triangular arrangement (Fig. 3.1). The $O \leftrightarrow H$ internuclear distance is 0.0958 nm, the bond angle is 104.4° and the dipole moment $M_e = 6.13 \times 10^{-30}$ Cm. As the $O \leftarrow H$ bond is very polar and the H_2O molecule is bent, water is a strongly polar substance. Within their nearest vicinity the water dipoles are attracted to each other by their opposite ends and cause association of water molecules by so-called hydrogen bonding, shown as a dotted line:

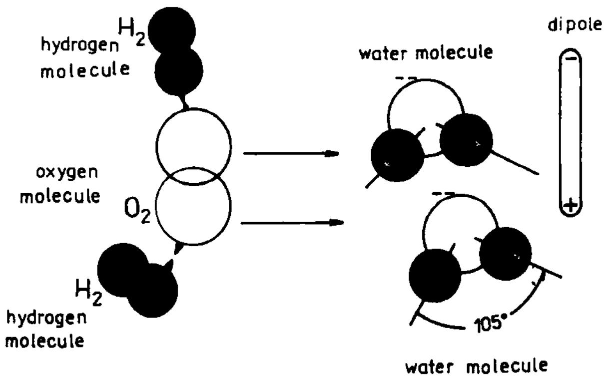
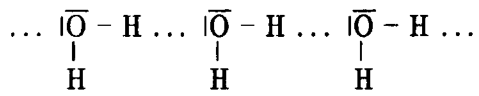


Fig. 3.1. A water molecule [3]



$$\ldots\ \underset{\underset{\mathrm{H}}{|}}{|\overline{\mathrm{O}}}-\mathrm{H}\ldots\ \underset{\underset{\mathrm{H}}{|}}{|\overline{\mathrm{O}}}-\mathrm{H}\ldots\ \underset{\underset{\mathrm{H}}{|}}{|\overline{\mathrm{O}}}-\mathrm{H}\ldots$$

Hydrogen is covalently bonded to one oxygen atom, and electrostatically to the other one. Intramolecular hydrogen bonding causes the high boiling temperature of water (100°C) as compared to the boiling temperature of a similar compound — hydrogen sulphide, H_2S (-61°C). In the gaseous phase, water associates only slightly at normal temperatures [3].

In nature, water occurs in the gaseous, liquid and solid states.

The structure of liquid water (Fig. 3.2) was determined by X-ray structural analysis and infrared spectroscopy. Each molecule of water is sur-

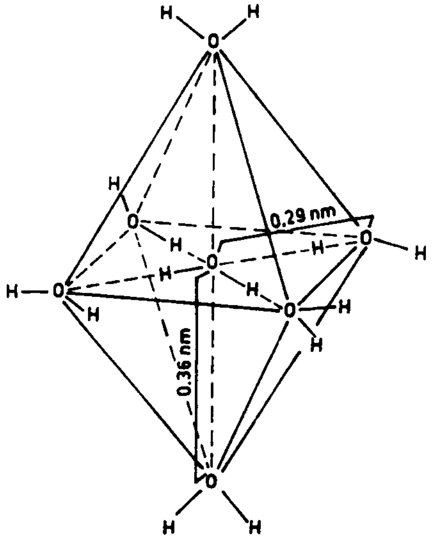


Fig. 3.2. A scheme of an octahedral molecule of liquid water structure [4]

rounded on average by six other molecules forming a deformed octahedron around it. At the same time, a similar arrangement of molecules can be found in small amounts of liquid water as is the arrangement in common ice, particularly at temperatures approaching the melting point of ice.

Water has seven crystal modifications in the solid state. At a normal pressure only the hexagonal modification — ice — is stable. Oxygen atoms form layers consisting of six-component chair-like bent circles (Fig. 3.3). Each oxygen atom is surrounded by other oxygen atoms in a tetrahedral arrangement, three of which belong to the same layer and one to the neighbouring upper or lower layer. The internuclear distance of the neighbouring oxygen atoms is 0.276 nm. Hydrogen atoms are located along the connecting lines of the oxygen atoms. Each oxygen atom has two hydrogen atoms in close vicinity (0.10 nm), forming covalent bonds with them, whereas two other hydrogen atoms are connected by hydrogen bonding at a greater distance (Fig. 3.4) [1, 4–6].

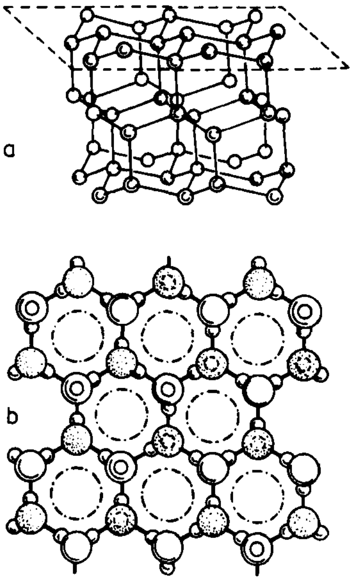


Fig. 3.3. Structure of ice. a — scheme of the arrangement of oxygen atoms and layer marking, b — arrangement of atoms in a layer; lower situated oxygen atoms are shown dotted [1]

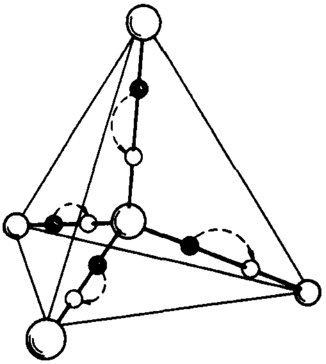


Fig. 3.4. Arrangement of hydrogen atoms along the lines connecting oxygen atoms [1]. ○ — oxygen atom, o — hydrogen atom, • — ion pair electrons

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3.2 Physical properties of water and aqueous solutions

3.2.1 Changes of state of water — the triple point

The changes of state of water can be schematically illustrated as follows:

$$\begin{aligned} \text{ice} &\rightleftarrows \text{water} \\ \text{water} &= \text{water vapour} \end{aligned}$$

Corresponding quantities of heat required for the change of state are called *specific latent heat of melting* or *solidification* (333.3 kJ kg^{-1}) and *evaporation* or *boiling* (2257 kJ kg^{-1}).

When water is transformed into ice (under normal conditions) the volume increases by approximately 9.2%. Then changes in the volume of water which take place around the freezing point, intensify the erosive activity of water in nature.

Water and ice evaporate (ice sublimes), therefore, they are always surrounded by water vapour. In a closed space at a given temperature and pressure an equilibrium is achieved after a certain time interval, the space being saturated with water vapour. This saturated vapour exerts the same partial pressure by which the original pressure of air is reduced. The higher the temperature, the greater is the pressure of saturated vapour (Table 3.3).

Table 3.3. Dependence of saturated water vapour pressure on temperature

t (°C)	0	5	10	15	20	25	30	50	100
Pressure of saturated water vapour (10^5 Pa)	6.1	8.7	12.3	17.0	23.37	31.65	42.42	123.3	1013.27

When the saturated vapour pressure reaches the value of the atmospheric pressure, vapour can be generated inside the liquid, and *boiling* starts. The *boiling temperature of water* is quite high considering the relatively low molecular weight of water (100°C at 101.325 kPa).

If liquid water is heated, only part of the supplied heat causes a rise in the temperature, the rest is employed in breaking the hydrogen bonding. This results in a high value of the heat capacity of water (4.1819 kJ kg^{-1} K^{-1} at 20°C) which undergoes an anomalous transformation with temperature — it decreases with increasing temperature, and then it begins to increase. On account of the high thermal capacity of water, the land becomes relatively warmer in winter and cooler in summer. Thus, large water surfaces (lakes, seas, oceans) participate significantly in the temperature control over the entire earth's surface.

As water evaporates under given conditions at any temperature, all three states can be studied at the same time. They can be in equilibrium only at a certain pressure and a certain temperature — this state is called the *triple point*. It is defined by the following values in the case of water:

$$p = 6.1 \times 10^2 \text{ Pa} \quad \text{and} \quad t = -0.0075^\circ\text{C} \tag{3.1}$$

Figure 3.5 shows a simplified phase diagram of water in which mutual relationships between the triple point (T), curves of evaporation (TK), melting and solidification (TA) and sublimation curve (OT), can be seen.

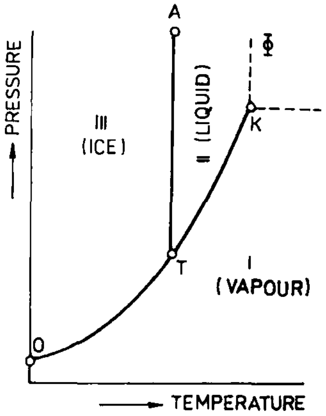

Fig. 3.5. Phase diagram of water. *T* — triple point, *OT* — sublimation curve, *TA* — curve of melting and solidification, *TK* — curve of evaporation, *Φ* — fluid zone, *K* — critical point

The three curves divide the diagram field into three unequal parts: vapour region (I), liquid water (II) and ice (III). In these regions always only a single state can exist (vapour, water, or ice). Under the conditions of pressure and temperature given by the points lying on the curves of the phase diagram only two states can exist in equilibrium:

- — along the TK evaporation curve — water and vapour,
- — along the curve of melting and solidification TA — water and ice,
- — along the sublimation curve OT — ice and vapour.

At the triple point T all three states can coexist.

The curve TK is not an infinite curve, it is terminated by the point K corresponding to the so-called *critical state.* The temperature and pressure corresponding to this state are called the *critical temperature* t_{cr} and *critical pressure* p_{cr}. In the critical states the densities of both states are equal and any differences between both phases — liquid and vapour — disappear, and they form one state only (the fluid zone *Φ*). At very high pressures the phase diagram of water becomes more complicated (Fig. 3.6). At such

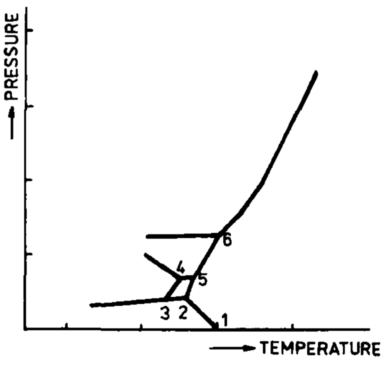

Fig. 3.6. Phase diagram of water for high pressures [5]

pressures six other ice modifications exist, which is evident from the six triple points in the phase diagram [1].

3.2.2 Density and viscosity

The density of liquid water increases from 0°C and reaches its maximum value at 3.98°C (ρ = 1000 kg m^{-3}); then, it continuously decreases up to the boiling point (at 100°C ρ = 958.4 kg m^{-3}) (Fig. 3.7). This anomaly of water has far reaching impacts on life in water, as well as on the uses of water. When cooled down to 4°C, water falls to the bottom, but if it is cooler than 4°C it remains on the surface as it is less dense than the water with a temperature of 4°C; here, it transforms into ice by further reduction of temperature. Because ice is less dense than water it floats on the water surface and protects the water against further cooling. If there were no such anomaly, water would freeze from the bottom upwards and all life in it would be destroyed.

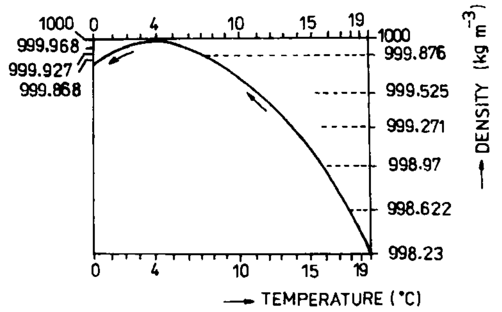

Fig. 3.7. Relationship between density and temperature of pure water [5]

The viscosity of water decreases with increasing temperature (by more than 1/6th if warmed from 0 to 100°C): i.e. resistance to motion is slightly lower in hot water than that in cold water.

The viscosity and density characteristics considerably influence the hydraulic behaviour of water.

3.2.3 Surface tension

Except for mercury, water has the highest surface tension of all common liquids. The reason for the surface tension is the mutual attraction of water molecules; the molecules on the surface are not surrounded by equal molecules in all directions and therefore, there is a net force acting into the

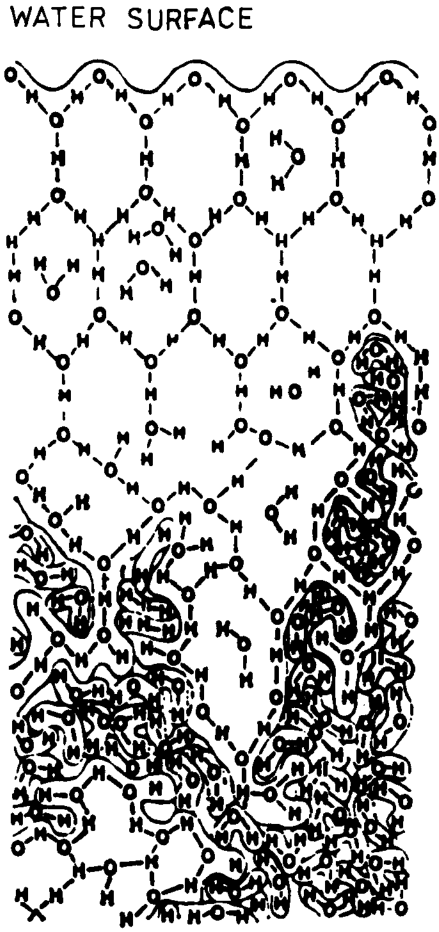

Fig. 3.8. Surface tension of water at the surface (water molecule arrangement)[5]

Table 3.4. Dependence of water surface tension on temperature

t (°C)	0	20	40	60	80
Surface tension (N m^{-1})	75.5×10^{-3}	72.6×10^{-3}	69.5×10^{-3}	66.0×10^{-3}	62.3×10^{-3}

water (Fig. 3.8). The surface tension of water decreases with decreasing temperature, and equals zero at the critical temperature. The dependence of the surface tension of water on temperature is shown in Table 3.4.

High surface tension results in capillary phenomena, such as capillarity of water in the capillaries of soil and rocks, wetting ability, foam formation, and the stability of dust, small insects and pollen grains on the water surface, etc. The surface tension is reduced by washing and wetting agents, which thus increase the wetting and cleaning capabilities of water.

3.2.4 Hydrogen ion and pH value

Combined hydrogen can form a hydrogen ion only if its compounds are dissolved in media able to solvate protons. The energy required for breaking the bond is provided by the solvation process:

$$\mathrm{H{-}X} + \underset{\text{solvent}}{\mathrm{Y}} \rightarrow \mathrm{X^-} + \underset{\substack{\text{protonated}\\\text{solvent}}}{\mathrm{H{-}Y^+}}$$

The bare proton H^+ never exists in condensed phases, it always occurs in the form of solvates (e.g. H_3O^+, R_2OH^+). The compounds which provide hydrogen ions in appropriate solutions or liquids, such as water, are called acids.

Hydrogen ion in water is more correctly called the *hydroxonium ion* H_3O^+. Although we usually write H^+ and talk about a "hydrogen ion", we always assume that this ion is hydrated (H_3O^+) similarly as in the case of ions such as Fe^{2+}, where it is known that hydrated particles $[Fe(H_2O)_6]^{2+}$ are present in aqueous solutions.

Water itself is very slightly dissociated:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (3.2)$$

or

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (3.3)$$

The dissociation equilibrium of water is characterized by the dissociation constant:

$$K_{H_2O} = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = \frac{\gamma_\pm^2}{\gamma_{H_2O}} \frac{c_{H^+} c_{OH^-}}{c_{H_2O}} \qquad (3.4)$$

where a is activity, c — mass concentration (mol l^{-1}), γ_{H_2O} — activity coefficient of non-dissociated water molecules, $\gamma_\pm$ – average activity coefficient of ionized water.

In diluted solutions the water activity can be considered to be constant (a_{H_2O} = const, $\gamma_{H_2O} = 1$), and these can be combined into the constant K_w termed the *ionic product of water*

$$K_w = K_{H_2O} a_{H_2O} = a_{H^+}, \qquad a_{OH^-} = \gamma_{\pm}^2 c_{H^+} c_{OH^-} \tag{3.5}$$

At 25°C $K_w = 1.008 \times 10^{-14}$ mol^{2}l^{-2}, i.e., approximately 10^{-14}. Values of K_w as a function of temperature are given in Table 3.5 [2]. In pure distilled water at 25°C

$$a_{H^+} = a_{OH^-} = 10^{-7} \text{ mol l}^{-1} \tag{3.6}$$

The hydrogen ion activity, a_{H^+} is a vitally important parameter in all branches of science, technology and industry where water is involved. In order to avoid using cumbersome figures such as, for example, $10^{-7.8}$, it is common practice to use the negative log (base 10) of the H^+ activity, and call it the pH:

$$\text{pH} = -\log a_{H^+} \tag{3.7}$$

Thus, if $a_{H^+} = 10^{-7.8}$, then the pH is 7.8. And conversely,

$$a_{H^+} = 10^{-\text{pH}} \tag{3.8}$$

Water whose pH 7 is neutral at 25°C as $a_{H^+} = a_{OH^-}$. Solutions with pH < 7 are acids, and those with pH > 7 are alkalies. The zero pH value corresponds to a strongly acid solution with a unit activity of H^+. The pH value also depends on the temperature. For example, pure water has a pH 7.472 at 0°C, and pH 6.12 at 100°C (see Table 3.5).

Table 3.5. Equilibrium constants for water [2]

t (°C)	K_w (mol^2 l^{-2})	pH of water at given temperature
0	1.13×10^{-15}	7.47
5	1.83×10^{-15}	7.37
10	2.89×10^{-15}	7.27
15	4.46×10^{-15}	7.18
20	6.75×10^{-15}	7.09
25	1.00×10^{-14}	7.00
30	1.45×10^{-14}	6.92
35	2.07×10^{-14}	6.84
40	2.91×10^{-14}	6.77

3.2.5 pE values in water

pE is defined as

$$\mathrm{pE} = -(\log a_{\mathrm{e}^-}), \tag{3.9}$$

where a_{e^-} is the activity of the electron in an aqueous solution.

Water may be oxidized

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \tag{3.10}$$

or it may be reduced

$$2\mathrm{H_2O} + 2\mathrm{e^-} \rightleftharpoons \mathrm{H_2} + 2\mathrm{OH^-} \tag{3.11}$$

Since these reactions involve hydrogen ion and hydroxide ion, the reactions are pH-dependent.

The pE–pH relationship for the oxidizing limit of water is given by

$$\mathrm{pE} = 20.75 - \mathrm{pH} \tag{3.12}$$

and for the reducing limit of water by

$$\mathrm{pE} = -\mathrm{pH} \tag{3.13}$$

The decomposition of water is very slow in the absence of a suitable catalyst. Therefore, water may have temporary non-equilibrium pE values more negative than the reducing limit or more positive than the oxidizing limit [3].

3.2.6 Conductivity

An important factor in the chemistry of water is its *electric conductivity* (*specific conductivity*) $\varkappa$. The electric conductivity $\varkappa$ is the conductivity of a cube of a conductor (solution) with an edge of 1 m. The unit is in the terms of $\mathrm{S\ m^{-1}}$. The electric conductivity of aqueous solutions is a function of the concentration of ions in a solution, the nature of dissolved substance and the temperature.

The electric conductivity of a water sample can be approximated using the following additive relationship:

$$EC = \sum_i (C_i f_i) \tag{3.14}$$

Table 3.6. Conductivity factors for ions commonly found in water [4]

Ion	Conductivity factor f_i (μS cm^{-1} per mg l^{-1})
Ca^{2+}	2.60
Mg^{2+}	3.82
K^+	1.84
Na^+	2.13
HCO_3^-	0.715
CO_3^{2-}	2.82
Cl^-	2.14
NO_3^-	1.15
SO_4^{2-}	1.54

where EC is electric conductivity (μS cm^{-1}), C_i — concentration of ionic species i in the solution (mg l^{-1}), f_i — conductivity factor for ionic species i (see Table 3.6).

In waters containing amounts of inorganic compounds (drinking water, majority of ground- and some wastewaters) electric conductivity is used as an approximate measure of the concentration of mineral electrolytes. In wastewaters containing salts of organic acids and bases the electric conductivity is an approximate measure of the concentration of mineral and organic electrolytes. Dissociated organic substances present in natural waters have little influence on the conductivity. In water analysis, the electric conductivity at 20°C is the standard.

Another electrochemical factor of great importance is the molar conductivity λ, which is a ratio of electric conductivity and mass quantity in 1 m^3 (concentration c):

$$\lambda = \frac{\varkappa}{c} \tag{3.15}$$

The values of measured molar conductivities can also be employed for checking the results of the chemical analysis of waters with pH ranging from 6 to 9 (concentration of ions H^+ and OH^- is very low, therefore, the determination cannot be influenced by their mobility). The concentrations of ions determined by analysis are multiplied by the values of mole conductivities at the given temperature and dilution. If electric conductivity calculated in this way lies within ± 2% of the experimentally determined one, the results of the analysis are considered to be in good agreement.

3.2.7 Aqueous solutions

An important property of water is its ability to dissolve substances. There are only very few compounds known which do not dissolve at least to some extent in water. The basic reason for the remarkable dissolving and ionization capability of water is its dipole character, as well as the high dielectric constant. An aqueous solution is a homogeneous system of water and other compounds whose particles are homogeneously dispersed in the volume, they do not agglomerate in certain localities in the form of grains, crystals, etc., larger than 1 nm. Aqueous solutions are prepared by dissolution, a spontaneous process, until thermodynamic equilibrium is attained, at which a saturated solution is formed coexisting with the substance to be dissolved without further net solution occurring.

3.2.7.1 Solubility of solid substances in water

Due to its dipole character, water is a good solvent of ionic compounds and is particularly suitable for the formation of addition compounds with ionic substances or with substances having a dipole character (Fig. 3.9). The surface ions of the crystalline lattice attract the opposite charged poles of water molecules which agglomerate around the ions in high quantities until the ions are released from the crystalline lattice. After being released

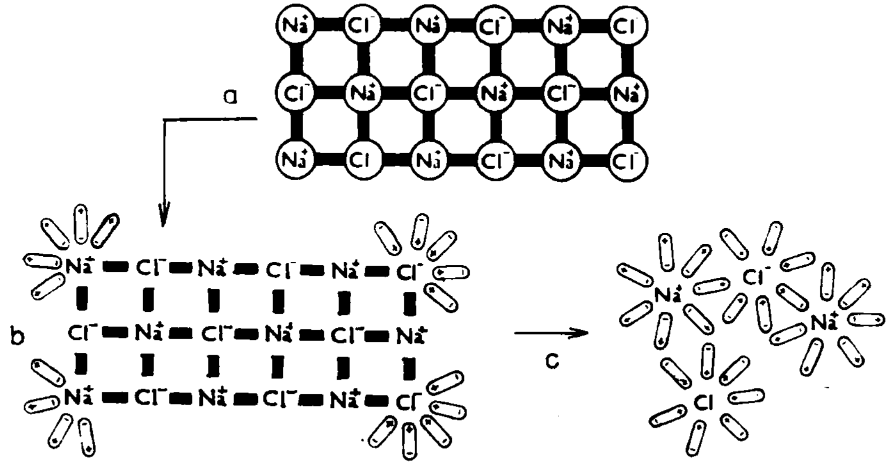

Fig. 3.9. The effect of polarity (of dipole character) of water molecules on the solution of ionic compounds. a — crystalline lattice of NaCl, b — water molecules surround the chloride anions and sodium cations, c — water molecules remove the Na^+ and Cl^- ions from crystalline lattice, surround them and prevent their return to the lattice

from the crystal, the ions are immediately surrounded on all sides by water molecules: this process is called *hydration*. The hydration envelopes of ions are sometimes very stable and the ions "carry" them during motion through the water. For example, in an aqueous solution of copper sulphate, the copper ions exist as complex hydrated ions rather than as simple Cu^{2+} ions (Fig. 3.10) [5].

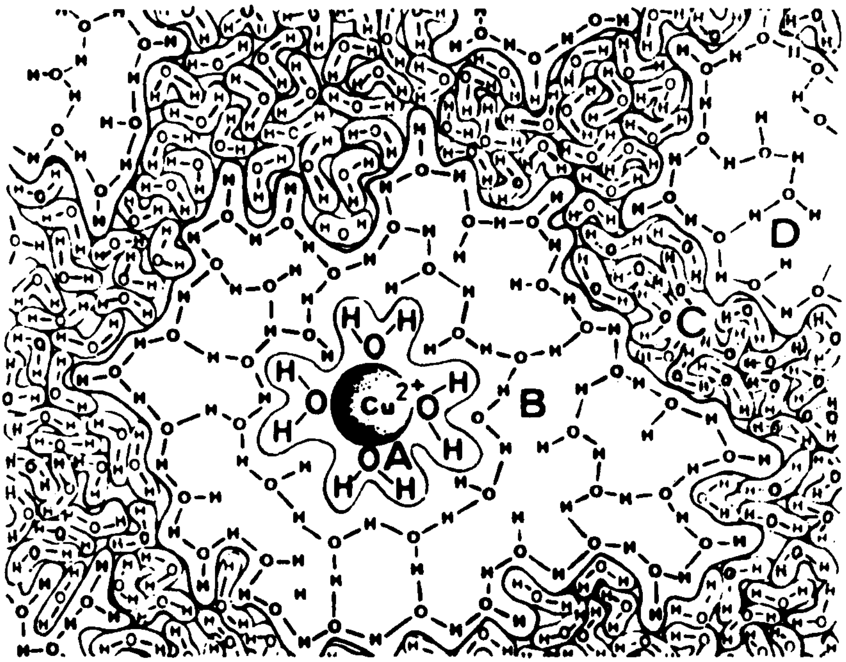

Fig. 3.10. Complex ions. A — $[Cu(H_2O_x)]^{2+}$, B, C and D — different structures existing in an aqueous solution

Due to diffusion the individual molecules or ions of the substance to be dissolved are thoroughly dispersed among the water molecules during dissolution. The greater the contact surface of the dissolved substance with water, the higher is the rate of dissolution. Increasing temperature usually increases the solubility of substances; on cooling a saturated solution to normal temperature the excess of the solid substance is separated in the form of crystals. And vice versa, in the case of relatively few other substances, the solubility decreases with increasing temperature (e.g. $CaSO_4$, $CaCO_3$, $MgCO_3$, $Ca(OH)_2$, $Mg(OH)_2$).

The solubility of substances in water is given in different terms, usually as g or mg of substance per 100 g or 1 litre of water. The dependence of the solubility of substances on temperature is expressed graphically by so-called *solubility curves*. Some of characteristic solubility curves are shown

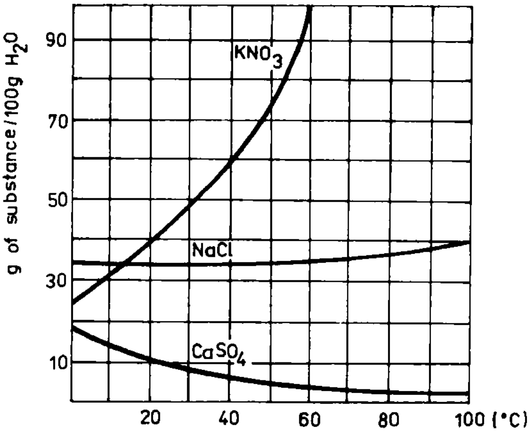

Fig. 3.11. Solubility curves

in Fig. 3.11. The diagram shows that the solubility of
— KNO_3 rapidly increases with the temperature,
— NaCl increases slowly with increasing temperature,
— $CaSO_4$ decreases with increasing temperature.

The solubility curves of the substances whose solubility changes irregularly with the temperature are irregular.

The solubility of inorganic substances depends — apart from the temperature — also on the presence of other substances. If a substance with a common ion is present, the solubility is reduced. Organic substances can be rendered less soluble by adding an ionic compound, when salting-out takes place. Many substances which are commonly considered to be insoluble, are significantly soluble from the toxicological viewpoint. For example, the solubility of mercury in oxygen-free water is 0.02–0.06 mg l^{-1}, however, the standard for drinking water allows only 0.001 mg l^{-1}.

3.2.7.2 Solubility of liquids in water

In water, as a polar liquid itself, polar liquids are readily dissolved (inorganic acids and some organic acids, some alcohols). Non-polar molecules of hydrocarbons do not dissolve well in water. The first members of the homologous series of alcohols (which contain a polar OH group) are readily water-soluble, however, higher members of these series containing long hydrocarbon chains are insoluble in water. Ethyl alcohol (C_2H_5OH) is miscible in water at any ratio, but cetylalcohol ($C_{16}H_{33}OH$) is water-insoluble. The hydrocarbon groups CH, CH_2, CH_3 are hydrophobic. If a monomolecular layer of fatty acid is formed on water, its polar hydrophilic groups —

COOH are immersed in it, and the hydrocarbon residue "protrudes" from the water surface (Fig. 3.12) [5].

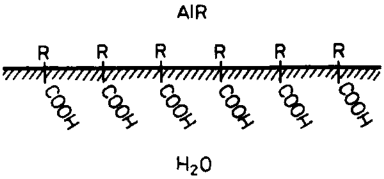

Fig. 3.12. Monomolecular layer of a fatty acid on the water surface. R — hydrocarbon group

3.2.7.3 Solubility of gases in water

The dependence of the solubility of gases in liquids on their pressure at a constant temperature is expressed as *Henry's Law*

$$c = kP \tag{3.16}$$

where c is the gas concentration in the saturated solution, P — pressure of gas above the solution, k — the proportionality constant dependent on temperature.

If more than one gas is dissolved in water, Henry's Law is valid for each component

$$c_i = k_i P_i \tag{3.17}$$

where k_i is the absorption coefficient of the i-th gaseous component, and P_i is partial pressure of the i-th gaseous component.

Henry's Law is valid for less soluble gases and those which do not react with the solvent (water) up to a pressure of about 0.1 MPa. Examples of solubilities for some gases are shown in Table 3.7.

Table 3.7. Solubility of some gases in water at a partial pressure of 101.325 kPa

t	Solubility (mg l^{-1})				
(°C)	Oxygen	Nitrogen	Carbon dioxide	Hydrogen sulphide	Chlorine
0	70	29.6	3380	7180	14600
10	54	23.5	2360	5230	9970
20	44	19.4	1730	3970	7280
50	—	13.7	860	2140	3880

Usually, the solubility of gases decreases with increasing temperature and thus, gases can be expelled from the liquid by heating (for example, when degasifying boiler feed waters). An increased content of salt in water reduces the solubility of gases. Therefore, the solubility of oxygen in the sea water is lower than that in the river water.

In the chemistry and technology of water the data on oxygen solubility are of the greatest importance. However, one should distinguish the solubility of pure oxygen and solubility of oxygen from air (containing ~ 21% vol. of oxygen). For example, at 10°C and a pressure of 0.1 MPa the pure oxygen solubility is 54 mg l^{-1} while that of oxygen from air is 11.3 mg l^{-1} [1, 6, 7].

3.2.7.4 Expression of quantitative composition of aqueous solutions

The composition of aqueous solutions is expressed in terms of *weight* (*mass*) *concentrations* (g l^{-1}, mg l^{-1}, μg l^{-1}, alternatively as kg m^{-3}, mg m^{-3}), or in the terms of the *mole concentrations of substances* (substance concentrations) (mmol l^{-1} or mol m^{-3}, mmol m^{-3}).

The definitions of the mole unit point to the necessity of specifying the species whose concentration is to be expressed. The quantity of the substance is usually expressed in moles of whole molecules, atoms or ions. However, according to the needs it can also be expressed in moles of chemical equivalents (e.g., calcium (Ca/2) = 1.00 mmol l^{-1}). Generally, for the conversion of the mole concentration of a substance (B) to the weight concentration the following is valid:

$$1 \text{ mmol } l^{-1} B \times \text{mol} \cdot \text{weight } B = \text{mg } l^{-1} B$$

Concentration data may be encountered in terms of ppm (mg kg^{-1}), or in ppb (μg kg^{-1}), however, these units should not be used. If water density approaches the value of 1000 kg m^{-3} (in the majority of surface and groundwaters), then ppm ≈ mg l^{-1} and ppb ≈ μg l^{-1}.

3.2.8 The sensory properties of natural waters

The sensory properties of waters involve those which affect the human senses, particularly taste, odour, appearance and touch. Among these temperature, taste, odour, colour and turbidity, are important characteristics.

3.2.8.1 Temperature

Depending on the type and source of water its temperature may vary over a wide range (from 0°C to almost the boiling point).

The temperature of groundwater depends particularly on the depth of layers from which the water is taken and on the water flow rate. The greater the depth the higher the average water temperature and smaller variation in the temperatures, and the minima and maxima of the water temperature lag behind the minimum and maximum of the temperature of air more markedly. Common groundwaters have temperatures ranging from 5 to 13°C. Mineral or thermal waters usually have a higher temperature. Waters with a temperature higher than 25°C at the point of emergence are *thermal waters*, and waters from boreholes with a temperature over 200°C are *hyperthermal waters.*

Running surface waters follow the minima and maxima of the atmospheric temperature.

The temperature of waters in reservoirs decreases with the water depth from the surface. The temperature of surface waters varies strongly during the seasons of the year as well as during a day (within a range from 0 to + 25°C). The temperature of surface waters strongly affects the intensity of self-purification processes: the lower the temperature, the slower the rate of these processes.

The optimum temperature of *drinking water* ranges from 8 to 12°C. Water which is warmer than 15°C is not refreshing [8].

3.2.8.2 Taste

The taste of water is influenced by substances introduced into water naturally, or by pollution.

Water taste is markedly influenced by amounts of iron, manganese, magnesium, calcium, zinc, copper, chlorides, sulphates, hydrogen carbonates, carbon dioxide, etc. An appropriate quantity of salts and the presence of free carbon dioxide give water a refreshing taste. A higher content of some salts has unfavourable effects (for example, higher amounts of the compounds of iron or manganese considerably worsen the taste of water; waters with a high content of magnesium and sulphates are bitter). The best pH for drinking water is 6–7. pH values above 8 cause an alkaline-soapy taste.

Threshold concentrations of the tastes of organic substances are in many cases lower than their highest permissible concentrations from the toxicity

Table 3.8. Threshold concentrations of the taste of some substances in water in mg l^{-1} [9]

Compound	c_m	Compound	c_m
Nitrochlorobenzene	0.05	Amylalcohol	0.10
1-Methylstyrene	0.09	Octylalcohol	0.24
Ethylbenzene	0.10	Chlorocyclohexane	0.20
Styrene	0.80	2,4-Dichlorophenoxyacetic acid	1.00
		Thiophos (pesticide)	0.08

viewpoint. The threshold concentrations of the taste of some organic substances are presented in Table 3.8 [9].

3.2.8.3 Odour

The odour of water is caused by volatile substances present in water which are perceived by the sense of smell. The sources of odour are of primary or secondary origin.

Primary sources are as follows:

— those which form a natural fraction of water (e.g. hydrogen sulphide),
— those of biological origin (formed by the life activity or extinction of plants, algae, bacteria, actinomycetes, fungi, mushrooms and protozoa),
— those contained in sewage and industrial wastewaters.

Secondary sources of odour can be produced during its technological treatment. For example, during water chlorination in the presence with phenols a typical chlorine-phenolic odour is generated.

The categories of offensive odours commonly encountered in water are listed in Table 3.9 [10].

Table 3.9. Categories of offensive odors commonly encountered in water [10]

Compound	Typical formula	Descriptive quality
Amines	$CH_3(CH_2)_nNH_2$	Fishy
Ammonia	NH_3	Ammoniacal
Diamines	$NH_2(CH_2)_nNH_2$	Decayed flesh
Hydrogen sulphide	H_2S	Rotten egg
Mercaptans	CH_3SH; $CH_3(CH_2)_nSH$	Skunk secretion
Organic sulphides	$(CH_3)_2S$; CH_3SSCH_3	Rotten cabbage
Skatole	$C_8H_5NHCH_3$	Fecal

3.2.8.4 Colour

The colour of water is a physical indicator of purity of surface and groundwaters. It is caused by soluble and insoluble substances (turbidity in the latter case).

Pure natural waters are usually colourless, or azure-blue in thick layers. The blue colour intensity increases with decreasing amount of smaller suspended matter present in water. The presence of finely-divided substances causes a change from blue into green colour. Greenish colour of water is also caused by the presence of calcium salts and the near-green colour of some lakes is due to the shape of the bottom. Yellow to brown colours of surface waters are caused by humic (soil) substances and three-valent iron compounds.

Some microorganisms give rise to a characteristic shade. Wastewaters have various shades depending on the source.

Table 3.10. Important properties of water [3]

Property	Effects and significance
Excellent solvent	Transport of nutrients and waste products, making biological processes possible in an aqueous medium
High dielectric constant of any pure liquid	High solubility of ionic substances and their ionization in solution
Higher surface tension than any other liquid	Controlling factor in physiology; governs drop and surface phenomena
Transparent to visible and longer wavelength fraction of ultraviolet light	Colourless, allowing light required for photosynthesis to reach considerable depths in bodies of water
Maximum density as a liquid at 4°C	Ice floats; vertical circulation restricted in stratified bodies of water
Higher heat of evaporation than any other material	Determines transfer of heat and water molecules between the atmosphere and bodies of water
Higher latent heat of fusion than any other liquid except ammonia	Temperature stabilized at the freezing point
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

3.2.8.5 Turbidity

The turbidity of water is caused by insoluble and colloidal compounds of inorganic origin (clay minerals, silicic oxide, hydrated oxides of iron and magnesium, etc.), or of organic origin (organic colloids, bacteria, plankton, etc.). In the groundwaters turbidity is caused mainly by the presence of inorganic substances. Turbidity causes an undesirable appearance of drinking and service waters.

In conclusion we have seen that water has a number of unique properties without which life could not exist. Many of these properties are due to hydrogen bonding in water. These characteristics are summarized in Table 3.10 [3].

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3.3 Chemical reactions and equilibria in waters

3.3.1 Kinetic and thermodynamic notes

The enormous number of chemical reactions and other chemical and physico-chemical interactions in waters considerably complicate their exact description. There are various co-existing dynamic equilibria in waters resulting from the protolytic, complex-forming, oxidation-reduction, polymerization, photochemical, hydrolytic, and other reactions. Inorganic and organic substances are determined in waters both quantitatively and qualitatively. The chemical characteristics and properties of water do not depend so much on the total concentration of dissolved substances but rather on the different species present. As in the majority of cases it is impossible to distinguish analytically all the particular species, their relative representation can in theory be calculated from the laws of chemical thermodynamics. Thermodynamics is defined as the science of mutual transformations of various forms of energy. Chemical thermodynamics deals with an analysis of phenomena related to chemical processes. The totality of substances studied by thermodynamics in a particular situation is called a system. The system is separated from its environment by walls determining the conditions of the processes taking place in the system. From the viewpoint of thermodynamics open, closed and isolated systems are distinguished. The open systems can exchange with the environment both energy and mass, the closed ones only energy, and the isolated ones cannot exchange either mass or energy. A system with identical properties in all its parts is called homogeneous (water, aqueous salt solution, air). A heterogeneous system consists of a number of homogeneous phases separated by phase boundaries (e.g. saturated salt solution in equilibrium with its crystals, a mixture of ice and water).

The state of the system is given by a set of values of properly chosen physical variables. To determine unambiguously the state of the simplest system (a pure substance in one phase) one should know two properties (e.g. temperature and pressure) in addition to the quantity (moles). To describe the state of more complex systems one should know more properties (e.g. the concentrations of individual species). The thermodynamic properties of the system depending only on the state and not on the way by which the system has reached the given state, are called state functions. The typical fundamental state functions are temperature, pressure, volume and concentration of the individual components of the system. The thermodynamic properties are usually classified into extensive and intensive ones. The extensive properties are proportional to the quantity of the substance in the system. Therefore, they are additive, i.e. the total extensive property of the system equals the sum of the extensive properties of the individual parts of the system. Typical extensive quantities are weight, energy, volume, number of moles. On the other hand, the intensive properties do not depend on the quantity of the substance in the system (pressure, temperature, concentration, specific quantities, specific resistance, molar heat, etc.).

If the state of the system changes then it can be said that a thermodynamic process takes place in it (for example, water freezing). Each thermodynamic process proceeds only up to that state at which no further thermodynamic processes occur and all thermodynamic quantities remain constant. This situation is called *thermodynamic equilibrium.* A perfect equilibrium can be achieved only in a system isolated from its environment. In an equilibrium system it is very easy to induce a process with an infinitesimally small change of the state in both directions. For example, in a heterogeneous mixture of ice and water (at a temperature of 0°C) a small addition of heat causes melting of ice, and vice versa, a small removal of heat results in water freezing.

In many chemical reactions, new products are formed. Chemical reactions are controlled both *kinetically* and *thermodynamically.* In the former case the ratio of the products at any moment equals the ratio of the rate constants of all competitive processes. If one of the competing reactions is reversible, the less stable, kinetically controlled products become more thermodynamically stable after a certain time interval, when the ratio of the products is determined by the ratio of the equilibrium constants. This is called a *thermodynamically controlled reaction.*

Temperature has a considerable effect on the outcome of a reaction. Generally, a higher temperature accelerates the achievement of equilibrium as also do increasing quantities of a catalyst [1–4].

Another factor which affects the course of chemical reactions is that of solvation. The strength of solvation of the resulting reagents, reaction intermediates and resulting products significantly influence other mutual interactions and thus also the yield or the result of the reaction itself.

Due to the very high relative permittivity ε_r (25°C) of water ($\varepsilon_r = 78.5$), water has a marked influence on chemical reactions as a solvent (and also as a catalyst) [5].

The real systems encountered in hydrochemistry are continuously open from the viewpoint of thermodynamics (dynamic, through-flow). With respect to the very difficult thermodynamic description of an open system, a real state is described by an approximately equilibrium state of a closed system. A continuous open system approaches the closed one in such a case (or, a stabilized state the equilibrium one) if the retention time is sufficiently long compared to the reaction rates of partial reactions. To simplify this, models considered to be closed systems are used most frequently. Using the laws of chemical thermodynamics it is possible to determine the possibility of the course of the given process in water, and to calculate the equilibrium state and distribution of the particular species [6, 7].

The criterion of the direction of reactions taking place in closed systems is the change in the Gibbs energy ΔG:

$$\Delta G = \Delta H - T\Delta S \tag{3.18}$$

where ΔH denotes a change in enthalpy, ΔS denotes a change in entropy, and T is the temperature.

The sign of ΔG indicates the direction of the reaction towards equilibrium. Processes are probable if ΔG is negative. At a state of chemical equilibrium $\Delta G = 0$. At a constant pressure and temperature the following equation is valid

$$\Delta G = \Delta G^0 + RT \ln Q \tag{3.19}$$

where Q is the activity quotient, and ΔG^0 — the standard change of free enthalpy for the given reaction. If the reaction system is in equilibrium ($\Delta G = 0$, $Q = K_a$) then the following equation is valid:

$$-\Delta G^0 = RT \ln K_a \tag{3.20}$$

$$-\Delta G^0 = 5.71 \times 10^3 \log K_a \qquad (25°\text{C; J mol}^{-1})$$

In the case of oxidation-reduction reactions a similar relationship is valid:

$$-\Delta G^0 = nFE^0 \tag{3.21}$$

where E^0 is the standard oxidation-reduction potential, F — the Faraday constant and n — the number of exchanged electrons. The relation between the equilibrium constant K_a and standard potential E^0 is evident from the equation for a partial oxidation-reduction system

$$\ln K_a = \frac{nF}{RT} E^0 \tag{3.22}$$

A complete oxidation-reduction reaction can be expressed as follows:

$$\log K_a = kn(E_1^0 - E_2^0) \tag{3.23}$$

where E_1^0 is the standard potential of a more positive system, and E_2^0 of a more negative one in volts, k — a constant. From the equilibrium constant expressions, mass and charge equilibria it is possible to calculate the equilibrium concentrations of particular species. The composition of all natural waters depends on the large number of physico-chemical, chemical and biological processes taking place in both homogeneous and heterogeneous systems. These may involve dissolution, precipitation, adsorption, ion exchange, membrane processes, acid-base reactions, complex-forming reactions, oxidation-reduction reactions, and, if there are biochemical processes, denitrification, nitrification, desulphurization, assimilation, photosynthesis, etc., also need considering. The exact description of such a system is extremely complex, so that attention is generally focused mainly on the chemical equilibria formed at the contact of water with the atmosphere, minerals, and the contact among the liquid phase components [8–11]. It is of interest from the historical viewpoint that analyses of the Dead Sea waters were performed as early as in the 18th century [12].

The solution of chemical equilibria is of great significance in the water technology. The most complicated situation involves the application of chemical thermodynamics to the equilibria in organically polluted wastewaters. Therefore, these problems are documented by only a few examples of reactions of organic substrates in water. They are mostly hydrolytic, homolytic, oxidation-reduction and photochemical reactions [13]. All these reaction types are either individually or in parallel applied to waters containing inorganic, biological or organic pollutants.

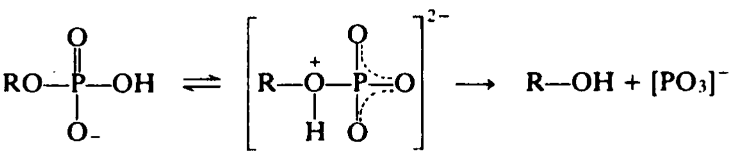
3.3.2 Chemical reactions in waters

3.3.2.1 Hydrolytic reactions

The hydrolytic reactions are of great importance from the viewpoint of chemical degradation of some water pollutants [14–17]. Both inorganic and organic water pollutants frequently have a chemical structure which renders them liable to hydrolysis.

3.3.2.1.1 Hydrolytic reactions of inorganic esters

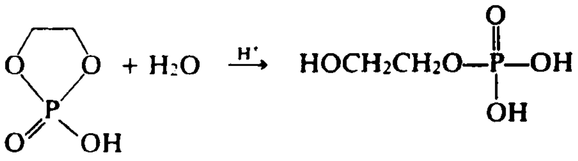
From the aspects of widespread occurrence, phosphate and sulphur esters are of the greatest importance. The study of hydrolysis of monophosphate esters shows that alcohol or phenolic forms split more readily



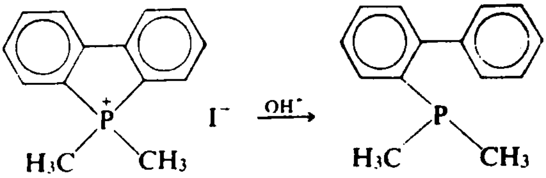
$$\mathrm{RO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}{-}OH} \rightleftharpoons \left[\mathrm{R{-}\overset{+}{\underset{\underset{\displaystyle H}{|}}{O}}{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{|}}{P}}{\doteq}O}\right]^{2-} \longrightarrow \mathrm{R{-}OH} + [\mathrm{PO_3}]^- \qquad (3.24)$$

than the alkoxide or phenoxide anion.

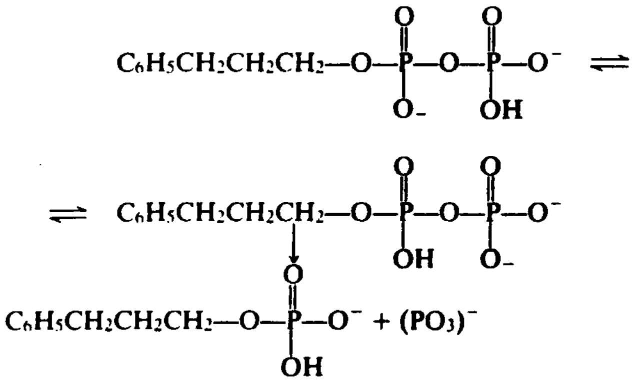
In the hydrolysis of cyclic esters an open form is obtained


(3.25)

Cyclic phosphenium salts also undergo the alkaline hydrolysis


(3.26)

Polyphosphates split off a monophosphate on hydrolysis, for example,


(3.27)

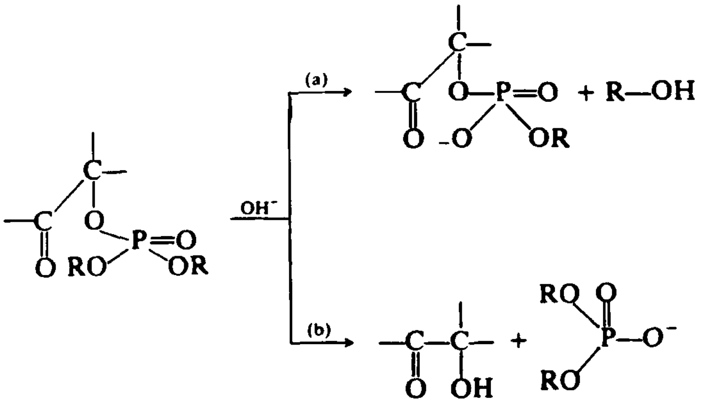
$$C_6H_5CH_2CH_2CH_2{-}O{-}\underset{O^-}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{OH}{\overset{O}{\overset{\|}{P}}}{-}O^- \rightleftharpoons$$

$$\rightleftharpoons C_6H_5CH_2CH_2CH_2{-}O{-}\underset{OH}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{O^-}{\overset{O}{\overset{\|}{P}}}{-}O^-$$

$$\downarrow$$

$$C_6H_5CH_2CH_2CH_2{-}O{-}\underset{OH}{\overset{O}{\overset{\|}{P}}}{-}O^- + (PO_3)^-$$

Depending on the conditions of hydrolysis and the character of the ester substituent, different products can be obtained:



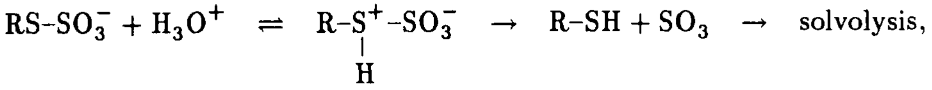
(3.28)

Where R = CH_3 only 3% of the initial substance reacted via the way (a), however, for R = phenyl (b) it was as much as 98%.

Hydrolytic reactions of inorganic esters of sulphur can be illustrated by several typical examples. Monoesters react as follows:

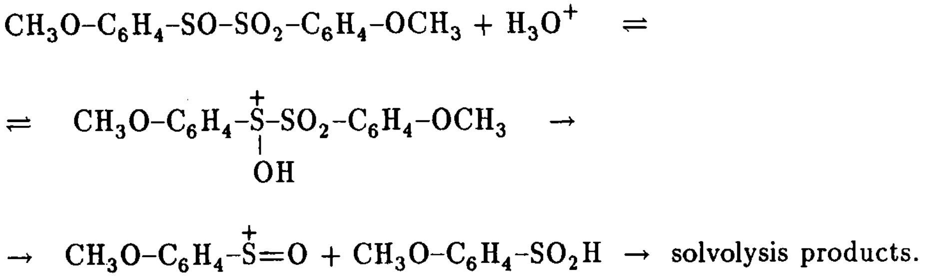
$$\begin{array}{rcl} RO\text{-}SO_3^- + H_3O^+ & \rightleftharpoons & RO\text{-}SO_3H + H_2O \\ ROSO_3H & \rightarrow & R\text{-}OH + SO_3 \end{array} \qquad (3.29)$$

In this way chemical degradation of, for example, tensides, can take place. A similar reaction is that of thioesters:



$$RS\text{-}SO_3^- + H_3O^+ \rightleftharpoons \underset{\textstyle H}{R\text{-}\overset{+}{S}}\text{-}SO_3^- \rightarrow R\text{-}SH + SO_3 \rightarrow \text{solvolysis,}$$

(3.30)



$$CH_3O\text{-}C_6H_4\text{-}SO\text{-}SO_2\text{-}C_6H_4\text{-}OCH_3 + H_3O^+ \rightleftharpoons$$

$$\rightleftharpoons CH_3O\text{-}C_6H_4\text{-}\underset{\textstyle OH}{\overset{+}{S}}\text{-}SO_2\text{-}C_6H_4\text{-}OCH_3 \rightarrow$$

$$\rightarrow CH_3O\text{-}C_6H_4\text{-}\overset{+}{S}{=}O + CH_3O\text{-}C_6H_4\text{-}SO_2H \rightarrow \text{solvolysis products.}$$

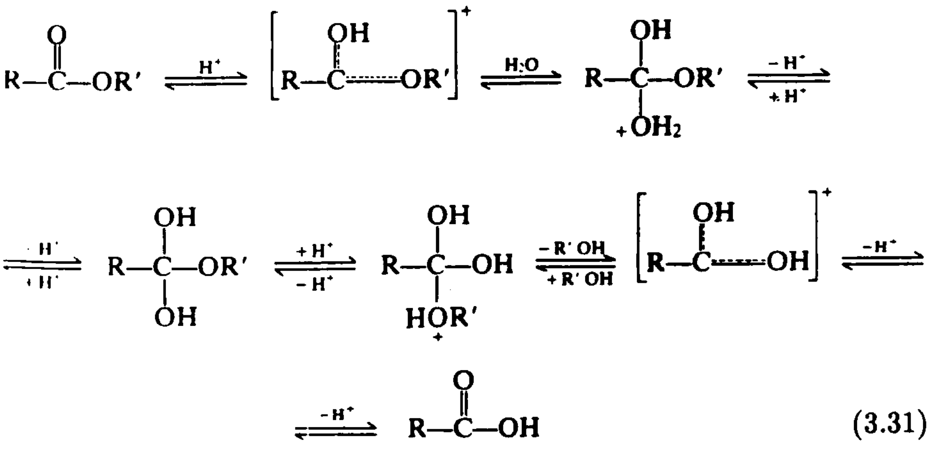
3.3.2.1.2 Hydrolytic reactions of organic acid derivatives

The reactivity of organic acid derivatives in nucleophile reactions decreases in the following order:

Acid halides > acid anhydrides > acid esters.

The most reactive of halides of acids are iodides, in the case of esters the most reactive are generally methylesters of carboxylic acids. The most important transformations of carboxylic acids and their derivatives include esterification and hydrolysis of esters and amides. Esters and amides are hydrolysed in both acid and alkaline media.

The acid hydrolysis of esters and esterification are mutually reversible processes, and, therefore, they take place by the same mechanism ($A_{AC}1$, $A_{AC}2$) in the direction:

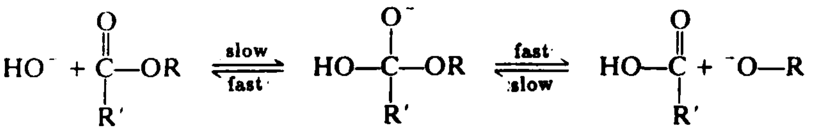


$$R{-}\overset{\overset{O}{\|}}{C}{-}OR' \xrightleftharpoons{H^+} \left[R{-}\overset{\overset{OH}{\vdots}}{C}{\cdots}OR'\right]^+ \xrightleftharpoons{H_2O} R{-}\underset{\underset{+OH_2}{|}}{\overset{\overset{OH}{|}}{C}}{-}OR' \xrightleftharpoons[+H^+]{-H^+}$$

$$\xrightleftharpoons[+H^+]{H^+} R{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}{-}OR' \xrightleftharpoons[-H^+]{+H^+} R{-}\underset{\underset{\underset{+}{HOR'}}{|}}{\overset{\overset{OH}{|}}{C}}{-}OH \xrightleftharpoons[+R'OH]{-R'OH} \left[R{-}\overset{\overset{OH}{\vdots}}{C}{\cdots}OH\right]^+ \xrightleftharpoons{-H^+}$$

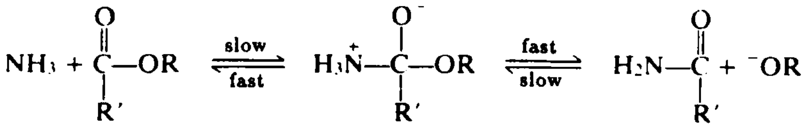
$$\xrightleftharpoons{-H^+} R{-}\overset{\overset{O}{\|}}{C}{-}OH \qquad (3.31)$$

Alkaline hydrolysis of esters by the $B_{AC}2$ mechanism takes place in the following way:



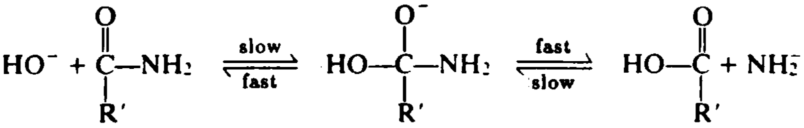
$$HO^- + \underset{\underset{R'}{|}}{\overset{\overset{O}{\|}}{C}}{-}OR \xrightleftharpoons[fast]{slow} HO{-}\underset{\underset{R'}{|}}{\overset{\overset{O^-}{|}}{C}}{-}OR \xrightleftharpoons[slow]{fast} HO{-}\underset{\underset{R'}{|}}{\overset{\overset{O}{\|}}{C}} + {}^-O{-}R \qquad (3.32)$$

Formation and hydrolysis of amides take place as follows ($B_{AC}2$):



$$NH_3 + \overset{O}{\overset{\|}{\underset{R'}{\underset{|}{C}}}}-OR \underset{fast}{\overset{slow}{\rightleftharpoons}} H_3\overset{+}{N}-\overset{O^-}{\overset{|}{\underset{R'}{\underset{|}{C}}}}-OR \underset{slow}{\overset{fast}{\rightleftharpoons}} H_2N-\overset{O}{\overset{\|}{\underset{R'}{\underset{|}{C}}}} + {}^-OR \quad (3.33)$$

The hydrolysis of amides can take place in an alkaline medium by the $B_{AC}2$ mechanism

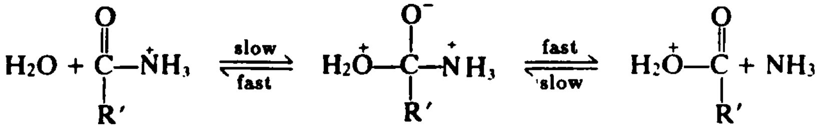


$$HO^- + \overset{O}{\overset{\|}{\underset{R'}{\underset{|}{C}}}}-NH_2 \underset{fast}{\overset{slow}{\rightleftharpoons}} HO-\overset{O^-}{\overset{|}{\underset{R'}{\underset{|}{C}}}}-NH_2 \underset{slow}{\overset{fast}{\rightleftharpoons}} HO-\overset{O}{\overset{\|}{\underset{R'}{\underset{|}{C}}}} + NH_2^- \quad (3.34)$$

and finally:

$$R'COOH + NH_2^- \xrightarrow{fast} R'COO^- + NH_3$$

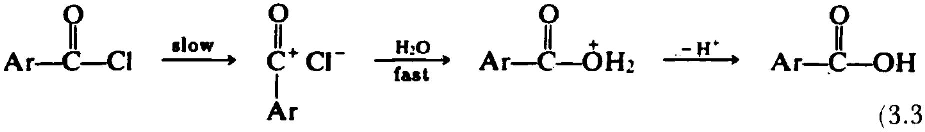
The acid hydrolysis takes place via the $A_{AC}2$ mechanism:



$$H_2O + \overset{O}{\overset{\|}{\underset{R'}{\underset{|}{C}}}}-\overset{+}{N}H_3 \underset{fast}{\overset{slow}{\rightleftharpoons}} H_2\overset{+}{O}-\overset{O^-}{\overset{|}{\underset{R'}{\underset{|}{C}}}}-\overset{+}{N}H_3 \underset{slow}{\overset{fast}{\rightleftharpoons}} H_2\overset{+}{O}-\overset{O}{\overset{\|}{\underset{R'}{\underset{|}{C}}}} + NH_3 \quad (3.35)$$

i.e. $R'CO\overset{+}{O}H_2 + NH_3 \xrightarrow{fast} R'COOH + NH_4^+$.

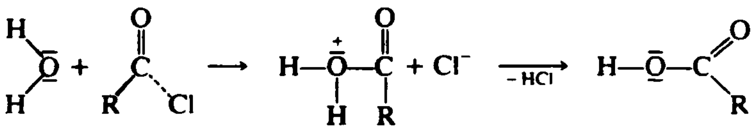
Another example is that of hydrolysis of acylhalides which can take place by either the following S_N1 mechanism:



$$Ar-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{slow} \overset{O}{\overset{\|}{\underset{Ar}{\underset{|}{C^+}}}}\,Cl^- \xrightarrow[fast]{H_2O} Ar-\overset{O}{\overset{\|}{C}}-\overset{+}{O}H_2 \xrightarrow{-H^+} Ar-\overset{O}{\overset{\|}{C}}-OH$$

(3.36)

or the S_N2 mechanism

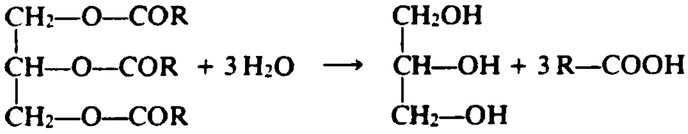


(3.37)

The reaction of acid anhydrides with water is also a nucleophilic substitution taking place in a similar way as hydrolysis of acylchlorides, for example,

$$(CH_3CO)_2O + H_2O \longrightarrow 2\,CH_3COOH \qquad (3.38)$$

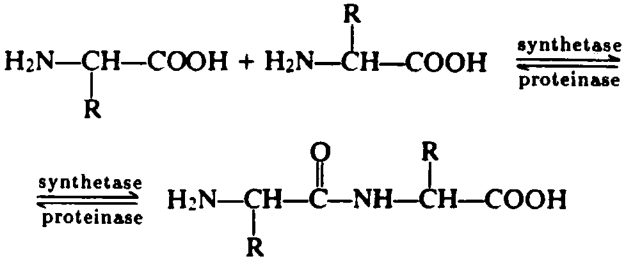
Of these reactions, the fat hydrolysis into glycerol an fatty acids is quite important in systems containing biological materials:



$$\begin{array}{l} CH_2{-}O{-}COR \\ | \\ CH{-}O{-}COR \\ | \\ CH_2{-}O{-}COR \end{array} + 3\,H_2O \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array} + 3\,R{-}COOH \qquad (3.39)$$

where R-COOH is palmitic acid.

Enzymatic hydrolysis of proteins results in the production of amino acids:



$$H_2N{-}\underset{\displaystyle R}{\underset{|}{C}H}{-}COOH + H_2N{-}\overset{\displaystyle R}{\overset{|}{C}H}{-}COOH \underset{\text{proteinase}}{\overset{\text{synthetase}}{\rightleftharpoons}} H_2N{-}\underset{\displaystyle R}{\underset{|}{C}H}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}\overset{\displaystyle R}{\overset{|}{C}H}{-}COOH \qquad (3.40)$$

By mainly similar mechanisms polysaccharides, saccharides and many other inorganic and organic pollutants present in waters undergo corresponding hydrolytic transformations.

3.3.2.2 Decomposition reactions of organometallic compounds

Organometallic compounds are rather frequent, and from the biological viewpoint dangerous pollutants of the environment.

In general, a degradation reaction of bivalent metals can be illustrated as follows:

$$\begin{array}{rcll} R{-}M{-}R & \rightarrow & R{-}M^{\bullet} + {}^{\bullet}R, & M = Zn, Cd, Hg, \\ R{-}M^{\bullet} & \rightarrow & M + {}^{\bullet}R, & R = \text{alkyl, aryl.} \end{array} \qquad (3.41)$$

Subsequent and secondary reactions are then:

$$\begin{aligned} 2\mathrm{R}^{\bullet} &\rightarrow \mathrm{R{-}R} \\ \mathrm{R}^{\bullet} + \text{H-substrate} &\rightarrow \mathrm{R{-}H} + {}^{\bullet}\text{substrate, etc.} \end{aligned} \tag{3.42}$$

Trimethylaluminium can be used as a typical example of degradation reactions of trivalent organometallic compounds:

$$\begin{aligned} \mathrm{Al(CH_3)_3} &\rightarrow {}^{\bullet}\mathrm{Al(CH_3)_2} + {}^{\bullet}\mathrm{CH_3} \\ {}^{\bullet}\mathrm{CH_3} + \mathrm{Al(CH_3)_3} &\rightarrow \mathrm{CH_4} + \mathrm{(CH_3)_2AlCH_2^{\bullet}} \\ \mathrm{(CH_3)_2AlCH_2^{\bullet}} &\rightarrow \mathrm{CH_3AlCH_2^{\bullet}} + {}^{\bullet}\mathrm{CH_3} \\ 2\mathrm{CH_3^{\bullet}} &\rightarrow \mathrm{C_2H_6} \end{aligned} \tag{3.43}$$

Reactions of tetravalent organometallic compounds can be exemplified by tetraethyl lead, which is very widely used as a petrol additive:

$$\begin{aligned} \mathrm{Pb(C_2H_5)_4} &\rightarrow {}^{\bullet}\mathrm{Pb(C_2H_5)_3} + {}^{\bullet}\mathrm{C_2H_5} \\ {}^{\bullet}\mathrm{Pb(C_2H_5)_3} + \mathrm{Pb(C_2H_5)_4} &\rightarrow \mathrm{Pb_2(C_2H_5)_6} + {}^{\bullet}\mathrm{C_2H_5} \\ \mathrm{Pb_2(C_2H_5)_6} &\rightarrow \mathrm{Pb(C_2H_5)_4} + \mathrm{Pb(C_2H_5)_2} \\ \mathrm{Pb(C_2H_5)_2} &\rightarrow \mathrm{Pb} + 2\mathrm{C_2H_5^{\bullet}} \end{aligned} \tag{3.44}$$

In these reactions it is important to note particularly the ability of radical intermediates to evoke a chain reaction with known effects on living organisms.

3.3.2.3 Induced reactions

The rate of reaction of substances which can mutually react to form one or several products can be greatly enhanced by induced reactions. Such a reaction can be exemplified by the very slow reaction of As(III) with $S_2O_8^{2-}$

which is rapidly accelerated in the presence of Fe(II) as an inductor

$$\begin{aligned}
\mathrm{Fe(II)} + S_2O_8^{2-} &\rightarrow \mathrm{Fe(III)} + SO_4^{2-} + SO_4^{\overline{\cdot}} \\
\mathrm{Fe(II)} + SO_4^{\overline{\cdot}} &\rightarrow \mathrm{Fe(III)} + SO_4^{2-} \\
\mathrm{As(III)} + SO_4^{\overline{\cdot}} &\rightarrow \mathrm{As(IV)} + SO_4^{2-} \\
\mathrm{As(IV)} + \mathrm{Fe(III)} &\rightarrow \mathrm{As(V)} + \mathrm{Fe(II)} \\
\mathrm{As(IV)} + (\mathrm{FeOH})^{2+} &\rightarrow \mathrm{As(V)} + \mathrm{Fe(II)} \\
\mathrm{As(IV)} + \mathrm{Fe}^{3+} &\rightarrow \mathrm{As(V)} + \mathrm{Fe}^{2+} \\
\mathrm{As(IV)} + \mathrm{Fe(II)} &\rightarrow \mathrm{As(III)} + \mathrm{Fe(III)}
\end{aligned} \qquad (3.45)$$

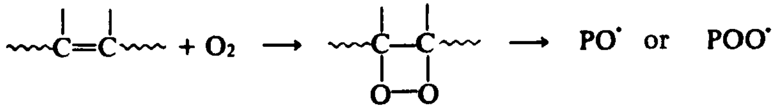
It results from the above presented mechanism that only Fe(II) reacts with $S_2O_8^{2-}$, and thus, the radical anion $SO_4^{\overline{\cdot}}$ is generated. These reactions are applied in oxidation-reduction processes.

3.3.2.4 Oxidation reactions of polymers

A polymer (PH) or other organic compounds can react with a molecular oxygen as follows:

$$\mathrm{PH} + O_2 \rightarrow \mathrm{P}^{\cdot} + \mathrm{HOO}^{\cdot} \qquad (3.46)$$

If the polymer contains double bonds the original adduct degrades into the products as follows:



(3.47)

Another illustrative reaction is the formation of a peroxy radical with $\mathrm{P}^{\cdot}$

$$\mathrm{P}^{\cdot} + O_2 \rightarrow \mathrm{POO}^{\cdot} \qquad (3.48)$$

Abstracting hydrogen, it reacts with another polymer (PH) generating hydroperoxides

$$\mathrm{POO}^{\cdot} + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P}^{\cdot} \qquad (3.49)$$

Thus, the homolytic POOH splitting off leads to the formation of the ($\mathrm{P}^{\cdot}$) intermediate which can cause generation of other degradation products (aldehydes and hydroxy compounds):

$$\begin{aligned} \mathrm{POOH} &\rightarrow \mathrm{PO}^{\cdot} + \mathrm{HO}^{\cdot} \\ \mathrm{PO}^{\cdot} + \mathrm{PH} &\rightarrow \mathrm{POH} + \mathrm{P}^{\cdot} \\ \mathrm{POOH} + \mathrm{HO}^{\cdot} &\rightarrow \mathrm{POO}^{\cdot} + \mathrm{H_2O}, \quad \text{etc.} \end{aligned} \tag{3.50}$$

Oxidative degradation can be initiated photochemically, or it can be catalysed by metals. This type of reaction can be exemplified by the catalytic effect of zinc oxide on the degradation of peroxides, brought about by UV radiation

$$\begin{aligned} \mathrm{ZnO} + \mathrm{O_2} &\xrightarrow{h\nu} (\mathrm{ZnO})^{+} + \mathrm{O}_2^{\overline{\cdot}} \\ \mathrm{O}_2^{\overline{\cdot}} + \mathrm{H_2O} &\rightarrow \mathrm{HO}_2^{\cdot} + \mathrm{HO}^{-} \\ 2\mathrm{HO}_2^{\cdot} &\rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \\ \mathrm{H_2O_2(ZnO)} &\xrightarrow{h\nu} 2\,\mathrm{HO}^{\cdot} \end{aligned} \tag{3.51}$$

In general, the interaction between a transition metal and oxygen can be summarized as follows:

$$\begin{aligned} \mathrm{M}^{n+} + \mathrm{O_2} &\rightarrow \mathrm{M}^{(n+1)+} + \mathrm{O}_2^{\overline{\cdot}} \\ \mathrm{O}_2^{\overline{\cdot}} + \mathrm{H}^{+} &\rightarrow \mathrm{HO}_2^{\cdot} \\ \mathrm{O}_2^{\overline{\cdot}} + \mathrm{RH} &\rightarrow \mathrm{RO}^{\cdot} + \mathrm{HO}^{-} \end{aligned} \tag{3.52}$$

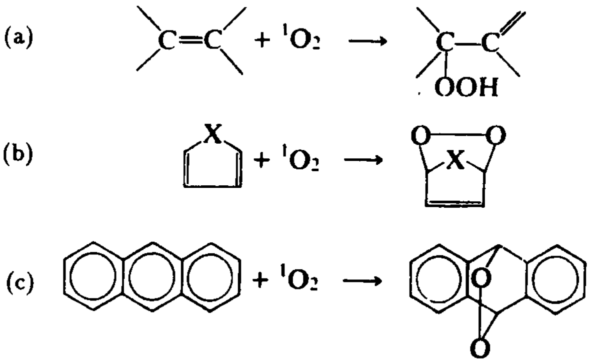
In the presence of hydrogen peroxide the following reactions take place:

$$\begin{aligned} \mathrm{M}^{n+} + \mathrm{H_2O_2} &\rightarrow \mathrm{M}^{(n+1)+} + \mathrm{HO}^{-} + \mathrm{HO}^{\cdot} \\ \mathrm{M}^{n+} + \mathrm{HO}^{\cdot} &\rightarrow \mathrm{M}^{(n+1)+} + \mathrm{HO}^{-} \\ \mathrm{HO}^{\cdot} + \mathrm{H_2O_2} &\rightarrow \mathrm{H_2O} + \mathrm{HO}_2^{\cdot} \\ \mathrm{HO}_2^{\cdot} + \mathrm{H_2O_2} &\rightarrow \mathrm{H_2O} + \mathrm{O_2} + \mathrm{HO}^{\cdot} \\ \mathrm{HO}_2^{\cdot} &\rightleftharpoons \mathrm{O}_2^{\overline{\cdot}} + \mathrm{H}^{+} \end{aligned} \tag{3.53}$$

In this type of reaction, during the oxidation of powder polypropylene in the presence of metallic salts of fatty acids it was found that the catalytic effect of these salts decreases in the following order:

$$\mathrm{Co} > \mathrm{Mn} > \mathrm{Cu} > \mathrm{Fe} > \mathrm{V} > \mathrm{Ni} > \mathrm{Ti} > \mathrm{Al} > \mathrm{Mg} > \mathrm{Ba}$$

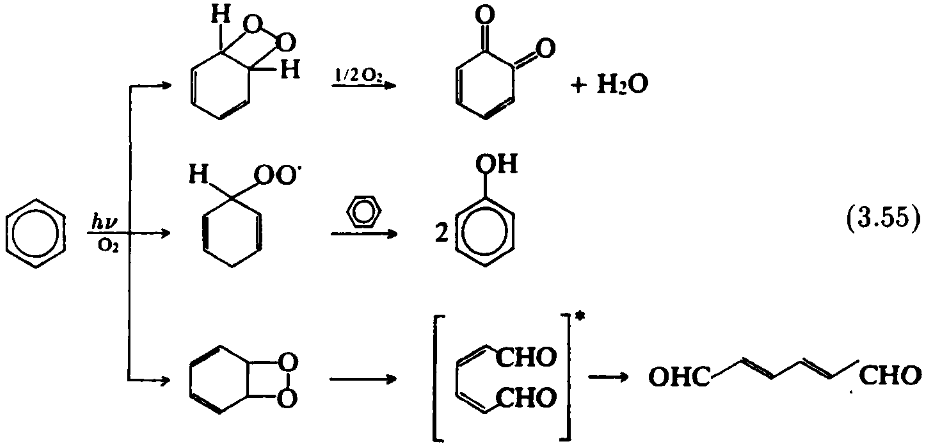
Other important oxidation reactions include the chemical reactions of the singlet oxygen ($^1\mathrm{O_2}$). Some examples illustrating the character and possible products of the reactions of a singlet oxygen with organic substrates are as follows [18–21]:



(d) insertion of $^1O_2$ into C–H bond

(3.54)

Quite frequently labile intermediates evoke further reactions, e.g.



(3.55)

Oxidation reactions can be expected in the surface films of polluted streams. Due to these reactions and other mutual interactions the number of possible products as water pollutants increases considerably.

3.3.3 Numerical and graphical solutions of chemical equilibria

Chemical equilibria can be solved either *numerically* or *graphically*. Based on the analytic results, firstly the types of the species of the individual components are determined. Then, all reactions between liquid, solid and gaseous phases are taken into consideration. Relevant equilibrium constants valid under the chosen conditions for a properly constituted equilibrium model are determined.

3.3.3.1 Numerical methods

When using the numerical methods, an identical number of mutually independent equations is arranged according to the number of unknown quantities (given by the number of the components of the chosen equilibrium model). The equations resulting from the definition of the corresponding equilibrium constants (including the ionic product of water), the equations expressing the mass balance, so-called equations of analytical concentrations and the equations expressing the precondition of electric neutrality, or equations expressing the proton balance (protolytic equilibria) are all taken into consideration. The ligand balance is performed in the case of complex-forming equilibria, and the balance of exchangeable electrons is performed for oxidation-reduction equilibria.

Numerical solution of the chemical equilibria becomes complicated in multicomponent systems as it results in many non-linear equations of higher degrees. Recently, the complex chemical equilibria in waters have been exactly solved using computers (e.g. seawater models). Morel and Morgan have solved a hypothetic model of a system containing 20 metals and 31 ligands (including organic ones). This resulted in distribution of 788 dissolved forms and 83 undissolved forms, which gives some idea of the complexity of the analysis [22].

3.3.3.2 Graphical methods

Graphical methods enable one to form a picture of the distribution of the particular species present, including the significant and negligible components of the system studied. In the numeric methods these values can then be used to simplify the calculation. However, the validity of the diagrams is limited by the conditions under which they were constructed.

Graphically the dependence of the composition of the studied system on one or two variables (pH, concentration, potential, etc.) can be illustrated. For the dependence on one variable, so-called *non-logarithmic* or *logarithmic distribution diagrams* are used, and for two variables, so-called *predominance area diagrams (stability fields diagrams)* are used. From such diagrams it is possible to read off the composition of the given system and the concentration of all its components. Both homogeneous and heterogeneous equilibria can be illustrated graphically. If a solid phase is present in the system, then solubility diagrams are involved. The problems of the solution of chemical equilibria are discussed in detail elsewhere [6–10].

3.3.3.2.1 Non-logarithmic distribution diagrams

The construction of non-logarithmic distribution diagrams is based on the equation of analytical concentrations and equations for the corresponding equilibrium constants. In the case of the reaction $MA \rightleftharpoons M + A$ with an equilibrium constant K it is necessary to take into consideration two components, i.e. MA and M, whose concentrations depend on the concentration of the predominant species A. When solving the two equations the following relations are obtained:

$$\delta_1 = \frac{[MA]}{c_M} = \frac{[A]}{K+[A]}, \quad \delta_2 = \frac{[M]}{c_M} = \frac{K}{K+[A]}, \tag{3.56}$$

where δ_1 and δ_2 are so-called *distribution coefficients* expressing proportional representation of the individual components in the total concentration c_M. The values of distribution coefficients can range from 0 to 1, and thus $\delta_1+\delta_2 = 1$. A graphical representation of $\delta_1 = f_1([A])$ and $\delta_2 = f_2([A])$ is shown in Fig. 3.13, and logarithmic dependence $\delta = f(\log[A])$ in Fig. 3.14.

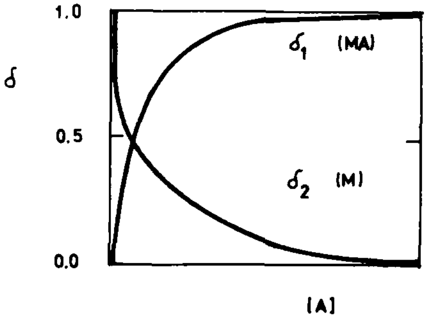


Fig. 3.13. Non-logarithmic distribution diagram

The shape of the distribution curves depends on the ratio of neighbouring partial equilibrium constants. From their values it is possible to assess the importance of the coexistence of the neighbouring species. The greater the difference between the corresponding equilibrium constants, the lesser the distribution curves overlap. When the share of both constants is equal to or greater than 10^3–10^4, then only one of the considered species prevails in a certain concentration range of the predominant species A. Others are negligible and the neighbouring equilibria practically do not influence each other (Fig. 3.15).

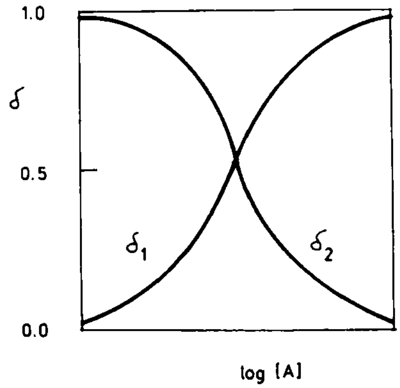


Fig. 3.14. Non-logarithmic distribution diagram

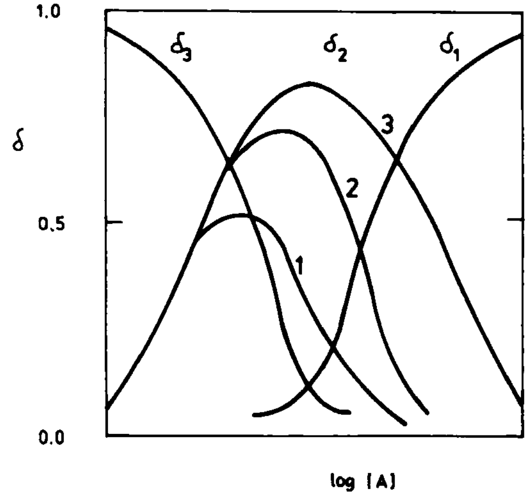


Fig. 3.15. Non-logarithmic distribution diagram with 3 species at different ratio of equilibrium constants. Curves 1, 2 and 3 are for the ratio $K_1 : K_2 = 2.5$, 10 and 100

Of great importance is the control of the predominant species A concentrations at which the distribution coefficient of the given species has the maximum value, and then, such concentrations at which the above forms are equally represented ($\delta_1 = \delta_2$ or $\delta_2 = \delta_3$; see Fig. 3.15).

Non-logarithmic distribution diagrams — due to their clear representation — are used for orientation search for significant and negligible species in the system in question (particularly the solution of the complex-forming equilibria).

3.3.3.2.2 Logarithmic distribution diagrams

The purpose of construction of logarithmic distribution diagrams consists in the representation of linear dependences within the widest concentration range. Again considering the reaction $MA \rightleftharpoons M + A$, the following relations can be derived for the molar concentrations of MA and M:

$$[MA] = \frac{[A]c_M}{K + [A]}, \quad [M] = \frac{Kc_M}{K + [A]} \tag{3.57}$$

Taking the logarithms of these relations the following expressions are obtained:

$$\begin{aligned} \log[MA] &= \log[A] + \log c_M - \log(K + [A]) \\ \log[M] &= \log K + \log c_M - \log(K + [A]) \end{aligned} \tag{3.58}$$

The concentrations MA and M are functions of $[A]$ and c_M (therefore, the total concentration c_M should be known). When constructing the diagram, first the c_M value is plotted and subsequently the point S of the system is determined whose coordinates are given by the values c_M and K ($\log c_M$ and $\log K$). Distribution curves cross in the point P when $[MA] = [M]$, i.e. $\log[A] = \log K$. The second coordinate P is found from the equation $c_M = [MA] + [M]$, from the relation $[MA] = [M] = 0.5\ c_M$, i.e. $\log[MA] = \log[M] = c_M - \log 2$. Thus, the coordinates of the point of intersection P are $\log K$ and $(\log c_M - 0.3)$. It is assumed that in certain regions $A \gg K$ and $A \ll K$. It results for $A \gg K$:

$$\begin{aligned} \log[MA] &= \log c_M \\ \log[M] &= \log K + \log c_M - \log[A] \end{aligned} \tag{3.59}$$

and for $A \ll K$:

$$\begin{aligned} \log[MA] &= \log[A] + \log c_M - \log K \\ \log[M] &= \log c_M \end{aligned} \tag{3.60}$$

These are linear dependences with the intersection point S. Concentrations of both MA and M components at the given concentration of the predominant variable A are found from the point of intersection of a normal line, erected for the considered A, with the lines MA or M (Fig. 3.16).

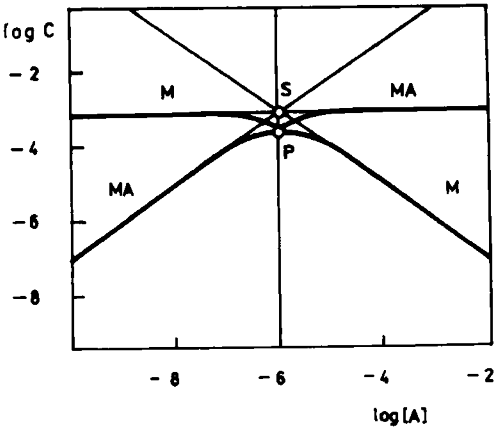


Fig. 3.16. Logarithmic distribution diagram with 2 species, $c_M = 0.001$ mol l^{-1}, $K = 10^{-6}$

Logarithmic distribution diagrams are constructed with an accuracy of 5%. Their advantage consists in their easy construction and in the possibility of a quite precise determination of low concentrations of individual components. After subtracting these values from the total concentration c_M it is possible to calculate the higher concentrations of the remaining principal species.

3.3.3.2.3 Logarithmic solubility diagrams

In the presence of a solid phase the distribution logarithmic diagrams are called *solubility log concentration diagrams.* From these diagrams it is possible to find the liquid phase composition (distribution of complexes and free-ion form) of the areas with predominating existence of the particular forms, total and minimum solubility of the solid phase and pH, or precipitant concentration required for separation of the solid phase at a given pH

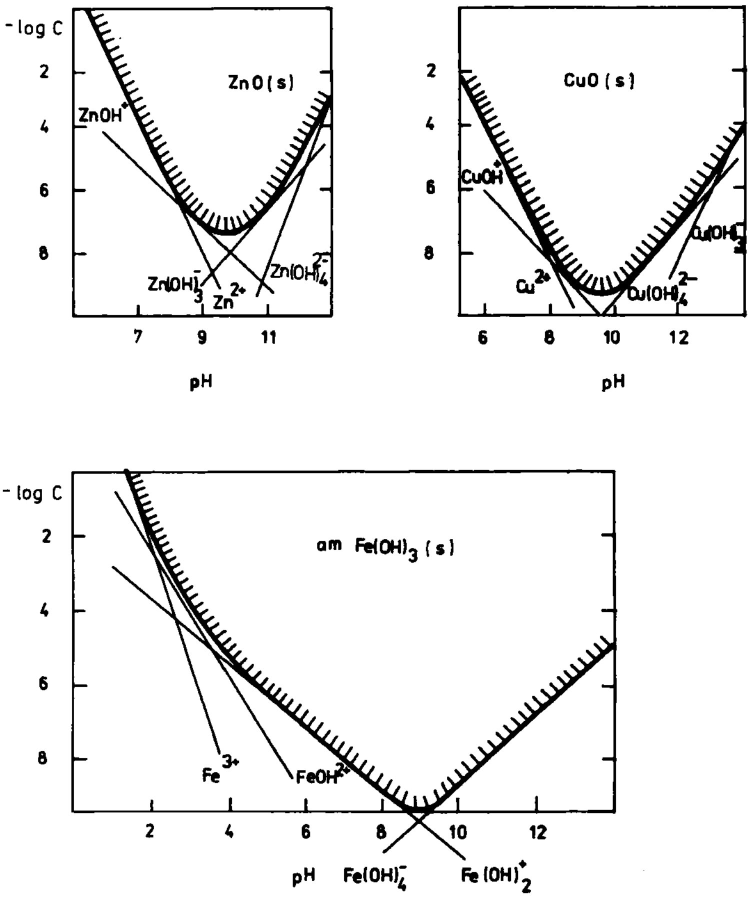


Fig. 3.17. Solubility of amorphous ZnO, CuO and $Fe(OH)_3$

or precipitant concentration. Examples are shown in Fig. 3.17 – logarithmic solubility diagrams of ZnO, CuO and $Fe(OH)_3$ influenced by hydrocomplex formation.

3.3.3.2.4 Predominance area diagrams

A system with two variables can be graphically illustrated either three-dimensionally or by projecting into a plane defined by axes on which the values of variables are plotted. So-called *diagrams of predominating existence area* (*stability field diagrams*) are obtained.

These diagrams consist of line segments limiting the areas (the so-called stability fields) in which — under the given conditions — a certain component prevails. The stability diagrams can be constructed for both homogeneous and heterogeneous systems. In hydrochemistry these diagrams are of great importance as a considerable part of chemical reactions in water can usually be expressed by equations possessing both redox and protolytic character at the same time (so-called E-pH diagrams), for example, the various species of Fe and Mn in waters. They are important in hydrochemistry for the formation of complexes and the different forms depend on the concentration of different ligands occurring in waters (SO_4^{2-}, HCO_3^-, Cl^-, PO_4^{3-}, CN^-, etc.).

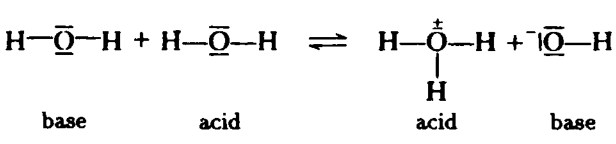
3.3.4 Protolytic equilibria

Acid-base reactions very strongly influence the composition of all waters.

According to the Arrhenius theory, acids are compounds which dissociate in solution forming ions H^+, and bases are compounds providing OH^- ions by dissociation. Acidity, and hence basicity of the solution are given by the concentration of these ions. However, this viewpoint is only valid for specific aqueous solutions. There is a large number of cases of acid-base phenomena which cannot be interpreted by the simple Arrhenius view. For example, urea behaves as an acid in liquid ammonia, and as a base in glacial acetic acid even though it does not provide any hydroxide ions. Ammonium salts in liquid ammonia behave as typical strong acids, they even dissolve metals with generation of hydrogen. Nitric acid behaves as a base, in a hard acid will react primarily with a hard base (or a soft acid with a soft base), and the products of this reaction will be stable. On the other hand, a soft acid and base with a hard acid or base and vice versa will react with difficulty and the products of this reaction will be unstable. From the viewpoint of the theory of hard and soft acids and bases, meanings of the terms of "neutralization" and "neutrality" lose their absolute character, as the resulting products appear as an acid base

$$\mathrm{ACID_1 + BASE_2 \rightleftharpoons ACID_2 + BASE_1} \qquad (3.61)$$

Also the term "amphoteric substance" loses its meaning. The only true amphoteric substance is water



$$\underset{\text{base}}{\mathrm{H{-}\underline{\overline{O}}{-}H}} + \underset{\text{acid}}{\mathrm{H{-}\underline{\overline{O}}{-}H}} \rightleftharpoons \underset{\text{acid}}{\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\pm}{\underline{O}}}{-}H}} + \underset{\text{base}}{\mathrm{{}^{-}|\underline{\overline{O}}{-}H}} \qquad (3.62)$$

Similarly, also the hydrolysis of water, e.g.,

$$\mathrm{Na^{+}\ {}^{-}|C{\equiv}N} + \overset{\delta+}{\mathrm{H}}\text{—}\overline{\underline{\mathrm{O}}}\text{—H} \rightleftharpoons \overset{\delta+}{\mathrm{H}} \longrightarrow \mathrm{C{\equiv}N} + \mathrm{Na^{+}\,{}^{-}|}\overline{\underline{\mathrm{O}}}\text{—H} \qquad (3.63)$$

is nothing more than a protolytic reaction of salts able to dissociate in the solvent into its ions. Examples of hard and soft acids and bases occurring in waters are presented in Table 3.11.

Table 3.11. Some hard and soft bases and acids occurring in waters

Hard base	Hard acid	Soft base	Soft acid	Medium base	Medium acid
HO^-	Al^{3+}	CN^-	Hg^+	ClO_4^-	H^+
HOH	$Al(CH_3)_3$	$R\text{-}S^-$	Hg^{2+}	NO_3^-	Na^+
$R\text{-}O^-$	CO_2	R-SH	CH_3Hg^+	NO_2^-	Zn^{2+}
R-OH	Mg^{2+}	SCN^-	Ag^+	Cl^-	Pb^{2+}
$R\text{-}COO^-$	Cr^{6+}	CO	Cu^+	Br^-	Fe^{2+}
SO_4^{2-}	Ca^{2+}	$S_2O_3^{2-}$	I_2	SO_3^{2-}	Cl_2
PO_4^{3-}	Fe^{3+}	I^-	Br_2	SO_2	SO_3^{2-}
CO_3^{2-}	SO_3	Benzene	DMSO	Aniline	Ni^{2+}

The many homogeneous and heterogeneous equilibria formed in waters between acids and bases determine the resulting pH of water, which is of great importance for hydrochemistry and water technology because it influences all physico-chemical, chemical and biochemical processes in waters. Dissociated and non-dissociated forms of some acids and bases liquid hydrogen fluoride.

J. J. Brønsted and T. M. Lowry (1923) explained these discrepancies using a new theory of acids and bases according to which acids are all compounds able to transfer a proton, and bases are compounds able to accept the proton. Thus, each acid is related to the base differing by one proton and providing a conjugated pair.

However, the protolytic theory cannot explain the distinctly acid or base properties of numerous substances which are not able to either split-off or accept a proton. This stimulated G. N. Lewis (1923) to a different generalization of the notion of acids and bases. According to the Lewis theory a base is a substance which is the donor of a free electron pair, whereas, acid can bond a free electron pair of another particle and thus, it is its acceptor. Neutralization of an acid by base is conditioned by the formation of coordination (donor–acceptor) bond. The Lewis theory is of importance particularly in the chemistry of coordination compounds where all central atoms as acceptors of electron pairs are Lewis acids, and all ligands as donors of electron pairs are Lewis bases. This theory is fairly general and leads to a wider understanding of the mechanism of the reactions between acids and bases, however, this can also be a certain disadvantage in some cases [23–25].

The theory of acids and bases postulated by Arrhenius, Brønsted and Lewis is presently generalized in the Pearson theory of hard and soft acids and bases [26–31].

The donor–acceptor relationships include oxidation-reduction, complex-forming, nucleophilic, electrophilic, acidobasic and other processes. A general principle of this theory, from the viewpoint of reactivity and stability of products, is that behave differently in waters. The dependence on pH of the concentrations of the various species is solved by calculation or graphically.

In the calculation of protolytic equilibria, the ionic product of water, equations for dissociation constants of acids and bases, equations of analytical concentrations and equations of electroneutrality or proton balance are taken for the starting point. Due to the difficulty of the numerical calculation of pH these systems are generally solved by graphical methods.

One of the most important aspects of hydrochemistry is the determination of the relative representation of the particular components of a protolytic equilibrium involving distribution coefficients δ. Graphical illustration of the relationship $\delta = f(\text{pH})$ can be expressed by either non-logarithmic or logarithmic distribution diagrams. Using these diagrams it is possible to read off the values of the concentrations of the particular species.

Logarithmic diagrams of protolytic equilibria can be employed for the assessment of pH of acids, bases and their salts. In the proton balances only those components are considered whose concentrations are important in the context of the particular study.

3.3.5 Complex-forming equilibria

Complex formation is important in the chemistry of natural and wastewaters from several standpoints. Complexes modify metal species in solution, generally reducing the free metal ion concentration so that effect and properties which depend on free metal ion concentration are altered. These effects include such aspects as the modification of solubility, the toxicity and possibly the biostimulatory properties of metals, the modification of surface properties of solids, and the adsorption of metals from solutions.

Coordination compounds or complexes consist of one or more central atoms or central ions, usually metals, with a number of ions or molecules, called ligands, surrounding them and attached to them. The complex can be non-ionic, cationic, or anionic, depending upon the balance of charges of the central ions and the ligands. Usually, the central ions and ligands can exist individually as well as combined in complexes. The number of attachments to a central atom or central ion or the total possible number of coordinated species is referred to as the coordination number. Ligands are attached to the central species by coordinate covalent bonds in which both of the electrons participating in the bond are derived from the ligand. Thus we can regard the central species as an electron acceptor and the ligand as an electron donor. The central species is hence a Lewis acid and the ligands are Lewis bases. Since metal ions have an affinity for accepting electrons, they all form coordination compounds, with a tendency that increases as the electron-accepting affinity of the metal ion increases. Molecules and ions with free electron pairs tend to form complexes whose strength is a function of their ability to donate or share that pair of electrons [6, 32–34].

Species forming a complex can be bonded immediately or solvated by water molecules if an ion pair is formed. In hydrochemistry this concerns, for example, the following ion pairs: $[CaSO_4\ (aq)]^0$, $[CaCO_3\ (aq)]^0$, $[MgHCO_3\ (aq)]^+$, $[CaHCO_3]^+$, $NaCO_3{}^-$, etc.

Reactions of the central atom M with the ligand L usually take place as subsequent reactions. The stability or instability of a given complex is measured by the stability constant β_{nm}, where n denotes the number of ligands and m the number of the central atoms in the complex

$$m\mathrm{M} + n\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_n, \qquad \beta_{nm} = \frac{[\mathrm{M}_m\mathrm{L}_n]}{[\mathrm{M}]_m[\mathrm{L}]_n} \tag{3.64}$$

When evaluating the effects of complex-forming reactions on the properties of waters it is necessary to take into consideration their rate, for example with respect to the protolytic reactions.

The problems of complex-forming reactions are solved either numerically or graphically. The distribution diagrams of complex-forming equilibria express the dependence of the distribution coefficient δ on the ligand concentration.

This can be exemplified by the solution of complex-forming equilibria in wastewaters from sodium chloride electrolysis which contains a number of chloro complexes of mercury ($HgCl^+$, $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$). In Table 3.12 partial and total stability constants are presented. A non-

Table 3.12. Partial and total stability constants of mercury chloro complexes

Reaction	K_n	Reaction	β_n
$Hg^{2+} + Cl^- = HgCl^+$	$K_1 = 10^{6.74}$	$Hg^{2+} + Cl^- = HgCl^+$	$\beta_1 = 10^{6.74}$
$HgCl^+ + Cl^- = HgCl_2$	$K_2 = 10^{6.48}$	$Hg^{2+} + 2Cl^- = HgCl_2$	$\beta_2 = 10^{13.22}$
$HgCl_2 + Cl^- = HgCl_3^-$	$K_3 = 10^{0.85}$	$Hg^{2+} + 3Cl^- = HgCl_3^-$	$\beta_3 = 10^{14.07}$
$HgCl_3^- + Cl^- = HgCl_4^{2-}$	$K_4 = 10^{1.0}$	$Hg^{2+} + 4Cl^- = HgCl_4^{2-}$	$\beta_4 = 10^{15.07}$

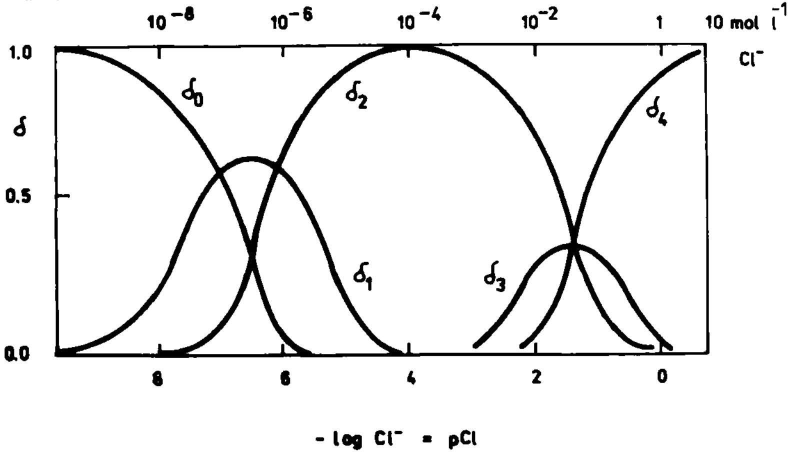


Fig. 3.18. Non-logarithmic distribution diagram of a system of mercury chloro complexes Hg^{2+}, $HgCl^+$, $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$

logarithmic distribution diagram is shown in Fig. 3.18. The distribution coefficients δ_0–δ_4 express the relative representation of the species Hg^{2+}, $HgCl^+$, $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$.

In addition to heavy metal equilibria, complex-forming reactions also take place between the basic inorganic components of waters (Mg^{2+}, Ca^{2+}, Na^+, HCO_3^-, SO_4^{2-}). These reactions become more significant in strongly mineralized waters. An important inorganic complex-forming substance in artificially polluted waters is the polyphosphate formation of stable chelates. The reason for a higher concentration of metals in natural waters also consists in the production of organic complexes of both natural and artificial origin. In polluted surface waters organic complexes of metals can be more prevalent than the inorganic ones.

3.3.6 Precipitation and dissolution equilibria

If a solid substance or liquid is in contact with water in which it dissolves without substantial chemical change an equilibrium state is established under the given conditions. A saturated solution is formed if a sufficient proportion of the solute is present.

The terms solubility and insolubility are only relative from the viewpoint of water treatment. It is indicated in Section 3.2.8 that the sensory properties of waters are influenced by relatively low concentrations. From the biological viewpoint also very low concentrations can be of great importance.

From a general equilibrium reaction of dissolution

$$M_m A_n(\mathrm{s}) \rightleftharpoons M_m A_n(\mathrm{aq}) \rightleftharpoons mM_{n+} + nA_{m-} \tag{3.65}$$

the solubility product K_s is

$$(K_s)_a = a_M^m a_A^n \tag{3.66}$$

where a_M, a_A are corresponding activities of the ions in equilibrium with undissolved solute. In the case of solutions with a low ionic strength the activities may be substituted by concentrations

$$K_s = [M]^m [A]^n \tag{3.67}$$

The reciprocal value of the solubility product is called a *solubility constant.*

In the technology of water the solubilities of hydroxides and carbonates are of the greatest importance, these are infuenced by metal ion hydrolysis. With metal cations water forms so-called aqua complexes. Usually, four or six molecules of water are coordinated around the central atom (e.g. $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$, $[Mn(H_2O)_6]^{2+}$, etc.).

Some reactions taking place in water and their equilibrium constants are presented in Table 3.13.

In water treatment practice the precipitation and hydrolytic reactions play an essential role particularly in determining the optimum pH of water and residual concentration of metals. Theoretical calculation of optimum conditions of precipitation (pH, quantity of precipitant) and residual concentration of the ion to be removed are always checked by experiment.

3.3.7 Oxidation-reduction equilibria

Oxidation-reduction equilibria play an important role in water technology particularly from the viewpoint of the calculation of a relative representation of individual oxidation degrees of the element in the system. Oxidation-reduction potentials are used in theoretical studies for checking the iron and manganese removal, water chlorination, in the study of the

Table 3.13. Equilibrium constants of oxides, hydroxides, carbonates, hydrogencarbonates, sulphates, sulphides, silicates and acids in water

Reaction	log *K* (25°C)	Conditions
I. Oxides and hydroxides		
$H_2O = H^+ + OH^-$	−14.00	A
	−13.77	B
$(am)Fe(OH)_3(s) = Fe^{3+} + 3OH^-$	−38.7	C
$(am)Fe(OH)_3(s) = FeOH_{2+} + 2OH^-$	−27.5	C
$(am)Fe(OH)_3(s) = Fe(OH)_2^+ + OH^-$	−16.6	C
$(am)Fe(OH)_3(s) + OH^- = Fe(OH)_4^-$	− 4.5	C
$2(am)Fe(OH)_3(s) = Fe_2(OH)_2^{4+} + 4OH^-$	−51.9	C
$(am)FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	3.55	C
α-$FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	1.6	C
α-$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	8.2	A
γ-$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	9.0	A
$(am)Al(OH)_3(s) + 3H^+ = Al^{3+} + 3H_2O$	10.8	A
$Al^{3+} + 4OH^- = Al(OH)_4^-$	32.5	A
$CuO(s) + 2H^+ = Cu^{2+} + H_2O$	7.65	A
$Cu^{2+} + OH^- = CuOH^+$	6.0 (18°C)	A
$2Cu^{2+} + 2OH^- = Cu_2(OH)_2^{2+}$	17.0 (18°C)	A
$Cu^{2+} + 3OH^- = Cu(OH)_3^-$	15.2	A
$Cu^{2+} + 4OH^- = Cu(OH)_4^{2-}$	16.1	A
$ZnO(s) + 2H^+ = Zn^{2+} + H_2O$	11.18	A
$Zn^{2+} + OH^- = ZnOH^+$	5.04	A
$Zn^{2+} + 3OH^- = Zn(OH)_3^-$	13.9	A
$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-}$	15.1	A
$Cd(OH)_2(s) + 2H^+ = Cd^{2+} + 2H_2O$	13.61	A
$Cd^{2+} + OH^- = CdOH^+$	3.8	D
$Mn(OH)_2(s) = Mn^{2+} + 2OH^-$	−12.8	A
$Mn(OH)_2(s) + OH^- = Mn(OH)_3^-$	− 5.0	A
$Fe(OH)_2$(active) $= Fe^{2+} + 2OH^-$	−14.0	A
$Fe(OH)_2$(inactive) $= Fe^{2+} + 2OH^-$	−14.5	A
$Fe(OH)_2$(inactive) $+ OH^- = Fe(OH)_3^-$	− 5.5	A
$Mg(OH)_2$(active) $= Mg^{2+} + 2OH^-$	− 9.2	A
$Mg(OH)_2$(brucite) $= Mg^{2+} + 2OH^-$	−11.6	A
$Mg^{2+} + OH^- = MgOH^+$	2.6	A
$Ca(OH)_2(s) = Ca^{2+} + 2OH^-$	− 5.43	A
$Ca(OH)_2(s) = CaOH^+ + OH^-$	− 4.03	A
$Sr(OH)_2(s) = Sr^{2+} + 2OH^-$	− 3.51	A
$Sr(OH)_2(s) = SrOH^+ + OH^-$	0.82	A
$AgOH(s) = Ag^+ + OH^-$	− 7.5	A

Table 3.13 (continued)

Reaction	log K (25°C)	Conditions
II. Carbonates and hydrogencarbonates		
$CO_2(g) + H_2O = H^+ + HCO_3^-$	−7.82	A
	−7.5	E
	−7.3	F
$HCO_3^- = H^+ + CO_3^{2-}$	−10.33	A
	−9.0	E
	−9.0	F
$CaCO_3$(kalcit) $= Ca^{2+} + CO_3^{2-}$	−8.35	A
	−6.2	E
$CaCO_3$(aragonit) $= Ca^{2+} + CO_3^{2-}$	−8.22	A
$SrCO_3(s) = Sr^{2+} + CO_3^{2-}$	−9.03	A
	−6.8	E
$ZnCO_3(s) + 2H^+ = Zn^{2+} + H_2O + CO_2(g)$	7.95	A
$Zn(OH)_{1,2}(CO_3)_{0,4}(s) + 2H^+ = Zn^{2+} + H_2O + CO_2(g)$	9.8	A
$Cu(OH)(CO_3)_{0,5}(s) + 2H^+ = Cu^{2+} + 3/2H_2O + 1/2CO_2(g)$	7.08	A
$CU(OH)_{0.67}(CO_3)_{0.67}(s) + 2H^+ = Cu^{2+} + 4/3H_2O + 2/3CO_2(g)$	7.08	A
$MgCO_3$(magnesite) $= Mg^{2+} + CO_3^{2-}$	−4.9	A
$MgCO_3$(nesquehonite) $= Mg^{2+} + CO_3^{2-}$	−5.4	A
$Mg_4(CO_3)_3(OH)_2.3H_2O$(hydromagnesite) $= = 4Mg^{2+} + 3CO_3^{2-} + 2OH^-$	29.5	A
$CaMg(CO_3)_2$(dolomite) $= Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	−16.7	A
$FeCO_3$(siderite) $= Fe^{2+} + CO_3^{2-}$	−10.4	A
$CdCO_3(s) + 2H^+ = Cd^{2+} + H_2O + CO_2(g)$	6.44	B
$MnCO_3(s) = Mn^{2+} + CO_3^{2-}$	−10.41	A
III. Sulphates, sulphides and silicates		
$CaSO_4(s) = Ca^{2+} + SO_4^{2-}$	−4.6	A
$H_2S = H^+ + HS^-$	−7.0	A
$HS^- = H^+ + S^{2-}$	−12.96	A
MnS(green) $= Mn^{2+} + S^{2-}$	−12.6	A
MnS(pink) $= Mn^{2+} + S^{2-}$	−9.6	A
$FeS(s) = Fe^{2+} + S^{2-}$	−17.3	A
SiO_2(quartz) $+ 2H_2O = H_4SiO_4$	−3.7	A
(am)$SiO_2(s) + 2H_2O = H_4SiO_4$	−2.7	A
$H_4SiO_4 = H^+ + H_3SiO_4^-$	−9.46	A
IV. Acids		
$NH_4^+ = H^+ + NH_3(aq)$	−9.3	A
$HOCl = H^+ + OCl^-$	−7.53	A

A — 0, B — 1 mol l^{-1} solution of $NaClO_4$, C — 3 mol l^{-1} solution of $NaClO_4$, D — 1 mol l^{-1} solution of $LiClO_4$, E — sea water, F — 5°C, sea water and $p = 20.265$ MPa.

Table 3.14. Standard and formal potentials (pH 7)

Equation	pE^0 (25°C)	$pE^{0'}$ (25°C)
$O_2(g) + 4H^+ + 4e = 2H_2O$	20.75	13.75
$2H^+ + 2e = H_2(g)$	0.0	− 7.00
$HCOO^- + 3H^+ + 2e = CH_2O + H_2O$	2.82	− 7.68
$CO_2(g) + 8H^+ + 8e = CH_4(g) + 2H_2O$	2.87	− 4.13
$NO_3^- + 10H^+ + 8e = NH_4^+ + 3H_2O$	14.90	6.15
$SO_4^{2-} + 9H^+ + 8e = HS^- + 4H_2O$	4.13	− 3.75
$SO_4^{2-} + 8H^+ + 6e = S(s) + 4H_2O$	6.05	− 3.30
$S(s) + H^+ + 2e = HS^-$	− 1.1	—
$S(s) + 2H^+ + 2e = H_2S$	2.4	—
$NADP^+ + H^+ + 2e = NADPH$	− 2.0	− 5.5
$CO_2(g) + 4H^+ + 4e = 1/8$ glucose $+ H_2O$	− 0.20	− 7.20
$CO_2(g) + 4H^+ + 4e = CH_2O + H_2O$	− 1.20	− 8.20
$CO_2(g) + H^+ + 2e = HCOO^-$	− 4.83	− 8.73
$O_3(g) + 2H^+ + 2e = O_2(g) + H_2O$	35.1	—
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	25.6	—
$Cl_2 + 2e = 2Cl^-$	23.1	—
$ClO^- + H_2O + 2e = Cl^- + 2OH^-$	15.2	—

course and automation of aerobic and anaerobic water treatment processes, in limnology for characterization of the surface water trophic level, and for checking the water quality in storage systems. However, this quantity is not widely used in practice particularly because of the difficulties over its accurate measurement.

The value of the oxidation-reduction potential can be calculated by substituting the activities of reacting substances into the Nernst–Peters equation

$$E = E^0 + \frac{2 \cdot 3RT}{nF} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \tag{3.68}$$

where F is the Faraday constant, n — total number of electrons taking part in the reaction, E^0 — standard redox potential, i.e. the potential at which the activities (concentrations) of the reacting components are equal. To simplify the calculations and graphic solutions the quantity pE is used in the Nernst equation, which — like pH — represents a dimensionless quantity expressing in this case the relative activity of electrons

$$pE = pE^0 + \frac{1}{n} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \tag{3.69}$$

Some pE^0 quantities valid for reactions modelling different chemical and biochemical processes in waters are shown in Table 3.14. Redox potentials E^0 of some biologically important systems are presented in Table 3.15.

Table 3.15. Redox potentials of some biologically important systems (pH 7)

System	E^0 (V)
$1/2O_2/H_2O$	+0.82
NO_3^-/NO_2^-	+0.42
Dopaquinone/dihydroxyphenylalanine	+0.37
$[Fe(CN)_6]^{3+}/[Fe(CN)_6]^{2+}$	+0.36
Cytochrome c Fe^{3+}/cytochrome c Fe^{2+}	+0.26
2,6-Dichlorophenol – indophenol, ox/red	+0.22
Methaemoglobin/haemoglobin	+0.17
Dehydroascorbic acid/ascorbic acid	+0.08
Fumaric acid/succinic acid	+0.03
Methylene blue, ox/red	+0.01
Haemin Fe^{3+}/haemin Fe^{2+}	+0.114
Flavoprotein (yellow enzyme), ox/red	−0.12
Pyruvic acid/lactic acid	−0.19
Acetaldehyde/ethanol	−0.20
$NAD^+/NADH + H^+$	−0.32
Glutathione, G–SS–G/G–SH	−0.34
Succinic acid – CO_2/α-ketoglutaric acid	−0.67

The measurement and quantitative evaluation of redox potentials in waters is difficult. It is of great importance in the systems with known composition. For the measurement, electrometric methods are used. At the same time, pH, temperature and oxygen concentration are determined. A saturated calomel electrode serves as a reference and a platinum one as the measuring electrode. Oxidation-reduction equilibria are described in detail elsewhere [6, 7].

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3.4 Chemical composition of water

3.4.1 Inorganic substances in water

Among the essential inorganic constituents of natural waters *calcium, magnesium, sodium* and *potassium* are the main cations, and the more important anions are *hydrogen carbonate, sulphate, chloride* and *nitrate*. In the majority of natural waters the concentration of these ions decreases in the given order. However, in strongly mineralized waters sodium prevails over calcium, and sulphate and chlorides over hydrogen carbonates.

These components make up the fundamental chemical composition of fresh waters and must be taken into consideration in all material balances. For example, electroneutrality equations are used for checking the results of the chemical analysis of water.

$$\begin{aligned} &2c(\mathrm{Ca}^{2+}) + 2c(\mathrm{Mg}^{2+}) + c(\mathrm{Na}^{+}) + c(\mathrm{K}^{+}) = \\ &= c(\mathrm{HCO}_3^-) + 2c(\mathrm{SO}_4^{2-}) + c(\mathrm{Cl}^-) + c(\mathrm{NO}_3^-) \end{aligned} \tag{3.70}$$

where $c(x)$ designates the molar concentration of the species x.

In natural waters *iron* and *manganese* are generally present in low concentrations and many other metals in trace concentrations; these enrich water when it is in contact with soil, different minerals and rocks.

Of the non-metal species, *ammonia* and *ammonium ions, nitrites, nitrates* and *phosphates* are present in low concentrations. The group of nonionic soluble substances includes *compounds of silicon, boron* and *titanium*. The most important dissolved gases are *oxygen* and *carbon dioxide*.

Total mineralization $\sum c_\mathrm{m}$ is the sum of mass concentrations of solid inorganic substances dissolved in water, electrolytes (cations and anions) as well as of non-electrolytes, and it is usually expressed in mg l^{-1}. For nonelectrolytes, particularly silicon and in the case of mineral water, boron should be considered. Very slightly mineralized waters are those with $\sum c_\mathrm{m} < 100$ mg l^{-1}, for example, relatively unpolluted atmospheric waters. In ground- and surface waters the total mineralization ranges from about 100 to 1000 mg l^{-1}. Waters with total mineralization over 1000 mg l^{-1} are classified as mineral waters.

The classification of inorganic substances in waters into electrolytes, nonelectrolytes, cations and anions is only formal grouping and not necessarily exact, since a given element can occur in water both in ionic and nonionic forms simultaneously, including different complex forms which will be discussed in following sections [1].

The relative concentrations of individual constituents can also differ in fresh waters depending on their genesis, such as atmospheric, mineral, mine and sea waters. This composition can be quite specific in wastewaters.

3.4.1.1 Sodium and potassium

In dissolved forms, mostly simple cations Na^+ and K^+ occur. In more strongly mineralized waters, ion associates such as $[NaSO_4]^-$, $[NaCO_3]^-$, $[NaHCO_3]^0$, $[KSO_4]^-$, $[KCO_3]^-$ and $[KHCO_3]^0$ can be expected to exist.

Sodium and potassium are common constituents of natural waters, with sodium being more prevalent than potassium. The Na:K ratio usually ranges from 10:1 to 25:1. In atmospheric waters, the ratio is reduced in favour of potassium to about 1.5:1–2:1. From the viewpoint of concentration of metals in waters, sodium usually occupies the 3rd position following calcium and magnesium. However, in highly mineralized natural waters sodium can prevail over both these metals.

From the health point of view, sodium and potassium are relatively unimportant in waters. Since about 1960 the possibility of an adverse effect of a high sodium concentration has been studied as it can influence negatively the health of people suffering from heart disease [2]. Sodium hydrogen carbonate mineral waters are important for the treatment of gastric diseases and the diseases of the biliary tract.

Potassium provides a natural radioactive background of waters because natural potassium contains 0.0118 % of the ^{40}K radioactive nuclide. The contents of sodium and potassium in waters for various industries is usually not significant. The exception is the requirement for water quality to be used for high pressure steam boilers, as under higher pressures insoluble sediments (incrustations) of the type $Na_2O.R_2O_3.xSiO_2.yH_2O$ can be formed.

Sodium and potassium play an important role in the classification of the chemistry of natural waters and the checking of the results of chemical water analysis. Therefore, the determination of these alkali metals should become a common procedure within the framework of chemical analysis of water.

3.4.1.2 Lithium, rubidium and caesium

These elements are present at significant concentrations only in mineral and sea waters. Lithium accumulates in plants and can inhibit their growth. Therefore, some countries recommend limiting the content of lithium in waters intended for irrigation. Lithium has a certain balneological importance, and is employed in the prevention of coronary diseases caused by atherosclerosis.

3.4.1.3 Calcium and magnesium

Calcium and magnesium occur in waters mostly as the simple ions Ca^{2+} and Mg^{2+}. Other forms in which they occur are complexes (ion associates) of $[CaSO_4\ (aq)]^0$, $[CaCO_3\ (aq)^0]$, $[CaHCO_3]^+$, $[CaOH]^+$, with similar species for magnesium. In strongly mineralized waters their content can be higher than 40% of the total content of calcium and magnesium.

Calcium and magnesium are usually the main cations in natural waters. With the limited solubility of $CaCO_3$ and $CaSO_4$, the calcium concentration is not higher than 1000 mg l^{-1} even in mineral waters. High concentrations of calcium and magnesium are due to the presence of a sufficient quantity of soluble carbon dioxide so that the following equilibrium is shifted to the right:

$$CaCO_3(s) + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (3.71)$$

The equilibrium constant for this is deduced from the solubility product of $CaCO_3$ (K_s), and the dissociation constants of carbonic acid to the first degree (K_1) and to the second degree (K_2); the equilibrium constant (K) is thus given by the relation $K = K_s K_1 K_2^{-1}$.

With increasing concentration of sodium in waters the calcium concentration decreases, and in some mineral waters sodium is the predominant cation.

Magnesium in natural waters usually occurs in lower quantities than calcium. The Ca:Mg weight ratio ranges from 4:1 to 2:1. However, in exceptional cases there can be more Mg than Ca, for example, in sea water and in some mineral waters. In these the concentration of magnesium can be as high as several g per litre, due to higher solubility of $MgCO_3$ in the presence of CO_2 and $MgSO_4$ in comparison with equivalent calcium compounds.

Depending on the pH, magnesium can be separated from natural waters containing hydrogen carbonates in the form of the hydroxy carbonate $(MgCO_3)_3\ Mg(OH)_2.3H_2O$ or magnesium hydroxide $Mg(OH)_2$. In the presence of phosphates $Mg_3(PO_4)_2$ can be separated. If it is necessary to remove magnesium from water through a chemical process, separation in the form of $Mg(OH)_2$ or $Mg_3(PO_4)_2$ is carried out.

Among the low-solubility compounds of *calcium*, calcium carbonate (calcite), calcium fluoride and some phosphates are important in hydrochemistry and water technology. Calcium carbonate is about 6 times less soluble than $MgCO_3$, but $Ca(OH)_2$ is quite soluble in comparison with

$Mg(OH)_2$. The solubility of $Ca(OH)_2$ is about 1200 mg l^{-1} at 20°C, whereas that of $Mg(OH)_2$ is only 10 mg l^{-1}. In the presence of phosphates, first the hardly soluble calcium hydrogen phosphate $CaHPO_4$ is formed, which reacts in alkaline media to produce *hydroxyapatite* $Ca_5(PO_4)_3(OH)$ whose formula can be written as $3Ca_3(PO_4)_2.Ca(OH)_2$. In fact, it is a complex compound with the assumed structure of $Ca_2[(OH)(CaPO_4)_3]$.

In the process of precipitation of calcium with phosphates a mixture of $CaHPO_4$ and hydroxyapatite is usually formed.

The ratio Ca:P in the precipitate is therefore not constant and it changes depending on the age of the precipitant and reaction conditions.

In hydrochemistry and water technology the kinetics of the separation of $CaCO_3$ is quite important, for instance in the processes of precipitation of protective coatings in pipes. Precipitation of $CaCO_3$ from weakly supersaturated solutions is slow and inhibited by many inorganic and organic compounds [3].

Calcium sulphate separates from water at temperatures below 65°C in the form of $CaSO_4.2H_2O$(gypsum), and at higher temperatures in the form of anhydrous $CaSO_4$ (anhydrite). The solubility of gypsum is about 2000 mg l^{-1}. It readily forms supersaturated solutions.

Calcium fluoride has a lower solubility than magnesium fluoride. Eventual production of CaF_2 is important in the fluoridation of water.

The so-called hardness of water is sometimes mentioned in connection with calcium and magnesium contents, but it is not unambiguously defined in the literature as it is based on either technology or analysis. As the term "hardness" does not correspond to the actual behaviour of water ("hard" water = ice) and because there are difficulties with the exact definition of various types of hardness, this term is gradually disappearing from the literature on hydrochemistry.

The term "water hardness" incorrectly attributes identical chemical and biological properties to calcium and magnesium. Positive or negative effects of "water hardness" mostly do not relate to the total calcium and magnesium concentrations, but only to the concentration of one of them. For example, from the viewpoint of the formation of incrustations in pipes, calcium plays a more important role than magnesium. There are also differences in biological and health aspects. It is therefore invariably more appropriate to evaluate the effects of calcium and magnesium separately [4].

At higher temperature, calcium and magnesium can cause the formation of sediment or boiler incrustation on the walls of technological equipment, particularly of steam boilers. Incrustations appear especially on sites where water vapours and saturated solutions of salts are formed due to the presence and growth of low-solubility crystals, particularly calcium carbonate, sulphate and silicate in admixture with some sparingly soluble compounds of magnesium, particularly magnesium silicate. Usually, three main types of incrustations are recognized: ***carbonate, sulphate*** and ***silicate*** ones. Incrustations act as a thermal insulator, thus hindering heat transfer through the boiler wall. They can be dangerous since under the layer of the incrustation the boiler can be overheated, thus losing its strength and elasticity, and permanent deformation can appear.

Therefore, it is sometimes necessary to remove calcium and magnesium from water (e.g. feed water for steam boilers). On the other hand, it is necessary to increase the content of calcium in some cases to reduce aggressivity of water due to soluble CO_2 or to improve the quality of drinking water.

In industrial water, higher concentrations of calcium and magnesium can negatively influence technological processes and the quality of the products (particularly for the textile industry, laundries, dye works, leather works and some branches of the foodstuffs industry). They cause precipitation of soap solutions, forming insoluble salts of higher aliphatic acids. In some operations not only calcium- and magnesium-free water is required, but also water free from all ions (*deionized water*) or even free from soluble non-ionic inorganic substances (*demineralized water*).

The content of calcium or magnesium in surface and normal groundwaters is unimportant from the viewpoint of health. As for the taste, the best waters are those which contain calcium and hydrogen carbonates. A magnesium content above 250 mg l^{-1} causes a bitter taste. Waters with high concentrations of magnesium and sulphates have laxative effects.

3.4.1.4 Strontium and barium

In fresh waters *strontium* is present at higher concentrations than barium, but some mineral waters can be an exception. Both elements occur in surface and normal groundwaters at concentrations of only units or tenths of $\mu g\ l^{-1}$.

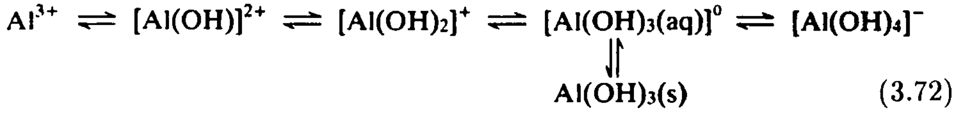
Barium belongs among the toxic elements. The content of strontium in drinking water is not the subject of an official standard. Strontium present in mineral waters has favourable effects when used for the treatment of skin diseases and also for the treatment of respiratory diseases.

3.4.1.5 Aluminium

Soluble forms of aluminium present in waters are the simple hydrated Al^{3+} cation, cationic and anionic hydroxo complexes, sulphate complexes of $[AlSO_4]^+$ and $Al[(SO_4)_2]^-$, and following fluoridation it also occurs as fluoroaluminates with 1–6 coordinated atoms of fluorine, for example $[AlF_6]^{3-}$.

Of the aluminium compounds with low solubility, hydrated aluminium oxide (usually called aluminium hydroxide with a non-stoichiometric structure) is of particular interest in hydrochemistry and the technology of water, and it is present mainly in the colloidal form. The structure $Al(OH)_3$ corresponds only to the compound formed by precipitation of aluminium solutions by introducing carbon dioxide. At a higher temperature during precipitation with ammonia, *aluminium oxide-hydroxide* AlO(OH) can also be formed. When removing phosphates from water aluminium phosphate plays an important role; it is stable in weakly acid media but is hydrolysed to $Al(OH)_3$ in alkaline media.

Aluminium ion hydrolysis. The aluminium cation is present in aqueous media not in the form Al^{3+}, but in the hydrated form, the so-called *aqua-complex* $[Al(H_2O)_6]^{3+}$. For simplicity, however, coordinated molecules of water are usually not shown. The hydrated ion is acidic, and the acidity of the hexaaqua-aluminium complex is lower than the acidity of hexaaqua-ferric complex. During hydrolysis different *hydroxo complexes* are formed. Gradual transformation of Al^{3+} ions takes place according to the following scheme (coordinated water molecules are omitted):



$$\begin{array}{ccccccccc} Al^{3+} & \rightleftharpoons & [Al(OH)]^{2+} & \rightleftharpoons & [Al(OH)_2]^+ & \rightleftharpoons & [Al(OH)_3(aq)]^0 & \rightleftharpoons & [Al(OH)_4]^- \\ & & & & & & \downarrow\uparrow & & \\ & & & & & & Al(OH)_3(s) & & \end{array} \qquad (3.72)$$

The reactions are reversible. The relative concentrations of particular species depend on the pH of the medium. In these reactions, polymerization processes also occur. *Polynuclear complex compounds* are formed; they are also called *hydroxo polymers* with a certain range of existence. Depending on the pH of the medium they are charged either positively or negatively. During the hydrolysis of aluminium, polynuclear complexes such as the following are formed: $[Al_6/OH)_{15}]^{3+}$, $[Al_8(OH)_{20}]^{4+}$, $[Al_{13}(OH)_{32}]^{7+}$, $[Al_2(OH)_2]^{4+}$, $[Al_2(OH)_8]^{2-}$, etc. The polymerization reactions occur fairly slowly. Polynuclear complexes with a higher molecular weight have a colloidal character, and they gradually agglomerate up to the formation of a precipitate of non-stoichiometric structure changing with time. The precipitate formed is *hydrated aluminium oxide.*

Thus, the hydrolysis of Al^{3+} is a rather complex process which should be taken into consideration when dealing with coagulation. The charge of the colloidal hydrated aluminium oxide is related to the charge of corresponding polynuclear hydroxo complexes. *The charge of the colloidal particles in acid media is positive, whereas that in the alkaline media is negative*, and the choice of pH for removal of either negatively or positively charged colloids from water by coagulation with aluminium salts depends on this fact.

In the last decade the chemistry of aluminium salts hydrolysis related to the application of the products of their partial hydrolysis in coagulation has been studied in detail [5]. It has been found that as well as the pH value, temperature, precipitate ageing and solution, the composition of the hydrolysis product also depends on the initial ratio of the concentration of OH^- ions and aluminium, as well as on the rate of the base addition. The hydrolysis of aluminium salts influences a number of side reactions depending on the overall composition of water, since aluminium forms complexes with other ligands, such as sulphate, phosphate and fluoride.

Evaluating the distribution diagram of different forms of the aluminium occurrence, at $pH < 4$ simple hydrated Al^{3+} cation predominates in the solution, and at $pH > 7$ anionic hydroxo complexes prevail. The lowest solubility of hydrated aluminium oxide is achieved at about pH 5.5. Solubility rapidly increases in the alkaline region. Low concentrations of soluble aluminium can be maintained within a rather narrow pH scale. Precipitation of aluminium salts appears at $pH < 4$ and at the initial Al concentration below 0.01 mol l^{-1}.

The solubility of hydrated aluminium oxide depends on the modifications connected with precipitate ageing. The precipitate ageing reduces the amount of hydrated aluminium oxide due to the formation of crystalline thermodynamically stable modifications, and the minimum solubility pH is shifted into the more acid pH region [6].

In surface and normal groundwaters aluminium occurs only in hundredths to tenths of mg l^{-1}. High aluminium content was found in acid waters from the vicinity of deposits of some sulphide-containing ores or slates, by the oxidation of which sulphuric acid was formed, which decomposed the neighbouring minerals.

For a long time aluminium was considered to have no adverse effects on health. Its determination is important for checking the wastewater treatment plant operation where aluminium sulphate is used for clarification. In the case of improper dosing and low temperatures, on coagulation the hydrated aluminium oxide may separate sufficiently in the water piping network thus deteriorating the sensory properties of drinking water. The World Health Organization recommends 0.2 mg l^{-1} as the highest Al concentration in water because of possible neurotoxic effects.

3.4.1.6 Iron

The forms of the occurrence of dissolved and undissolved iron depend on pH, redox potential and the presence of complex-forming inorganic and organic substances.

In the oxygen-free reduction environment of groundwaters and in the waters at the bottom of pools and lakes, iron is present in the oxidation state II. Soluble forms which occur are particularly Fe^{2+}, $[FeOH]^{+}$, $[Fe(OH)_3]^{-}$, and in the waters with high concentrations of sulphate and hydrogen carbonates also $[FeSO_4(aq)]^0$ and $[FeHCO_3]^{+}$. Organic substances in natural waters are mostly complexes of humic acids.

The Fe(II) solubility is influenced by the solubility of $Fe(OH)_2$, $FeCO_3$ and FeS. In natural waters it is mostly limited by the $FeCO_3$ solubility, but precipitation of $FeCO_3(s)$ is very slow and requires considerable super saturation. Only in strongly alkaline region $Fe(OH)_2$ is found. Within the range pH 8–11 different hydroxo carbonates are usually separated. In waters containing hydrogen sulphide and its ionic forms, the iron solubility can be limited by the FeS solubility over a wide range of pH. However, at high concentrations of hydrogen carbonates and a very low concentration of sulphidic sulphur the equilibrium moves in the favour of $FeCO_3$.

In waters containing soluble oxygen, iron in the oxidation state III is the most stable form. Fe^{3+}, $[FeOH]^{2+}$, $[Fe(OH)_2]^{+}$ are the predominating dissolved forms of Fe(III), and in the presence of higher concentrations of sulphates and in acid media ionic associates of $[FeSO_4]^{+}$, $[Fe(SO_4)_2]^{-}$ or $[FeHSO_4]^{2+}$ are also taken into consideration. Similarly, in strongly acid waters with a high concentration of chlorides $[FeCl]^{2+}$ and $[FeCl_2]^{+}$ can be formed, and in the presence of phosphates, ionic associates of $[FeHPO_4]^{+}$ and $[FeH_2PO_4]^{2+}$. The solubility of iron under aerobic conditions is influenced by the solubility of hydrated iron(III) oxide.

The equilibrium concentration of dissolved Fe(III) can also be limited by the presence of phosphate within a certain pH range. However, the effect of $FePO_4$ solubility is observed at $pH < 5$ at a phosphate concentration > 0.1 mmol l^{-1}. At $pH > 5$ $FePO_4$ slowly hydrolyses to $Fe(OH)_3$, simultaneously releasing phosphate ions. In anaerobic media phosphates can react with dissolved Fe(II) forms producing low soluble ferrous phosphate $Fe_3(PO_4)_2.8H_2O$.

Other anions with which Fe(III) forms complexes are the silicates; Fe(II) is less reactive with these species. This is used to limit the separation of hydrated Fe_2O_3 from waters, e.g. in water mains (this also concerns hydrated Mn(III) and Mn(IV) oxides). In waters containing 15–20 mg l^{-1} Si the Fe_2O_3 separates with difficulty. It is best stabilized in alkaline media at pH 7.5. The formation of cationic or anionic complexes is supposed, e.g. $[FeSiO(OH)_3]^{2+}$ and $[Fe(OH).O.Si(OH)_3]^-$. At higher concentrations of iron, polynuclear complexes can be formed.

We now consider Fe^{3+} hydrolysis. The hexaaquafferric cation $[Fe(H_2O)_6]^{3+}$ is more acid than hexaaquaferrous cation $[Fe(H_2O)_6]^{2+}$. The equilibrium constant of hydrolysis is approximately one order lower than that in phosphoric acid, whereas the equilibrium constant of the hydrolysis of Fe^{2+} is approximately one order higher than that in boric acid. During the hydrolysis the following essentially mononuclear complexes are produced: $[FeOH]^{2+}$, $[Fe(OH)_2]^+$, $[Fe(OH)_3(aq)]^0$ and $[Fe(OH)_4]^-$. By other reactions a series of polynuclear complexes is formed, for example, $[Fe_2(OH)_2]^{4+}$, $[Fe_3(OH)_4]^{5+}$, $[Fe_4(OH)_6]^{6+}$, etc. (for simplicity, the coordinated water molecules are omitted). First, colloid hydroxo complexes are formed and finally there is a precipitate of hydrated ferric oxide which is in fact a mixture of different polynuclear complexes. The distribution of polynuclear complexes depends not only on pH, but also on the initial concentration of iron. In diluted solutions of ferric salts a precipitate of hydrated Fe_2O_3 is separated only at a higher pH. The equilibrium between particular polynuclear complexes is established only very slowly.

We turn now to the *kinetics of* Fe(II) *oxidation.* The ability of Fe(II) and Fe(III) to undergo reversible oxidation and reduction plays an important role in the chemistry and biology af natural waters and water de-ironing. Dissolved iron is removed in the form of hydrated Fe_2O_3 from natural waters by oxidation with dissolved oxygen and subsequent hydrolysis and flocculation. The oxidation can be represented by the following equation:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \tag{3.73}$$

In hydrogen carbonate waters this reaction takes place as follows:

$$4Fe^{2+} + 8HCO_3^- + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8CO_2 \tag{3.74}$$

The rate of oxidation depends on pH, iron concentration and concentration of dissolved oxygen or its partial pressure [7]. As hydrogen ions are released during the reaction, the oxidation is accelerated in alkaline media. The oxidation rate within the pH range 5.0–7.5 can be described by the following kinetic equation:

$$\frac{\mathrm{d}c(\mathrm{Fe(II)})}{\mathrm{d}t} = kc(\mathrm{Fe(II)})c^2(\mathrm{OH}^-)p_{\mathrm{O}_2} \tag{3.75}$$

The dependence on pH is very marked. Within the above pH range the oxidation rate increases by about 100 times for a pH increase of one unit. In a more detailed description the effects of temperature and light are also taken into account. The positive or negative effect of different anions depends on the stability of their complexes with Fe(II) or Fe(III). If more stable complexes with Fe(III) are formed then the oxidation rate increases, and vice versa. Among the cations, copper has catalytic effects on the oxidation process. A higher buffer value of water has also a positive effect.

The Fe(II) oxidation rate is also influenced by organic matters which can be either complex-bonded or can have reduction effects. This concerns primarily humic substances. The complex-forming, oxidation-reduction and catalytic processes result in a condition in which iron of the oxidation state II can exist in humic waters in solution even in the presence of dissolved oxygen unless the organic substances are removed by a stronger oxidizing agent.

At low concentrations, hundredths to tenths of mg l^{-1}, iron is a common component of waters. Higher amounts of iron are found in the waters of peat moors where iron is bonded in complexes with humic substances and is kept in a stable colloid solution. In reservoirs and lakes the content of iron is stratified. On the bottom of reservoirs reduction processes take place to produce Fe(II) (anaerobic conditions). During spring and autumn circulation, Fe(II) is dispersed in the whole water column and it oxidizes at the surface to Fe(III) due to the contact with dissolved oxygen and is hydrolysed.

In oxygen-free groundwaters iron in the oxidation state II is present at concentrations of as many as tens of mg l^{-1}. Natural waters with amounts of iron above 10 mg l^{-1} are considered to be mineral waters and are called *ferruginous waters*.

The content of iron in surface and normal groundwaters is not significant from the viewpoint of hygiene. However, it influences the sensory properties of water. Taste is affected at concentrations from about 0.1–1.5 mg l^{-1}. At concentrations higher than 0.5 mg l^{-1} separation of the hydrated oxide under aerobic conditions can cause water turbidity unless the iron is bonded in stable complexes.

Low Fe concentrations in water can cause ***development of iron bacteria which can clog water piping***, and after they die out they cause an unpleasant odour in the water. Iron bacteria are autotrophic, obtaining energy by oxidation of Fe(II) to Fe(III), and they utilize CO_2 and its ionic forms as the source of carbon for the formation of new biomass.

Thus, iron in waters causes particular technological problems from the aspects of supplying drinking and service waters. Therefore, the concentration of iron in drinking waters should not exceed approximately 0.3 mg l^{-1}.

Iron is also undesirable in waters for industry as it causes rusty spots on materials. Its permissible concentration is sometimes lower than that in drinking water. For example, in the production of viscose staple, the maximum permissible quantity of iron in technological water is 0.05 mg l^{-1}. A strict limit is also imposed in the case of waters for textile and paper industries.

3.4.1.7 Manganese

In waters, manganese can occur in different oxidation states. In natural waters the oxidation states II, III and IV are of greatest importance. In water treatment, manganese in the oxidation state VII is sometimes used.

In the absence of soluble oxygen and other oxidizing agents Mn(II) *is the most stable form of occurrence in water.* For the dissolved forms, Mn^{2+}, $[MnOH]^+$, $[Mn(OH)_3]^-$, $[MnSO_4(aq)]^0$, $[MnHCO_3]^+$ should be considered, and at high concentrations of chlorides and in acid media also $[MnCl]^+$, $[MnCl_2]^0$ and $[MnCl_3]^-$ chloro complexes. As distinct from iron the relative representation of ion associates of $[MnSO_4]^0$ and $[MnHCO_3]^+$ can be quite significant in hydrogen carbonate and sulphate waters, and in some cases it can be as much as 50% of the total dissolved manganese. Among the organic complexes, those with humic substances are of particular significance.

The quantity of dissolved Mn(II) in natural waters depends on the solubility of hydroxide, carbonate and sulphide. In most natural waters the equilibrium concentration of dissolved manganese is determined by the $MnCO_3$ solubility. The production of $Mn(OH)_2$ is considered only in a stronger alkaline medium. In the presence of hydrogen sulphide and its ionic forms the Mn(II) solubility in alkaline media is limited by the MnS solubility and the equilibrium concentrations are the lowest under these conditions.

Manganese in the oxidation state II *is labile in waters containing dissolved oxygen under certain conditions.* It is oxidized and hydrolysed quickly in alkaline media. Relatively insoluble higher oxides of manganese in the oxidation states III and IV are separated.

Oxidation of Mn(II) and Mn(III) up to Mn(IV) accompanied by precipitation of hydrated oxides is an important process in the course of manganese removal from waters. *In comparison with* Fe(II), Mn(II) *is more resistant to oxidation.* Oxidation with dissolved oxygen proceeds more markedly only at pH > 9. On the contrary, it is easier to achieve reduction of Mn(III) or Mn(IV) to Mn and thus also dissolution and release of manganese from the sediments into the liquid media under conditions where the reduction of Fe(III) to Fe(II) does not yet take place.

The kinetics of Mn(II) *oxidation* with dissolved oxygen can be described by the following relationship:

$$\frac{\mathrm{d}c(\mathrm{Mn(II)})}{\mathrm{d}t} = k_0 c(\mathrm{Mn(II)}) + k_1 c(\mathrm{Mn(II)}) c(\mathrm{MnO_2}) p_{\mathrm{O_2}} \tag{3.76}$$

This kinetic equation involves an additive member containing the product of oxidation (in contrast to Fe(II) oxidation). *It is an autocatalytic reaction.* Therefore, when removing manganese from water, employing so-called *manganese filters*, it is first necessary to form a layer of higher hydrated oxides of manganese on the carrier, which is usually sand.

Complex forms of manganese in the oxidation state II are more resistant to oxidation by dissolved oxygen than a simple Mn^{2+} ion. Organic Mn(II) complexes with humic substances are very stable. Apart from the chemical oxidation of Mn(II) by dissolved oxygen, *biochemical oxidation with manganese bacteria* is also significant in waters. Fast biochemical oxidation takes place even in natural media. *The excessive growth of manganese bacteria can cause build up of biomass coating in water piping.*

Increased content of iron in water is usually observed together with increased content of manganese. The quantity of manganese is generally lower than that of iron, however, waters with roughly equal concentrations also exist. The concentrations are mainly lower than 1.0 mg l^{-1} due to the low solubility of $MnCO_3$, $Mn(OH)_2$ and MnS, respectively. High concentrations of manganese are found only in acid mine waters. In reservoirs and lakes the content of manganese is usually stratified, as in the case of iron.

Manganese has no adverse effects on health when present in the concentrations occurring in natural waters. However, it markedly influences the sensory properties of water, more so than iron does. The taste of water can be adversely influenced at concentrations greater than 0.1 mg l^{-1}. As distinct from iron, materials in contact with water change its colour at low concentrations. This also concerns the possibility of a more intense growth of manganese bacteria. Since manganese is more harmful than iron, its content in drinking and industrial waters is strictly limited. The World Health Organization recommends for drinking water a maximum concentration of 0.1 mg l^{-1}. However, the limits are even lower for waters used by textile and foodstuff industries.

3.4.1.8 Copper

Among the soluble forms of Cu^{2+} present in natural waters the following are to be taken into consideration: carbonate complexes $[CuCO_3(aq)]^0$ and $[Cu(CO_3)_2]^{2-}$, and hydroxo complexes $[CuOH]^+$, $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$. Important complex-forming substances are polyphosphates which can bond copper into stable chelate structures. Silicates, sulphates and nitrates do not form complexes with copper. Of the organic complexes, production of compounds with amino acids, polypeptides and humic substances are of interest.

The solubility of copper in natural waters in acid media is limited by the solubility of the alkaline carbonate, malachite $Cu_2(OH)_2CO_3$, and in the alkaline media by the solubility of $Cu(OH)_2$. However, it depends on the concentration of hydrogen carbonates. Depending on pH and hydrogen carbonates, only limited quantities of copper can be kept in the soluble form, this being of practical importance for the evaluation of its algicidal effects in reservoirs.

In surface waters the dissolved forms of copper are mostly complex compounds. Organic complexes with amino acids and humic substances, and the $[CuCO_3(aq)]^0$ carbonate complex prevail. Only a small fraction consists of the simple ionic form [8].

In common surface and groundwaters copper occurs only in tens of $\mu g\ l^{-1}$. Water stagnating in copper piping can contain even units of mg l^{-1}. Acid waters from the vicinity of ore deposits contain high concentrations of copper ranging from tens through hundreds of mg l^{-1}.

Copper is not so poisonous for humans as was assumed in the past. However, a concentration of 1–5 mg l^{-1} causes a very unpleasant taste of water. Compounds of copper are fairly toxic for fish.

When suppressing the excessive growth of algae a concentration of about 1.0 mg l^{-1} is usually applied which rapidly decreases since, depending on the composition of water, only a certain equilibrium concentration can be kept in the soluble form, this being lower than 1.0 mg l^{-1}.

3.4.1.9 Silver

Significant concentrations of silver occur only in some mine and industrial wastewaters (particularly the photographic industry). In natural waters it is present in trace amounts only. Slightly higher concentrations of silver can be found in the waters which were disinfected by silver ions because of their *oligodynamic properties.* Water in contact with silver or its slightly soluble compounds shows a decrease in the concentration of bacteria. Bactericidal effects are explained by the reaction of Ag^+ ions with proteins of living matter; such effects are observed at concentrations as low as 25 $\mu g\ l^{-1}$.

3.4.1.10 Zinc

The following soluble forms of zinc occur: Zn^{2+}, $[ZnOH]^+$, $[Zn(OH)_3]^-$ and $[Zn(OH)_4]^{2-}$. In waters with a higher concentration of hydrogen carbonates the $[ZnCO_3(aq)]^0$ ion associate is also significant and in waters with a higher concentration of sulphates, $[ZnSO_4(aq)]^0$. In industrial wastewaters from metal plating, various cyano complexes and amino complexes can also be present. The solubility of zinc is limited particularly by the solubility of $ZnCO_3$, $Zn_5(OH)_6(CO_3)_2.H_2O$, and in alkaline region also by the solubility of $Zn(OH)_2$. In normal surface and groundwaters usually 5–200 $\mu g\ l^{-1}$ are present. In water remaining in zinc vessels the Zn concentration can reach 5 $mg\ l^{-1}$. Exceptionally high concentrations are present in acid waters from ore mines.

The content of zinc in drinking water is limited by the World Health Organization to a value of 5 $mg\ l^{-1}$ with respect to organoleptic properties of water. As zinc has rather adverse effects on fish and other aquatic organisms only 0.05 $mg\ l^{-1}$ is permissible for streams.

3.4.1.11 Cadmium

Among the dissolved forms particularly Cd^{2+}, $[CdOH]^+$, $[CdCO_3(aq)]^0$, $[CdSO_4(aq)]^0$ occur, and in alkaline media mainly the hydroxo complexes $[Cd(OH)_3]^-$ and $[Cd(OH)_4]^{2-}$. Humic substances provide important organic complexes.

Cadmium in waters occurs together with zinc, but at much lower concentrations. The background in natural waters ranges from units to tens of $\mu g\ l^{-1}$. The artificial sources of cadmiun are wastewaters from the surface finishing of metals, photographic and printing industries. It can be leached from plastic piping as it is a component of their stabilizers.

The solubility of cadmium is limited by the solubility of $CdCO_3$, alkaline carbonates and $Cd(OH)_2$. Cadmium has quite a high accumulation coefficient which ranges from 5000 to 50,000. This concerns not only bottom sediments but also aquatic organisms.

Cadmium is one of the very dangerous poisons, therefore, the World Health Organization limits its maximum permissible concentration in drinking water to 0.005 mg l^{-1}.

3.4.1.12 Mercury

Among the soluble inorganic forms, Hg^0, Hg^{2+}, Hg_2^{2+}, $[HgOH]^+$, $[HgCl_2]^0$, $[HgCl_3]^-$, $[HgCl_4]^{2-}$, $[HgCl]^+$ and $[HgS_2]^{2-}$ are significant and in the organic forms particularly monoalkylmercury compounds and dialkylmercury compounds. The presence of Hg_2^{2+} is limited because of the disproportionation into Hg^0+Hg^{2+} in water. The concentration of elementary mercury, whose solubility in an oxygen-free medium is about 25 μg l^{-1}, can be significant. The solubility increases in waters containing dissolved oxygen, due to the formation of slightly soluble $Hg(OH)_2$. Mercury in natural waters bonds in the form of slightly soluble HgS in sediments under anaerobic conditions. In alkaline media the solubility of HgS increases due to the formation of the complex anion $[HgS_2]^{2-}$ which is of practical importance for mercury-containing wastewater treatment by precipitation with sodium sulphide. In the presence of higher concentrations of chlorides chloro complexes with 1–4 atoms of chlorine coordinated round the central atom are to be taken into consideration, particularly in wastewaters resulting from electrolysis.

In the group of organo-mercury compounds, phenylmercuric chloride used as pesticide should be mentioned. By biological processes either CH_3HgCl or CH_3HgCH_3 is formed from inorganically bonded mercury. These compounds are easily accumulated in the meat of fish living in the mercury-containing waters.

Mercury has one of the highest accumulation coefficients. It accumulates exceptionally intensively in sediments and aqueous flora and fauna. The values of accumulation coefficients presented are as high as 10^6.

The maximum Hg concentration recommended by the World Health Organization in drinking water is only 0.001 mg l^{-1} — the lowest value among all the toxic metals.

3.4.1.13 Lead

In natural waters, Pb^{2+} and $[PbCO_3(aq)]^0$ are the significant soluble forms. In the alkaline region also $[Pb(CO)_3]^{2-}$, $[Pb(OH)_2(aq)]^0$ and $[PbOH]^+$ complexes are to be considered. In waters with a high concentration of sulphates the $[PbSO_4(aq)]^0$ complex is also important. In addition, at high concentrations of chlorides different chloro complexes must also be taken into consideration.

The solubility of lead in hydrogen carbonate waters is chiefly dependent on the $PbCO_3$ solubility. In alkaline media $Pb_3(OH)_2(CO_3)_2$ and $Pb(OH)_2$ can be considered which, however, again dissolve in strongly alkaline media to form $[Pb(OH)_3]^-$. The solubility can also be significantly influenced by the presence of organic complex-forming substances.

Artificial and increasingly important sources of lead are exhaust gases of motor vehicles, which contain degraded products of tetraethyl lead. Via atmospheric precipitation, lead is introduced into surface waters. Since it has a high accumulation coefficient its major portion is removed from surface waters by sorption on the bottom sediments.

Lead is a traditional poison and it is very dangerous when present in waters. Therefore, no lead pipes are nowadays used for the distribution of drinking water.

The maximum concentration of lead in drinking water recommended by the World Health Organization is 0.5 mg l^{-1}. Comprehensive results on lead in the environment are presented elsewhere [9].

3.4.1.14 Arsenic

Arsenic usually occurs in water as As(V), but also in labile forms of As(III), it is frequently bonded in complexes with organic ligands. As(III) undergoes chemical and biochemical oxidation to form As(V). The most stable form in aerobic environment of waters is As(V). In neutral media particularly the ionic forms, $H_2AsO_4^-$ and $HAsO_4^{2-}$ should be taken into consideration. In neutral media and at a redox potential of approximately zero As(III) predominates, particularly its non-ionic form, H_3AsO_3.

In natural waters arsenic usually occurs at concentrations ranging from units to tens of μg l^{-1}. Mineral waters containing more than 0.7 mg l^{-1} of arsenic are called *arsenic waters*. Since the compounds of arsenic appear in company with phosphates, used as additives in detergents, as much as 0.1 mg l^{-1} can be found in the waters from laundries.

Arsenic has a considerable ability to accumulate in river sediments and aquatic organism. Similarly to mercury, organic methyl derivatives can be formed by the biological activity.

The arsenic compounds are poisonous, especially As(III), causing chronical diseases. The maximum concentration of arsenic in drinking waters recommended by the World Health Organization is 0.05 mg l^{-1}.

3.4.1.15 Selenium

Selenium occurs in waters in the oxidation state IV in the form of simple or complex anions, for example, SeO_3^{2-}, $HSeO_3^-$, $[Se(OH)_6]^{2-}$, and the like. In natural waters it is present only in trace quantities. However, in some areas its amount in water can be very high, reaching tens of mg l^{-1}.

The compounds of selenium are fairly dangerous. The maximum concentration of selenium in drinking waters permitted by the World Health Organization is 0.01 mg l^{-1}.

3.4.1.16 Chromium

Chromium can occur in water either in the oxidation state III or VI. Cr(III) possesses significant complex-forming properties. The Cr(VI) forms are stable in aerobic media. In anaerobic media Cr(VI) can be reduced to Cr(III), chromium is eliminated from the liquid phase in the form of low soluble hydrated chromic oxide.

The oxidation of Cr(III) to Cr(IV) by oxygen dissolved in water is very slow and takes place only in alkaline media.. On the other hand, reduction of Cr(VI) in natural waters by bivalent iron is possible especially in acid media and by sulphites and hydrogen monosulphide. The maximum concentration of Cr(VI) in drinking water permitted by the World Health Organization is 0.05 mg l^{-1}.

3.4.1.17 Other metals

Nickel can enter natural waters primarily from wastewaters discharged from plants involved in the surface finishing of metals.

Organically bonded *cobalt* occurs in the sludge from biological wastewater treatment plants in the form of vitamin B_{12}.

Molybdenum can be toxic at higher concentrations. It is intensively accumulated by plants.

Vanadium, when present in waters at certain concentrations, is considered to be an indicator of crude oil occurrence and it perhaps has balneological effects. At low concentrations it probably has static effects on dental caries, however, it is toxic at higher concentration.

Most of the elements of the periodic system occur in waters, including the elements of rate earths. However, these concentrations are very low and do not cause any hygienic or technological problems. Recently, attention has been paid to the remarkable toxicity of *beryllium*. The compounds of beryllium are used in the production of rocket fuels, fluorescent lamps and they occur in wastewaters from beryllium processing works.

3.4.1.18 Fluorine and chlorine

Fluorine occurs in waters largely in the form of the simple anion F^-, sometimes also as hexafluorosilicates SiF_6^{2-} and complex compounds with metals, particularly with Fe(III) and Al(III) (fluoroferrates and fluoroaluminates). The concentration of fluorides in waters is limited by the solubility of CaF_2 and MgF_2. As CaF_2 is less soluble than MgF_2 the equilibrium concentration of fluorides in water depends primarily on the concentration of calcium.

The concentration of fluorides in natural waters ranges from hundredths to tenths mg l^{-1}. Concentrations exceeding 1 mg l^{-1} are exceptional.

Fluorine in waters is of special hygienic importance from the viewpoint of stomatology. Health disorders can occur in the case of both deficiency and excess of fluorine in drinking water. At higher concentrations a chronical disease occurs — fluorosis which is manifested by spots on the teeth (*dential fluorosis*). Therefore, the limiting content of fluorides in drinking water is 1.5 mg l^{-1}. On the other hand, concentrations of fluorine in drinking water lower than 0.5 mg l^{-1} can result in more intensive occurrence of caries, particularly in children. The optimum concentration of fluorides in drinking water is 1.0 mg l^{-1} as it has both *caries-prophylactic* and *caries-static effects.* Since most natural waters contain only a low content of fluorine, fluorides are often added to drinking waters (*fluoridation*) to prevent the formation of caries. The biological activity of fluorine depends on the form of its occurrence. It appears that fluoroaluminates are biologically less effective. However, it seems that in natural waters with $pH > 7$ and at a concentration of a free fluoride ion of approximately 1.0 mg l^{-1} no fluoroaluminates are formed because the competing capability of hydroxyaluminates is quite significant [10]. For fluoridation, fluorides or fluorosilicates are recommended. Fluorosilicates are gradually hydrolysed in water according to the equation:

$$SiF_6^{2-} + 2H_2O = 6F^- + 4H^+ + SiO_2 \tag{3.77}$$

Mineral waters with a concentration of fluorides more than 2.0 mg l^{-1} are called *fluorine* (*fluoride*) *waters.*

Chlorine is present in waters primarily in the form of the simple Cl^- anion, and in some cases also in the form of chloro complexes, for example, $[FeCl]^+$, $[FeCl_2]^+$, $[FeCl]^{2+}$, $[FeCl_3]^-$, $[FeCl_4]^{2-}$, etc. Of other forms of occurrence of chlorine, elementary chlorine, non-dissociated hypochlorous acid HClO, ClO^- anion and different chloramines should be considered, followed by organically bonded chlorine which may originate from the wastewaters of chemical industry, and from chlorinated pesticides. However, it can also enter the water via the chlorination of polluted waters.

Chlorine occurs most widely in the form of *chlorides.* In nature this anion is present in all waters at fairly high concentrations. *Together with hydrogen carbonates and sulphates chlorides are the chief anions in waters.* In surface and normal groundwaters they are present in amounts ranging from units to tens of mg l^{-1}. Chlorides may predominate in groundwaters from great depths.

Man excretes about 9 g of chlorides per day in urine, which increases the original content of chlorides in sewage. If chlorides are of animal origin, they indicate faecal pollution. High concentrations of chlorides occur in some industrial wastewaters (salting-out of products with sodium chloride, neutralization of HCl-containing waters).

Chlorides are relatively stable, both chemically and biochemically. They do not change in natural waters. During infiltration they are only slightly adsorbed on different soil minerals. They have no adverse effects from the viewpoint of hygiene, however, they affect the taste of water. But the threshold concentration of taste also depends on the relative amounts of some cations. A concentration of 150 mg l^{-1} does not influence the sensory properties of water. The maximum concentration of chlorides in drinking waters recommended by the World Health Organization is 250 mg l^{-1}.

The presence of *elementary chlorine* in water is not natural. It is introduced into waters via disinfection by chlorination or where chlorine is used as an oxidizing agent. Chlorine react with water according to the following equation:

$$\begin{aligned} Cl_2 + H_2O &\rightleftharpoons HClO + H^+ + Cl^- \\ HClO &\rightleftharpoons H^+ + ClO^- \end{aligned} \tag{3.78}$$

A solution of chlorine in waters is not stable when exposed to sunlight and it undergoes a photochemical decomposition according to the following reaction:

$$2HClO \rightarrow 2H^+ + 2Cl^- + O_2 \tag{3.79}$$

Depending on pH and redox potential the following forms can occur in water: Cl_2, HClO, ClO^- and Cl^-. In the presence of ammonia nitrogen, chloramines are formed during the chlorination of water. In neutral media primarily HClO reacts:

$$\begin{aligned} NH_3 + HClO &\rightarrow NH_2Cl + H_2O \\ NH_2Cl + HClO &\rightarrow NHCl_2 + H_2O \\ NHCl_2 + HClO &\rightarrow NCl_3 + H_2O \end{aligned} \tag{3.80}$$

Distribution of mono-, di- and trichloramines depends on pH, temperature, time of reaction and mass ratio of chlorine and ammonia nitrogen. At a certain ratio chloramines are degraded to form elementary nitrogen or dinitrogen monoxide. This process can be represented by the following summary reactions:

$$\begin{aligned} 2NH_3 + 3Cl_2 &\rightarrow N_2 + 6H^+ + 6Cl^- \\ 4NH_3 + 7Cl_2 + H_2O &\rightarrow N_2 + N_2O + 14H^+ + 14Cl^- \end{aligned} \tag{3.81}$$

Chlorine dissolves in water to form chlorine water. At 10°C about 10 g l^{-1} can be dissolved, and the above reactions (3.78) take place. The solution of chlorine has both chlorinating and oxidizing effects. In hydrochemistry the term "active chlorine" denotes all forms of chlorine which oxidize iodides into iodine in acid media. It is necessary to differentiate between *free active chlorine* (molecular chlorine, hypochlorites, chlorine dioxide) and *bonded active chlorine* (active chlorine in chloramines). In water, chloramines are slowly hydrolysed into hypochlorites, and they are weaker oxidizing agents than chlorine. The oxidation of Fe(II) and Mn(II) by chloramines is not very effective.

To ensure hygienically safe drinking water it is necessary to remove the remaining concentrations of chlorine from the water; active chlorine at higher concentrations also influences the sensory properties. Therefore, the concentration of active chlorine in drinking water should range from 0.05 to 0.3 mg l^{-1}. Active chlorine is rather harmful for fish as well as for other aquatic organisms. Its concentration in surface waters should not be higher than 0.15 mg l^{-1}.

3.4.1.19 Bromine and iodine

These elements are present in waters predominantly in the form of simple Br^- and I^- anions. The amount of iodides is usually lower than that of bromides. In atmospheric waters they are of either ***natural origin*** (coastal areas) or ***artificial*** (industrial air pollution). In normal ground- and surface waters, they are usually present in trace quantities only; there are higher concentrations in the sea and in mineral waters.

Mineral waters containing at least 5 mg l^{-1} of iodides are called *iodine (iodide) waters.* They are important in the treatment of some forms of tuberculosis and positively influence the function of glands with internal secretion. Deficiency of iodine causes hypertrophy of the thyroid gland.

3.4.1.20 Sulphur compounds

In natural and wastewaters, inorganic compounds of sulphur in the oxidation states II, 0, IV and VI may be present. They include sulphates, sulphites, thiosulphates, thiocyanates, hydrogen sulphide and its ionic forms, polysulphides and elementary sulphur.

Sulphates occur in water predominantly in the form of simple $SO_4{}^{2-}$ anions; in waters with high concentrations of sulphates ionic associates with some cations, e.g. $[CaSO_4(aq)]^0$, $[MnSO_4(aq)]^0$ and others are also present. *Together with hydrogen carbonates and chlorides they provide the essential part of the anions in natural waters.* In normal ground- and surface waters the content of sulphates ranges from tens to hundreds of mg l^{-1}. Some mineral waters are particularly rich in sulphates.

From the chemical viewpoint sulphates are quite stable. However, *under anaerobic conditions they fairly easily undergo biochemical reduction to hydrogen sulphide and can almost disappear from water.* Under certain conditions elementary sulphur can also separate as a transient oxidation state. These processes can be represented as follows:

$$\begin{array}{rcl} SO_4^{2-} + 8H^+ + 6e^- & \rightarrow & S(s) + 4H_2O \\ S(s) + 2H^+ + 2e^- & \rightarrow & H_2S \end{array} \qquad (3.82)$$

Sulphates at concentrations occurring in surface and usually in groundwaters are irrelevant from the aspects of hygiene. However, high concentrations can influence the taste of water and have laxative effects. The maximum concentration of sulphates recommended by the World Health Organization is 400 mg l^{-1}.

A higher content of sulphates in water causes aggressiveness towards concrete. Permissible concentration of sulphates depends on the quality of concrete and other factors. The aggressive effects on concrete are due to the formation of ettringite (Candlot's salt), $Ca_6Al_2[SO_4(OH)_4]_3$ which crystallizes with 30–33 molecules of water, thus considerably increasing its volume and influencing the neighbouring material via crystallization pressure.

Sulphites rarely occur in natural waters. They are chiefly of artificial origin (wastewaters from the production of sulphite cellulose and thermal processing of coal). They are washed out into atmospheric waters from urban and industrial air pollutants. In waters, sulphites are slowly oxidized into sulphates, consuming dissolved oxygen. Chemical oxidation is accelerated by catalytic effects of various metals, particularly the Co(II) compounds. In water treatment, sulphites are used for dechlorination, removal of oxygen from feed waters for steam boilers, and in the technology of wastewaters for reduction of Cr(VI) to Cr(III).

Thiosulphates occur in natural waters only exceptionally. They are of natural origin in some mineral waters in which they accompany hydrogen sulphide and its ionic forms. Their artificial origin in wastewaters comes from the thermal processing of coal, dying plants, leather plants, etc.

Thiocyanates do not occur naturally in waters, but they are present in wastewaters from the thermal processing of coal. They can also be formed by secondary processes, chemical reactions of biochemical processes between cyanides and some compounds of sulphur.

We now consider *hydrogen sulphide and its ionic forms.* Sulphidic sulphur can occur in waters in the form of either non-dissociated hydrogen sulphide, H_2S, simple HS^- and S^{2-} ions, or some complex ions, e.g. $[HgS_2]^{2-}$. Within the range of pH 7.5–12 the HS^- ion predominates. At $pH < 6$ non-dissociated H_2S predominates in water. The second dissociation of H_2S is significant only in strongly alkaline media. Apart from these forms, polysulphides can also be present in water probably as intermediates in the oxidation of hydrogen sulphide.

Hydrogen sulphide and its ionic forms are labile in waters since they can be oxidized to sulphates via chemical or biochemical reactions. In waters they can occur permanently only in anaerobic media and therefore they are evidence of reduction processes taking place in such waters. Chemical oxidation of hydrogen sulphide by oxygen dissolved in water is a very complex process. Intermediates of the oxidation are probably polysulphides, sulphites, thiosulphates and elementary sulphur. The oxidation rate depends on pH (it is very low at pH < 6) and on the presence of catalysts (Mn^{2+}, Ni^{2+} and Co^{2+}) [11, 12].

Mineral waters containing at least 1 mg l^{-1} of sulphide and thiosulphate sulphur are called *sulphur* (*hydrogen sulphide*) *waters.* Mineral waters of oil origin are particularly rich in hydrogen sulphide.

Hydrogen sulphide and its ionic forms can cause corrosion of concrete sewage piping. In anaerobic media in sewage, hydrogen sulphide is generated and escapes into the atmosphere, where it is biochemically oxidized to free sulphuric acid via the sulphur bacteria from slimy layers on the walls of sewers. This acid can seriously damage the lining of the sewer roofs. For such aggressive effects, concentrations of about 1 mg l^{-1} of H_2S in wastewaters is sufficient [13].

Hydrogen sulphide seriously affects the sensory properties of water. The threshold odour concentration depends on pH because this odour is caused by non-dissociated H_2S. Drinking water should have concentrations not greater than 0.01 mg l^{-1} H_2S. Hydrogen sulphide is very poisonous for fish.

3.4.1.21 Phosphorus compounds

Inorganically bonded dissolved phosphorus occurs in water in simple or complex ionic or non-ionic forms, or in the form of polyphosphates.

Orthophosphates occur particularly in the following forms: PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, $[CaHPO_4]^0$, $[FeHPO_4]^0$, etc.

Polyphosphates occurring in water have either linear structures (catena-polyphosphates) or cyclic structures (cyclo-polyphosphates).

Of the *catena-polyphosphates*, particularly catena-diphosphates $P_2O_7^{4-}$, $[CaP_2O_{10}]^{2-}$ and eventually catena-triphosphates $P_3O_{10}^{5-}$, $[CaP_3O_{10}]^{3-}$ and others are to be considered in the hydrochemistry and technology of water. This group involves the polyphosphate frequently also used in the technology of water, incorrectly called *hexametaphosphate.* It is a catena-polyphosphate with 20–60 atoms of phosphorus per molecule. A general formula of the *cyclo-polyphosphates* is $(HPO_3)_n$, for example, cyclo-triphosphates $P_3O_9^{3-}$ ($n = 3$) or cyclo-tetraphosphates $P_4O_{12}^{4-}$ ($n = 4$).

Polyphosphates are able to bond different cations into complexes keeping them in this way in the soluble form even in the presence of some anions with which they would otherwise form insoluble compounds. Therefore, they find wide application possibilities in the textile industry, laundries, in the treatment of cooling and boiler waters in all places where higher concentrations of calcium, magnesium, iron, manganese and other cations cause problems.

The solubility of orthophosphates in water is limited by the solubility of hydroxylapatite, $Ca_5(PO_4)_3(OH)$, $Mg_3(PO_4)_2$, $FePO_4$, $AlPO_4$, $Fe_3(PO_4)_2$, etc. The formation of these low-soluble phosphates is used for chemical removal of phosphates from water. In the case of anaerobic stabilization of sludge, piping can get clogged by very low soluble $MgNH_4PO_4$ as the recycling sludge water contains higher concentrations of ammonia nitrogen and phosphates, and the pH is in the alkaline region [6].

The formation of many low-soluble compounds with commonly occurring cations in waters causes very low concentrations of phosphates in both natural and wastewaters. The concentration of phosphates in surface waters can be several tenths mg l^{-1}. More rich in phosphates are waters from peat moors which can sometimes contain as much as 1 mg l^{-1}. Due to detergents and application of phosphates in agriculture their content is continually increasing in natural waters. To prevent further undesirable increase of phosphates in surface waters their application in the production of synthetic detergents is now limited.

Man excretes about 1.5 g phosphorus per day which is discharged into sewage wastewaters; the use of synthetic detergents for washing in households thus resulted in a doubled amount of phosphates in sewage.

The compounds of phosphorus play an important role in the natural turnover of substances. They are of vital importance for lower and higher organisms. After the death and decay of organisms phosphates are again released into the environment. Phosphates are particularly important for the growth of green organisms in water. For the synthesis of 100 mg of biomass of algae about 1 mg phosphorus is required. Higher concentrations of phosphates in surface waters are not desirable as they support intensive growth of algae and cyanobacteria. They contribute to the so-called *eutrophication* of water.

The content of phosphates in groundwaters to be used for drinking water supplies is considered to be an indicator of faecal pollution if they are of organic origin. As phosphates are well retained in soil, their indicator value is significant.

Polyphosphates hydrolyse in water according to the following reaction:

$$P_3O_{10}^{5-} + 2H_2O \rightleftharpoons 3PO_4^{3-} + 4H^+ \tag{3.83}$$

The rate of hydrolysis is influenced by pH, temperature and calcium concentration. Calcium shifts the chemical equilibrium of this reaction to the right as it bonds the orthophosphate ions formed. In addition to chemical hydrolysis, biochemical hydrolysis also takes place in waters, particularly in sewage with a dense biological population. A considerable part of polyphosphates in sewage fed into wastewater treatment plants is hydrolysed. The half-time of polyphosphates in surface waters is given in days and tens of days.

The peptization capabilities of polyphosphates depend on their sorption on aluminosilicates and colloidal particles of hydrated oxides of iron, aluminium and manganese. In practice, this causes problems in water treatment by coagulation when already rather low concentrations of polyphosphates can cause improper agglomeration of colloidal particles into sedimentable floccules.

3.4.1.22 Nitrogen compounds

Together with phosphorus, nitrogen is one of the most important macrobiogenic elements. The compounds of nitrogen are involved in all biological processes in natural and wastewaters, and such compounds can be of either *inorganic* or *organic origin.* Sewage is one of the sources of organic nitrogen. Man produces about 12 g of N per day. The nitrogen compounds in wastes from agricultural operations (manure, silage waste) are also of organic origin. Inorganic sources of nitrogen are wastes from agricultural land fertilized with mineral nitrogen fertilizers, atmospheric waters particularly in the period of storms, and some industrial wastewaters (e.g. from thermal processing of coal). Elementary nitrogen is considered in Section 3.4.1.26.

Nitrogen compounds undergo numerous biochemical transformations in water. Organic nitrogen substances are decomposed by microbial activity and nitrogen is usually released by deamination in the form of ammonia nitrogen. On the other hand, ammonia nitrogen is utilized by microorganisms as a source of nitrogen for the synthesis of new biomass. In some cases molecular nitrogen can be transformed by some bacteria and algae directly to organically bonded nitrogen. If the degradation of organic nitrogen compounds takes place under anaerobic conditions the ammonia nitrogen formed is not further changed. Under aerobic conditions ammonia nitrogen can be oxidized by nitrifying bacteria into nitrite and even to nitrate nitrogen. This process is called *nitrification* and takes place in two steps:

$$\begin{array}{rcl} 2NH_3 + 3O_2 & \rightarrow & 2NO_2^- + 2H^+ + 2H_2O \\ 2NO_2^- + O_2 & \rightarrow & 2NO_3^- \\ \hline 2NH_3 + 4O_2 & \rightarrow & 2NO_3^- + 2H_2O + 2H^+ \end{array} \qquad (3.84)$$

For complete oxidation of 1 g of ammonia nitrogen, 4.57 g of oxygen is consumed.

During nitrification hydrogen ions are released which react with hydrogen carbonates commonly present in waters. If the buffering capacity of water is insufficient, the pH value drops significantly.

In the reverse direction, under anaerobic conditions reduction of nitrites and nitrates into elementary nitrogen, and eventually to N_2O and NO can take place. This process is called *denitrification*, in which nitrogen is removed from the liquid phase into the atmosphere. Biochemical reduction to ammonia nitrogen is rare; it does, however, take place, for example, during fixation of elementary nitrogen by some green organisms. Denitrification can result in the loss of nitrogen during biological wastewater treatment. For denitrification, an organic substrate as the source of energy is essential. Denitrification can take place in either strictly aerobic environment or at very low concentrations of dissolved oxygen. In acid media the rate of denitrification is lower and more oxides of nitrogen are formed. Nitrates are biologically reduced in priority to sulphates. Therefore, in an oxygen-free media hydrogen sulphide is not formed by the reduction of sulphates until there are no more nitrates in the water.

We now consider in turn the various forms in which nitrogen may occur in the environment, ammonia, nitrite, nitrate, cyanide and cyanate.

Ammonia nitrogen occurs in the form of either non-dissociated ammonia, NH_3, which is hydrated in water, or the cation NH_4^+. Relative representation of the two forms depends on pH. At a pH of approximately 9.3 the ratio of molar concentrations is approximately 1:1.

Ammonia nitrogen is the primary product of the decomposition of organic animal and plant substances. Therefore, it occurs at high concentrations in sewage and in the wastes from agricultural production plants (silage liquids, urine). It is of inorganic origin in wastewaters (from thermal processing of coal), in atmospheric waters, and its other sources are washings from soil to which nitrogen fertilizers have been applied.

As there is always a small amount of ammonia nitrogen in the atmosphere, its traces can be found in almost every surface water. There are usually tenths mg l^{-1} of ammonia nitrogen in atmospheric waters, but in industrial waters its concentration can increase to units of mg l^{-1}. Organically polluted surface waters can also contain ammonia nitrogen in units of mg l^{-1}. This is also the case for waters from peat moors, where it is produced via degradation of organic nitrogen substances of plant origin. Exceptionally high concentrations are found in some industrial wastewaters and waste from agricultural plants.

Ammonia nitrogen is very labile under aerobic conditions in natural waters. It is transformed into nitrites and even nitrates by biochemical oxidation (nitrification). *Chemical oxidation is difficult.* Ozone, potassium permanganate and potassium dichromate are ineffective. In only a few cases can partial oxidation be achieved in aqueous solutions using catalysts. An efficient oxidizing agent is chlorine which — depending on the reaction conditions — can provide a mixture of different chloramines, elementary nitrogen or nitrogen monoxide.

Ammonia nitrogen is essential for the production of a new biomass of microorganisms. Due to the activity of heterotrophic and autotrophic microbes it is transformed into organically bonded nitrogen. The NH_4^+ ions are strongly absorbed in soil, undergoing ion exchange. Ammonia nitrogen markedly increases corrosion of copper and its alloys, especially if the concentration of ammonia nitrogen is higher than 10 mg l^{-1} and the pH is greater than 8.5.

Ammonia nitrogen is of great importance from the viewpoint of hygiene as it is one of the primary product of degradation of organic nitrogen substances and one of the important chemical indices of groundwater pollution with animal wastes. However, it is necessary first to rule out any possible inorganic origin.

Ammonia nitrogen is fairly toxic for fish, the toxicity being caused primarily by non-dissociated ammonia and not the NH_4^+ ions. Non-toxic concentrations of NH_3 for fish range from 0.01 to 0.04 mg l^{-1}.

Nitrites occur as the simple NO_2^- anion. It is formed particularly by biochemical oxidation of ammonia nitrogen or biochemical reduction of nitrates. Some industrial wastewaters are very rich in nitrites, for example those from the production of some dyestuffs or from engineering works employing cutting liquids for cooling of machine tools; such liquids contain nitrites as corrosion inhibitors. Nitrites in waters occur with nitrates and ammonia nitrogen only at low concentrations since they are *biochemically and chemically labile.* In clean ground- and surface waters only trace amounts are present. Higher contents of nitrites can be found in iron and peat moor waters, where they are formed by reduction processes. In seriously polluted natural waters they occur exceptionally at concentrations > 1 mg l^{-1}.

Nitrites are insignificant from the viewpoint of hygiene at the concentrations occurring in ground- and surface waters. The problems concerning their higher concentrations are discussed in the section dealing with nitrates. They cause *methaemoglobinaemia.*

Nitrites are one of the important indicators of pollution of groundwaters, if formed by transformations from organically bonded nitrogen in animal wastes. Industrial water for the wool industry should not contain nitrites which could cause a yellow colour of wool in more acid media as well as difficulties during dyeing.

Nitrates, occurring most frequently as the simple NO_3^- anion, are found in much higher concentrations than nitrites. They are formed especially by secondary pathways during nitrification of ammonia nitrogen. Another source is the drainage from agricultural land to which nitrogen fertilizers have been applied. In the case of electric discharges in the atmosphere, nitrates are formed by oxidation of elementary nitrogen; they are then transported into atmospheric waters. Nitrates are the final step of degradation (mineralization) of organic nitrogen substances in an aerobic environment.

Nitrates occur at low concentrations in almost all waters. Higher concentrations can be found in groundwaters in the vicinity of large towns and old settlements, as well as in groundwaters of agricultural areas. In clean normal ground- and surface waters, concentrations of units mg l^{-1} are usually present. However, in some areas waters containing tens to hundreds mg l^{-1} of nitrate nitrogen are present.

Nitrates are stable in water under aerobic conditions.

Under anaerobic reduction conditions they are biochemically reduced to nitrites, elementary nitrogen or nitrogen monoxide, and eventually even to ammonia nitrogen. The chemical reduction of nitrates is also possible, in iron waters in alkaline media.

Denitrification due to which the nitrogen compounds are lost from water in the form of N_2 or N_2O is of particular importance in the technology of water. It has been suggested for the removal of excessive amounts of inorganically bonded nitrogen from wastewaters after their biological treatment so that the recipient is not overloaded with nutrients supporting an excessive growth of undesirable organisms. After exhaustion of dissolved oxygen in water, nitrates can temporarily serve as the source of oxygen for biological oxidation of organic substances.

Nitrates themselves have little direct adverse effects on man. However, they can become harmful indirectly as they are reduced in the gastrointestinal tract by microbial activity into the more toxic nitrites. Nitrites react with haemoglobin to form methaemoglobin which is not able to transfer oxygen in blood. A risk dose of nitrites for adults is approximately 500 mg; for sucklings it is about 1–10 mg NO_2^-. The forms of diseases depend on the amount of methaemoglobin in blood. A low-level clinical form is manifested by cyanosis and tachycardia. The condition is called nitrate alimentary methaemoglobinaemia, and it can be observed in regions with drinking water containing high amounts of nitrates which is used for the preparation of artificial nourishment for sucklings.

Furthermore, nitrites formed by the reduction of nitrates can react with secondary amines in the gastrointestinal tract to produce potentially carcinogenic nitrosoamines.

The World Health Organization recommends limiting the concentrations of nitrite and nitrate nitrogen to 10 mg l^{-1}, emphasizing that this value exceeds the content of nitrates in water which can be used for the preparation of nourishment for sucklings.

Organically bonded nitrogen occurring in natural waters is of either animal or plant origin, or it originates from some of industrial wastewaters, primarily from the foodstuff industry. The main forms of organic nitrogen in natural and sewage wastewaters are proteins and their degradation products (peptides, peptones, amino acids) and urea. The resulting product of biological transformations of organic nitrogen is most frequently ammonia nitrogen. It is determined particularly in waste- and sometimes in surface waters, and is important for tracing the technological processes of wastewater treatment and for the evaluation of biological sludge.

Cyanides occurring in natural waters are never of natural origin. They originate from industrial wastewaters, for example, from electroplating and the thermal treatment of coal. Cyanides can occur in waters in the form of *simple* (HCN, CN^-) or *complex* forms. The sum of the various species forms gives total amount of cyanides.

Hydrogen cyanide is a very weak acid in aqueous solution with a dissociation constant of approximately 10^{-9}. In neutral and acid media non-dissociated HCN predominates, so that hydrogen cyanide can be eliminated from simple cyanide solutions by such weak acids as H_2CO_3 or H_3BO_3. If non-dissociated HCN predominates it can be removed from the solution by simple aeration.

The CN^- anion has a great ability to coordinate as a ligand and to provide a series of complex cyanides which are common in wastewaters from metal surface finishing. The most stable are complexes of Fe(II), Fe(III), $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and complex cyanides of cobalt. The complex cyanides of cadmium, zinc, copper and nickel, for example $[Cd(CN)_4]^{2-}$, $[Zn(CN)_4]^{2-}$, $[Cu(CN)_2]^-$, $[Ni(CN)_4]^{2-}$ and others, have lower stabilities. Their behaviour depends on the magnitude of the stability constants; the stability constants of cyano complexes of cadmium and zinc are so low that the complexes are almost completely dissociated into simple cyanides in diluted solutions.

Simple cyanides and some less stable complex cyanides undergo, in water, chemical and biochemical decomposition processes, hydrolysis and oxidation. The decomposition is stimulated by free CO_2 in water:

$$CN^- + CO_2 + H_2O \rightarrow HCO_3^- + HCN \quad (3.85)$$

$$HCN + 2H_2O \rightarrow HCOOH + NH_3 \quad (3.86)$$

Simple cyanides are very toxic. In the case of complex cyanides, the toxicity depends on the stability constants as given by that fraction of HCN which is able to split off.

The maximum allowed concentration of CN^- in drinking water recommended by the World Health Organization is 0.1 mg l^{-1}

Cyanates occurring in waters are not of natural origin. They are formed during chemical treatment of cyanide wastewaters by oxidation with chloride, or during biological treatment of wastewaters containing cyanides. They are about one thousand times less toxic than free cyanides. They are stable only in alkaline media, readily undergoing hydrolysis in neutral and acid media according to the following equation:

$$OCN^- + 2H_2O + H^+ \rightarrow NH_4^+ + HCO_3^- \quad (3.87)$$

3.4.1.23 Silicon

Silicon is observed in waters following the decomposition of aluminosilicates under the effects of CO_2 and H_2O. The solubility of amorphous and crystalline SiO_2 (quartz) is also quite significant. Artificial sources of silicon in waters are some industrial wastewaters of inorganic-based industry (e.g. in glass and ceramic production).

In natural waters with pH < 9 *silicon occurs primarily in the soluble monomer non-ionic form as orthosilicic acid,* $Si(OH)_4$ *and partially in the colloidal form. In the past it was assumed that the colloid-soluble forms predominated.*

Tetrahydrogensilicic acid is very weak, dissociating at the first step into the $[SiO(OH)_3]^-$ anion which is frequently written as $HSiO_3^-$.

In water, about 120 mg l^{-1} of amorphous SiO_2 dissolves at 25°C and 6–12 mg l^{-1} of quartz. Supersaturated solutions are formed easily and polymerization is initiated. However, the equilibrium is achieved only very slowly. Ionic forms of silicon in waters can be considered only in stronger alkaline media, at $pH > 9$. This concerns, for example, mononuclear complexes, such as $[SiO(OH)_3]^-$, $[SiO_2(OH)_2]^{2-}$, $[Si(OH)_5]^-$ and $[Si(OH)_6]^{2-}$. At $pH > 9$ and at higher concentrations different polynuclear hydroxo complexes of polysilicates can be formed, for example, $[Si_4O_6(OH)_6]^{2-}$, $[Si_2O_3(OH)_4]^{2-}$ and others.

By acidification of the silicate solutions colloid polymer forms, colloidal hydrated SiO_2, are slowly separated. Absorbed silicate anions give the colloidal particles a negative charge. Silicates can form complexes with Fe(III) and Mn(II); their importance was mentioned in the section dealing with iron.

Because of very wide distribution of the silicon compounds in nature, silicates occur in almost all natural waters. In surface and fresh groundwaters concentrations are commonly up to 10 mg l^{-1}. Exceptionally high contents of silicon are found in hot waters of geysers, hundreds mg l^{-1}, from which hydrated SiO_2 is separated in the form of opal by cooling and evaporation after the emergence of the water at the surface.

For some microorganisms (diatoma) silicon compounds are of vital importance. They form a cell wall containing hydrated SiO_2. Siliceous shells of diatoms from ancient geological eras form layers, making the so-called *diatomaceous earth* which is important in the technology of water as a filtering material.

The silicon compounds are not significant in waters, from the viewpoint of hygiene. Higher silicon concentrations are undesirable in waters to be used for the textile industry and breweries. They cause special problems in the case of feed and boiler waters because they form dangerous silicate coatings (silicate boiler incrustation) via the reaction with calcium, magnesium, iron, aluminium and sodium. These coatings have a very low heat conductivity. At higher pressures, so-called hard coatings of the type $Na_2O.R_2O_3.xSiO_2.yH_2O$ can be formed.

3.4.1.24 Boron compounds

Boric acid, $B(OH)_3$ is a very weak acid. It forms the anion $[B(OH)_4]^-$ in aqueous solutions. At concentrations < 0.025 mol l^{-1} it is usually present in the monomolecular form. At higher concentrations polymers are formed which can have either chain or circular structures. Depending on the pH the monomolecular form can occur in either a non-ionic or an ionic form. At the pH of natural waters the non-ionic form predominates and therefore boron in waters is considered to be a non-electrolyte. The considerable tendency of boric acid to form complex compounds complicates the distribution and increases the number of the possible forms of the occurrence in waters.

An artificial source of boron in waters is sewage containing borates from detergents, and some industrial wastewaters, e.g. from glass, ceramic, photographic and foodstuff industries. In surface waters the content of boron of natural origin ranges from thousandths to hundred thousandths mg l^{-1}. Higher concentrations can be found in surface waters which are recipients of sewage. In such cases the concentrations of borates can exceed even a value of 1 mg l^{-1}.

The content of boron in sewage is gradually increasing due to the increase of the use of washing agents; concentrations as high as 5 mg l^{-1} can be found.

Boron does not represent any health hazard if present at the concentrations occurring in clean surface and fresh groundwaters. However, its presence is not suitable in irrigation waters as it inhibits the growth of plants. Therefore, the concentration of boron in these waters should be limited to values ranging from 0.5–2.0 mg l^{-1}

3.4.1.25 Oxygen (elementary)

Oxygen enters water via diffusion from the atmosphere and it is generated by photosynthetic activity of aqueous plants. It is consumed during aerobic decomposition of organic substances, oxidation of some inorganic compounds and respiration of the organisms present.

In clean surface waters the concentration of dissolved oxygen is about 85–95% of saturation and varies throughout the day. These diurnal variations depend on the intensity of photosynthesis and changes in the temperatures. In the case of intensive photosynthetic assimilation of green organisms or in turbulent stretches in streams, water can easily become *oversaturated by oxygen*. At 15°C water is saturated by oxygen at a concentration of about 10 mg l^{-1}.

As opposed to surface waters, groundwaters are poor in dissolved oxygen but after springing at the surface they are promptly saturated. The presence or absence of dissolved oxygen determines whether aerobic or anaerobic processes will take place in water. *It is essential in order to ensure* *aerobic processes during self-purification of surface waters, and for aerobic biological wastewater treatment.* If oxygen is exhausted from water, microorganisms obtain their oxygen for biochemical oxidation first of all by reduction of some inorganic susbstances (e.g. nitrates), and after exhaustion of these sources reduction of organic substances starts and different bad smelling products are formed, including mainly hydrogen sulphide.

It follows that the content of dissolved oxygen is an important *indicator of the quality of streams*, as one of the first indications of surface water pollution by organic substances is a decrease in the oxygen content downstream from the source of pollution. Oxygen in water is of vital importance for fish, a concentration of 3–4 mg l^{-1} is usually considered to be the lower limit, but this depends on the sensitivity of fish. The salmon-like fish require a concentration of approximately 6 mg l^{-1}.

Oxygen in water is important when evaluating aggressivity of water towards metals (so-called oxygen corrosion), and it is an important index for checking the operation of biological wastewater treatment plants.

3.4.1.26 Nitrogen (elementary)

The source of nitrogen in waters is primarily atmospheric nitrogen. It can also be generated directly in water or soil by biochemical denitrification processes from nitrates and nitrites. Although nitrogen is less soluble in water than oxygen its concentration in surface waters is higher because of its higher partial pressure in the atmosphere.

Nitrogen dissolved in water does not undergo chemical transformations. However, it can be biochemically transformed into organic nitrogen (fixation of elementary nitrogen by some bacteria or algae). Nitrogen in water has neither hygienic nor technological importance, therefore, it is not determined in waters.

3.4.1.27 Methane and aliphatic hydrocarbons

These compounds are present in some groundwaters and their origin is mostly biochemical. Methane is one of the base gases present in waters from oil deposits where it was generated by the activity of methane bacteria. It is also generated, together with a lower amount of *hydrogen*, during anaerobic stabilization of sludge from treatment plants and anaerobic treatment of some industrial wastewaters.

3.4.1.28 Carbon dioxide and its ionic forms. Carbonate equilibrium. Aggressive carbon dioxide

Unpolluted air contains about 0.03% by volume of CO_2 which corresponds to its partial pressure of 3×10^{-5} MPa. Under these conditions approximately only 0.7 mg l^{-1} CO_2 is dissolved at 10°C in distilled water. Although the content of *carbon dioxide* in the air of large towns and in the neighbourhood of industrial sites is higher, it is not the reason of high concentrations of CO_2 in waters.

Carbon dioxide of biochemical origin is an important source of CO_2 in fresh ground- and surface waters. It is formed during biological decomposition of organic substances present in both water and soils. The content of CO_2 in the surrounding air can be many times higher than that in the atmosphere. Its partial pressure usually ranges from 5×10^{-4} to 1×10^{-2} MPa.

Another source of CO_2 can be thermal decomposition of carbonate minerals, or their destruction by acid waters during the oxidation of sulphide ores.

Hydrogen carbonates get into water via chemical weathering of aluminosilicates by CO_2 and H_2O and the reaction between carbonate minerals and CO_2.

Carbonates occur in natural waters at higher concentrations only very rarely. Concentrations which can be analytically determined are formed during intensive photosynthetic assimilation of green organisms in waters when dissolved CO_2 is exhausted and thus, the carbonate equilibrium is shifted in favour of the formation of CO_3^{2-} ions. By this process the pH value is increased ($pH > 8.3$).

Carbon dioxide is dissolved in the molecular form as a free hydrated CO_2 and is usually denoted by the symbol $CO_2(aq)$. Slightly less than 1% reacts with water to form non-dissociated molecules of H_2CO_3. Carbon dioxide dissolved in water is called *free carbon dioxide* and this term is used for the sum of the concentrations of free hydrated CO_2 and H_2CO_3.

In chemical reactions usually only CO_2 *or* H_2CO_3 *is written, but it always expresses the total quantity of dissolved* CO_2 *in the form of both hydrated* CO_2 *and non-dissociated carbonic acid.*

The dissolution of CO_2 in water and the dissociation of carbonic acid can be expressed by the following equations:

$$K_0 = \frac{c(H_2CO_3)}{p_r(CO_2)}, \quad K_1 = \frac{c(H^+)c(HCO_3^-)}{c(H_2CO_3)}, \quad K_2 = \frac{c(H^+)c(CO_3^{2-})}{c(HCO_3^-)} \tag{3.88}$$

where c is the concentration of the relevant component in mol l^{-1}, and p_r (CO_2) is the relative partial pressure of carbon dioxide above the liquid phase, $p_r = p/p_0$, where p_0 is the standard pressure 101,325 Pa and p is the pressure of CO_2 in Pa.

The ionic forms of carbon dioxide are represented by the HCO_3^- and CO_3^{2-} ions. Here, *carbon dioxide* is chemically bound and is specified as a *hydrogen carbonate* and *carbonate*. The sum of all three forms, is denoted as *total carbon dioxide*:

$$c(CO_2)_T = c(H_2CO_3) + c(HCO_3^-) + c(CO_3^{2-}) \tag{3.89}$$

At $pH < 4.5$ the HCO_3^- ions practically do not occur in water and free CO_2 predominates. At pH 8.3 the HCO_3^- ions are predominant and at $pH > 10.5$ the ions CO_3^{2-} prevail.

Dissolved free CO_2 can be found in almost all natural waters with pH < 8.3. In running surface waters CO_2 is present only in units of mg l^{-1} and does not exceed 30 mg l^{-1}. In deep reservoirs and lakes the content of CO_2 is stratified due to photochemical assimilation of phytoplankton. In surface waters the CO_2 demand can be so high during photosynthetic assimilation in summer that the content of free CO_2 is exhausted and thus the pH of the water becomes higher than 8.3.

Fresh groundwaters usually contain several tens mg l^{-1} of free CO_2 and mineral waters frequently more than 1000 mg l^{-1}.

From the hydrogeological viewpoint the *partial pressure of CO_2 corresponding to the given composition of water* is important as it enables one to assess the state of water saturation in comparison with the atmosphere or soil air. Its value is calculated by solving the equations for equilibrium constants K_0 and K_1:

$$\log p_r(CO_2) = \log c(HCO_3^-) - pH - \log K_0 K_1 \tag{3.90}$$

where $p_r(CO_2)$ is the relative partial pressure. The actual pressure of CO_2 is calculated by multiplying the relative pressure by the standard pressure of 101,325 Pa.

Hydrogen carbonate is an ion which is common to all natural waters and it is the predominant anion. Apart from the simple HCO_3^- ions, part of hydrogen carbonates occur in ionic associates with calcium and magnesium, $[CaHCO_3]^+$ and $[MgHCO_3]^+$.

Atmospheric waters contain units and tens of mg l^{-1} of HCO_3^-. In fresh ground- and surface waters their quantity ranges from tens to hundreds mg l^{-1}, and in mineral waters their concentration is even higher.

Carbonates are difficult to determine in fresh ground- and surface waters. Only in the case of intensive photosynthetic assimilation when free CO_2 is exhausted from water, the carbonate equilibrium shifts towards the formation of carbonates which results in an increase of pH above 8.3. They are present in alkaline wastewaters from the textile industry and laundries.

Carbon dioxide is quite soluble in water; at 10°C about 2.360 mg l^{-1} dissolves. A very low degree of hydration of CO_2 to H_2CO_3 causes slight expulsion of carbon dioxide from water by aeration and slight transformation of the HCO_3^- ions into carbonates by boiling.

The CO_2 content in waters does not have any hygienic significance. However, it influences the taste of water very positively and in higher concentrations it can mask the unpleasant taste caused by other substances. *Carbon dioxide in water is of considerable technological importance from the viewpoint of aggressivity.*

Hydrogen carbonates also favourably affect the taste of water. To ensure non-aggressivity of water, minimum values of HCO_3^- have been defined for water transported by piping. It is recommended that the concentration of hydrogen carbonates in drinking water should be higher than 0.8 mmol l^{-1}.

We now consider the *calcium carbonate equilibrium and aggressive carbon dioxide.* Of the various chemical equilibria in natural and service waters, *the calcium carbonate equilibrium is of the greatest theoretical and practical importance.* It is concerned with the evaluation of water aggressivity, control of deacidification processes, limnology, evaluation of buffering capacity of water, etc.

The solubility of $CaCO_3(s)$ in clean waters is given by the solubility product K_s which is defined by the equilibrium *constant of the reaction*: $K_s = c(Ca^{2+})c(CO_3^{2-})$

$$CaCO_3(s) \rightleftharpoons [CaCO_3(aq)]^0 \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad (3.91)$$

Calcium carbonate can dissolve to a larger extent only in the presence of dissolved CO_2, according to the reaction:

$$CaCO_3(s) + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (3.92)$$

An equilibrium is established between the Ca^{2+} and HCO_3^- ions, and CO_2. Carbonate dioxide which is in equilibrium according to the above presented reaction and which is required to prevent $CaCO_3$ separation from the solution or, vice versa, for prevention of its dissolution, is called *equilibrium carbon dioxide.* If a higher quantity of free CO_2 than that corresponding to the carbonate equilibrium is present in water, then the water has a tendency to dissolve calcium carbonate. The difference between the free and equilibrium CO_2 is called *excess carbon dioxide.* A part of the total excess CO_2 *has aggressive effects* on various materials. On the other hand, if a lower amount of free CO_2 is present in water than that corresponding to the equilibrium, then water has a tendency to separate $CaCO_3$ and to form incrustations. In this connection one talks about the stability of water, which represents the condition in which it neither separates $CaCO_3$ from the solution, nor dissolves it.

Many authors discuss the theoretical and experimental solution of the calcium–carbonate equilibrium [14]. The methods are based on various simplifying assumptions and they solve calcium-carbonate equilibrium and thus also aggressivity of water with greater or lesser success. In the majority of cases the aggressivity of water can be evaluated only semi-quantitatively.

Water aggressivity should be evaluated with respect to the material it is in contact with. Most frequently, its aggressivity against iron or calcium carbonate is evaluated, in connection with the effect of water on some building materials (mortar, concrete). If water is in contact with calcium carbonate the excess CO_2 reacts as above specified. 1 ml of free CO_2 provides 2 moles of hydrogen carbonates. If the content of free CO_2 is reduced during dissolution of $CaCO_3$ by a certain quantity, the content of hydrogen carbonates is doubled. Water is enriched in hydrogen carbonates and thus the quantity of equilibrium CO_2 is increased. In this case only part of excess CO_2 is *aggressive against limestone.* It is evident that aggressivity of CO_2 towards limestone is lower than the aggressivity of CO_2 against iron.

The Langelier index of saturation, which is one of the so-called *indices of unequilibrium* (equilibrium indices, saturation indices), is commonly used in practice. The Langelier index specifies whether a water of given composition is or is not in equilibrium with solid $CaCO_3$. Water in a condition of calcium–carbonate equilibrium (so-called stable water) or slightly oversaturated $CaCO_3$ has a tendency to form protective layers in metallic pipings and thus to limit its corrosion. In the opposite case (undersaturation) water has a tendency to dissolve $CaCO_3$ in both the building industry (mortar, concrete) and in metallic piping.

The behaviour of water towards $CaCO_3$ can be characterized by the difference pH − pH_s, where pH_s is pH of water which is in equilibrium with $CaCO_3$. This difference is called the *Langelier saturation index* and is usually denoted by I_s. If $I_s = 0$ the water is in calcium-carbonate equilibrium, if $I_s < 0$, water has a tendency to dissolve $CaCO_3$ (aggressive water), and if $I_s > 0$ water has a tendency to precipitate $CaCO_3$ (incrustating water). Thus, if I_s is greater or less than zero, one can talk about *unstable water.*

The index I_s is not a quantitative measure of aggressivity but only an indicator of a general tendency to separate or dissolve $CaCO_3$. Therefore, the values ranging from +0.25 to -0.25 are still considered to be an equilibrium state.

For the calculation of pH_s it is possible to derive the following equation from the equation for the second dissociation constant of carbonic acid K_2 and the solubility product of calcium carbonate, K_s:

$$\mathrm{pH}_s = \log \frac{K_s}{K_2 \gamma(\mathrm{Ca}^{2+}) \gamma(\mathrm{HCO}_3^-)} - \log c(\mathrm{Ca}^{2+}) - \log c(\mathrm{HCO}_3^-) \qquad (3.93)$$

where c is the mass concentration in mol l^{-1} and γ is the activity coefficient of the corresponding species.

The value of pH_s calculated in this manner expresses pH of water which would be achieved if it was in equilibrium with $CaCO_3$ at the given ionic composition. It is not pH_s achieved after the contact of aggressive water with $CaCO_3$ since by dissolving of $CaCO_3$ the content of calcium and hydrogen carbonates changes and so does the ionic strength, so that the original state is not known. *This difference between actual and fictive pH is neglected in practice.* The difference can be significant only in slightly mineralizated waters with a high content of aggressive CO_2.

The evaluation of aggressivity according to the Langelier index of saturation is not ideal. The calculated pH_s values are usually higher than the actual ones. The aggressivity of waters with low mineralization is normally overestimated, and that of the waters with high mineralization is underestimated.

Ryznar suggested an empirical expression similar to the Langelier saturation indices. The term $2pH_s$ − pH which assumes only positive values was called the *stability index.* If the stability index ranges from 7.5–8.5 water is aggressive. If the index values are lower than 6 it means that the water will probably cause incrustations. If the stability index is approximately 7 the water is in equilibrium.

It seems that the calculation of oversaturation or undersaturation of water by $CaCO_3$ is more important for the evaluation of aggressive or incrustation effects of waters [14, 15]. It is the quantity of calcium or $CaCO_3$ either in mmol l^{-1} or mg l^{-1} which can be separated from oversaturated water or dissolved in unsaturated water.

None of these methods of pH_s calculation and water oversaturation by $CaCO_3$ take into consideration the formation of ionic associates in the calculation of ionic strength as well as in the calculation of actual and equilibrium concentrations of calcium and hydrogen carbonates which are primarily used for the calculation of calcium-carbonate equilibrium. More exact calculations of calcium-carbonate equilibrium, more exact calculations with regard to the formation of ionic associates may be found elsewhere [16, 17].

In the USA the use of the *Caldwell and Lawrence diagrams* is widespread [14]. These are graphic solutions of the problems concerning calcium-carbonate equilibrium. Each diagram is valid only for certain temperature and ionic strength. The diagram itself consists of isolines connecting the points with identical concentration of calcium, pH values and acid neutralizing capacity to pH 4.5 ($ANC_{4.5}$) (alkalinity). The point where these curves cross is the point of the calcium-carbonate equilibrium of water.

As the theoretical calculation does not always result in entirely correct results, practical corrosion tests are carried out. Aggressivity towards $CaCO_3$ is experimentally determined by the so-called *Heyer's test* (marble test). In these experiments water is brought in contact with $CaCO_3$ and after achieving equilibrium the increase or the loss of calcium or hydrogen carbonates is determined.

3.4.1.29 The pH value, buffering and neutralization capacity of water

The pH value considerably influences the course of chemical and biochemical processes in waters. It causes the differentiation of the specific forms of occurrence of some elements, it is one of the aspects for the evaluation of the aggressivity of water and it influences the efficiency of many technological processes employed for the treatment and purification of waters.

In clean natural waters the pH value ranging from 4.5–8.3 *is given by the equilibrium between free and bonded* CO_2 (carbonate equilibrium) unless another protolytic system is present at higher concentrations. This dependence can be affected by humic substances, a higher content of cations easily undergoing hydrolysis, a higher content of hydrogen sulphide and its ionic forms, and a higher content of phosphates, etc. Decrease in pH of water below 4.5 is caused by free inorganic and organic acids. Waters with $pH > 8.3$ contain CO_3^{2-} or OH^- ions or organic bases.

In clean natural water the pH can be calculated from the content of free CO_2 and hydrogen carbonates using the expression for the first dissociation constant of carbonic acid. Dissociation to the 2nd degree can be neglected as its effect becomes significant only as $pH > 8.3$. Due to the inaccurate determination of free CO_2 the calculation provides only rough results. On the contrary, from a known value of pH and the content of HCO_3^- the content of free CO_2 can be calculated.

Distilled water which is in equilibrium with CO_2 in clean air (0.03% by volume) contains about 0.55 mg l^{-1} CO_2 at 20°C. By calculation it results that its pH is 5.65.

Surface waters, except the waters from peat moors, have a pH ranging from 6.5–8.5. The shift into the alkaline region above 8.0 is caused by intensive photosynthetic assimilation of the organisms present. Waters from peat moors containing humic substances have relatively low pH values. The pH value of fresh groundwaters usually ranges from 5.5–7.5. Waters in the neighbourhood of sulphide ores have strongly acid reactions.

The pH value can be markedly influenced by its biological processes. For example, during biological nitrification hydrogen ions are released which react with the hydrogen carbonates present to release free CO_2 and the pH of the water decreases. Conversely the increase of pH of water can be observed during biological denitrification or reduction of sulphates.

The *buffer value* of water (BV) expresses the ability to resist, or buffer, pH changes after addition of acids and bases. It can be defined as a ratio of an infinitesimal addition of a strong base c_b or strong acid c_a in mol l^{-1} to the corresponding pH change induced in the following way:

$$\mathrm{BV} = \frac{\mathrm{d}c_b}{\mathrm{dpH}} = -\frac{\mathrm{d}c_a}{\mathrm{dpH}} \tag{3.94}$$

The buffer value of a solution can be evaluated from the course of the neutralization titration curve. It is a reciprocal value of the tangent to the titration curve expressing the dependence $pH = f(c_b)$ for the given points. The buffer value is given in mmol l^{-1} and is always positive.

A number of *homogeneous and heterogeneous buffer systems* can be found in water. The most important buffer system in natural waters is CO_2–HCO_3–CO_3^{2-}. Maximum buffer values in this system are achieved at equal concentrations of hydrogen carbonates and carbonates which are at pH of about 6.3 when $c(H^+) = K_1$ and at pH of about 10.3 when $c(H^+) = K_2$. The carbonate system has the minimum capacity at pH 8.3, i.e. when the concentrations of free CO_2 and carbonates are equal, when $c(H^+) = \sqrt{K_1 K_2}$. Other buffer systems which may occur in natural waters involve borates and silicates, which are observed in some mineral waters and sea water.

In wastewaters the NH_3–NH_4^+ buffer system needs to be considered. The total buffer value is given by the sum of partial buffer values; for natural water this ranges from tens to units of mmol l^{-1}.

The buffer mechanism in water can also be induced by some heterogeneous systems where exchange reactions between the ions in water and bottom sediments or minerals occur, or dissolution and precipitation of some minerals take place.

During the anaerobic stabilization of sludges from wastewater treatment plants, the buffer value of undissolved carbonates is particularly important.

The ability of water to bond hydrogen or hydroxyl ions is called the *neutralizing capacity*. This ability is a general property of all waters, involving different protolytic systems; in natural waters the carbonate system predominates. However, in the case of many wastewaters (sludge from anaerobic stabilization, agricultural wastes, etc.) a number of other protolytic systems are of interest. Neutralizing capacity is determined by titration of a sample of water with acid (*acid neutralizing capacity*, ANC) or base (*base neutralizing capacity*, BNC) up to the determined pH value which can be chosen on analytical grounds (inflexion point of the titration curve) or technological grounds (determination of acid or base consumption for neutralization of wastewaters) [1, 10].

For the titration of a carbonate system, titration indices 4.5 and 8.3 are used, but for the analysis of sludge water from anaerobic stabilization of sludge the value of pH 5.78 has been recommended [18]. To determine the consumption of acid or base for neutralization of wastewaters titration to pH 7.0 is recommended.

Acid or base neutralizing capacity is that quantity of a strong monobasic acid or monoacidic base in mmol which is used by 1 litre of water to achieve a certain pH value.

Acid or base capacities are therefore measured in mmol l^{-1}. The pH value up to which the titration takes place, is presented as the index of the relevant abbreviation, e.g. $ANC_{4.3}$, $ANC_{5.75}$, $BNC_{7.0}$, etc. The neutralizing capacity is an integral of the buffer value within given pH range.

In natural waters with the main protolytic system of carbon dioxide and its ionic forms, the determination of acid capacity up to pH 4.5 ($ANC_{4.5}$) (so-called alkalinity) is the most important from the analytical viewpoint; in this case hydrogen carbonates react to form free CO_2:

$$HCO_3^- + H^+ \rightleftharpoons CO_2 + H_2O \tag{3.95}$$

The acid consumption corresponds to the content of hydrogen carbonates. As well as free HCO_3^- ions, hydrogen carbonate complexes bonded in ionic pairs with calcium, magnesium, etc. are also determined.

If the pH of water is higher than 8.3 it indicates the presence of CO_3^{2-} ions or OH^- ions, which can occur either separately or in combinations, HCO_3^- + CO_3^{2-} + OH^-. The combination of HCO_3^- + OH^- is not possible as the reaction takes place to form CO_3^{2-} ions. To determine the concentration of individual ions the *acid capacity* to pH 8.3 ($ANC_{8.3}$) must be determined. Carbonates react as follows:

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{3.96}$$

The determination of *base capacity* up to pH 8.3 ($BNC_{8.3}$) also has analytical importance in natural waters. Free CO_2 reacts according to the reaction:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{3.97}$$

However, all weak inorganic and organic acids and their salts (phosphates, borates) and cations of metals being hydrolysed to release H^+ ions are titrated at the same time. In the majority of less-mineralized natural waters with pH > 4.5 which do not originate from peat moor regions, *the content of free* CO_2 *in water can be calculated from* $BNC_{8.3}$ (so-called acidity).

The following acid and base capacities of a carbonate system can be determined:

$$\begin{aligned}
ANC_{4.5} &= c(HCO_3^-) + 2c(CO_3^{2-}) + c(OH^-) - c(H^+) \quad \text{(alkalinity)} \\
ANC_{8.3} &= c(CO_3^{2-}) + c(OH^-) - c(H_2CO_3^x) - c(H^+) \\
BNC_{4.5} &= c(H^+) - c(OH^-) - c(HCO_3^-) - 2c(CO_3^{2-}) \\
BNC_{8.3} &= c(H^+) + c(H_2CO_3) - c(CO_3^{2-}) - c(OH^-) \quad \text{(acidity)}
\end{aligned} \tag{3.98}$$

For the total acid capacity of a carbonate system $ANC_{4.5}$ can be considered, when all forms of carbon dioxide are transformed into free CO_2.

In the case of wastewaters, the determination of neutralizing capacity at pH 7 *or another point in the neighbourhood of this is of the greatest importance from the technological viewpoint.* The determination of neutralizing capacities to pH 4.5 or 8.3 has neither practical, nor theoretical nor analytical importance in wastewaters as the calculation of the CO_2 forms is usually meaningless.

3.4.1.30 Radioactive substances

Radioactivity originates in natural sources (*natural radioactivity*) as well as in artificial ones (*artificial radioactivity*).

Natural radioactivity is caused by the presence of radionuclides such as ^{226}Ra, ^{222}Rn, ^{238}U, ^{230}Th, ^{210}Po, ^{210}Pb, ^{40}K and others. Except for some mineral waters and waters from the neighbourhood of radioactive ore deposits, ^{40}K participates to the greatest extent in the activity of groundwaters. Natural potassium contains about 0.012% of the radioactive isotope ^{40}K. In atmospheric waters also, natural radionuclides can be found which are formed in the atmosphere due to the effects of cosmic radiation, for example ^{3}H, ^{14}C.

The artificial radioactivity of waters is caused particularly by radionuclides formed by nuclear fission reactions (nuclear explosions, nuclear reactors). The contribution of artificial radioactivity from scientific and medical institutions is small. The following radionuclides in particular can be considered in this case: ^{90}Sr, ^{90}Y, ^{131}I, ^{132}I, ^{137}Cs, ^{141}Ce, ^{144}Ce, etc. Other radionuclides are formed due to the effects of neutron radiation on materials contained in reactors and nuclear weapons (^{59}Fe, ^{60}Co, ^{51}Cr, ^{54}Mn), or the constituents of the atmosphere (^{3}H, ^{14}C).

Radionuclides can be present in waters in both soluble and insoluble forms, as simple and complex ions.

One of the main components of the natural acitivity of mineral waters is gaseous radon. Other components of natural radioactivity of groundwaters are uranium and radium. Waters with an activity > 370 Bq l^{-1} are considered to be *radioactive mineral waters.*

Following the prohibition of nuclear weapons testing the most important source of radioactive pollution of surface water is the radioactivity of wastes from exploitation and processing of uranium ores. Wastewaters with artificial radionuclides are less dangerous for surface water pollution.

The most dangerous are radionuclides with half-lives, emitting radiation with a high density of ionization and remaining in organisms. Particularly toxic are ^{226}Ra, ^{90}Sr, ^{90}Y, ^{210}Pb and ^{210}Po.

In drinking water indirect indicators are allowed from the viewpoint of radiology, such as total volume activity alpha and total volume activity beta, which help to assess the occurrence of alpha or beta active radionuclides in waters without the necessity to identify actual radionuclides whose analysis would be complicated. The level of total alpha and beta activities was chosen so that the actual exposure of consumers would not be higher than 0.05 mSv per year at a daily consumption of 2 l of water. A "no action level" has been chosen, i.e. a level which does not require other analyses or action by the health care authorities. For the total alpha activity this is 0.1 Bq l^{-1} and for the total beta activity 1.0 Bq l^{-1}. The level for the alpha activity was determined with respect to the presence of ^{226}Ra and for beta activity the reference was ^{90}Sr. If these values are exceeded then detailed measurement is required and it is necessary to determine the content of individual radionuclides.

After the discharge of radioactive waste the following processes take place in the recipient: precipitation, accumulation in the aquatic flora and fauna, and bottom sediments. Some radionuclides are accumulated selectively in certain organisms or organs. Contamination of fish is a very serious matter. Therefore, for total evaluation of radioactive pollution not only the liquid phase must be analysed, but also sediments, and aquatic flora and fauna.

3.4.2 Organic substances in waters

The contamination of the hydrosphere of our environment by organic substances shows an ever increasing trend. This does not concern only their concentration, but also quantity and detrimental effects. Organic matter is present in both surface and groundwaters; the origin of such matter is diverse. Natural organic pollution of natural waters is caused by elutions from soil and sediments as well as by products of the biotic activities of plant and animal organisms living in water. Artificial organic pollution is due to the industrial activity of human society, which produces a remarkable variety of chemical wastes. From the biological viewpoint substances undergoing biological degradation or biochemically and chemically resistant substances which may accumulate in the hydrosphere, need to be considered. A very important factor resulting from the environmental contamination by organic substances is often forgotten, that is, their influence on the biological microworld living in symbiosis with the macroworld. Upsetting the biological balance in the realm of microorganisms can bring about unpredictable negative impacts on the biological macroworld.

From the viewpoint of effects the organic substances in water can be categorized into *harmful* and *harmless* groups. In drinking water, organic matters are present in quantities of tenths to units of mg l^{-1}. Their amount in surface waters increases approximately 10-fold, and in severely polluted industrial wastewaters amounts expressed in terms of g l^{-1} are present. In surface waters from 100 to 1000 organic coumpounds can be expected to occur.

Organic substances influence primarily the quality and properties of natural waters. Some organic substances are toxic, and they can manifest carcinogenic, mutagenic and teratogenic effects. Others, even though nontoxic, can very negatively influence the oxygen balance of the river or the sensory properties of water.

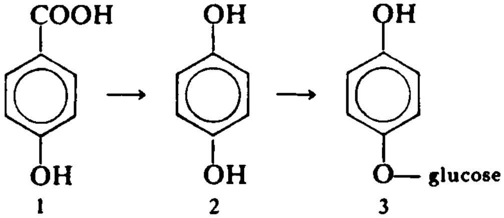
With regard to the very broad spectrum of organic substances present in waters, it is particularly important to identify those organic substances which are resistant from both chemical and biological viewpoint. From the viewpoint of biotransformations [20–23] it is necessary to know the possibilities of biodegradability of particular substances and the properties of the metabolites thus formed. On account of the immense quantity of individual chemicals occurring in waters which even increase after biotransformation, it is evident that the evaluation of the behaviour of specific substances is practically impossible. Only in some cases is this behaviour completely and precisely known. Therefore, in the following sections organic substances will be considered from the viewpoint of both their chemical affinity and their origin. Negative effects of organic substances in the biosystem will be briefly mentioned. Other properties and effects will be discussed in some of the following chapters.

The very extensive problems of the pollution of the hydrosphere by organic substances have been elaborated from different aspects in books, for example [24–29] and in numerous papers. Not all organic pollutants of the environment are considered here. For example, organic dyestuffs are missing, and so are the chlorinated dioxins and related derivatives [35] which are so topical from the environmental viewpoint [30–34], the chemical transformations of organic pollutants of the hydrosphere [36] whose importance is illustrated by few examples only from the field of photochemical transformations of pesticides, asbestos in waters [37] and other important groups of organic pollutants of the hydrosphere.

3.4.2.1 Phenols and phenolic compounds

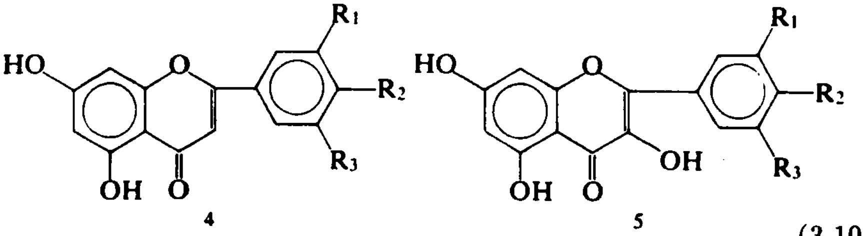
A large group of organic substances in water is that consisting of phenols and related compounds [38–42]. Phenolic compounds belong to very important biological substances occurring in nature. They are present in plants and tree species, and therefore, they are designated as plant phenolic compounds.

A huge amount of these substances is formed by secondary metabolism [22]. For example, p-hydroxybenzoic acid, a metabolic intermediate (1) undergoes oxidation decarboxylation to form 1,4-dihydroxybenzene (2) which is further transformed into arbutine (3)



(3.99)

Another example of phenols occurring as secondary metabolites, are flavones (4) and flavonols (5)



(3.100)

In general, phenols behave as organic acids. Therefore, phenolic compounds of natural and artificial origin are eluted by water. The content of naturally occurring phenols eluted increases in the vegetation period and can reach as much as several tenths of mg l^{-1}. The acid properties of phenols of natural and artificial origin are listed in order of the pK_a values measured in water (Table 3.16). Polyphenols occurring in water involve biologically difficult-to-degrade substances of different colours of either natural or artificial origin. They cause a yellow to brown-yellow colour of water. They are mostly both chemically and biochemically considerably resistant.

3.4.2.1.1 Simple plant phenols

Simple plant phenols are monomeric monohydroxy- to polyhydroxyphenolic compounds. In the plant kingdom a great number of these substances is present, and in the majority of cases their biochemical function is not yet known. As already mentioned, they participate particularly in secondary metabolism. They are formed as products of metabolic transformations

Table 3.16. pK_a constants of different phenols in water

Compound	pK_a
Phenol	10.00
o-Cresol	10.29
m-Cresol	10.09
p-Cresol	10.26
2,4-Xylenol	10.47
2,5-Xylenol	10.32
2,6-Xylenol	10.60
3,5-Xylenol	10.09
2,4,6-Trimethylphenol	10.80
2-(*n*-Propyl)phenol	10.55
2,6-Diisopropylphenol	10.08
2-(*t*-Butyl)phenol	11.35
2,6-Di(*t*-butyl)phenol	11.70
2,4,6-Tri(*t*-butyl)phenol	12.19
Pyrocatechol	9.45
Resorcinol	9.44
Hydroquinone	9.96
1-Naphthol	9.85
2-Naphthol	9.63
o-Nitrophenol	7.21
m-Nitrophenol	8.39
p-Nitrophenol	7.16
2,4-Dinitrophenol	4.11
2,4,6-Trinitrophenol	0.38

of aromatic compounds. They enter water primarily by the humification process on the elution of humus with water. Examples of simple plant phenols are shown in Fig. 3.19.

3.4.2.1.2 Plant tanning materials

Plant tanning materials are phenolic compounds which dissolve in water. They have a low degree of polymerization, and they are used in the leather industry for tanning.

Tanning materials are present in the tissues of living plants, particularly in vacuoles. In bark (dry tissue) they accumulate in higher amounts and undergo further chemical transformations. The content of tanning materials in bark depends on many factors, and in the case of technically important types of tanning raw materials it ranges from 5 to 20% in domestic raw materials, and from 20 to 60% in some foreign ones.

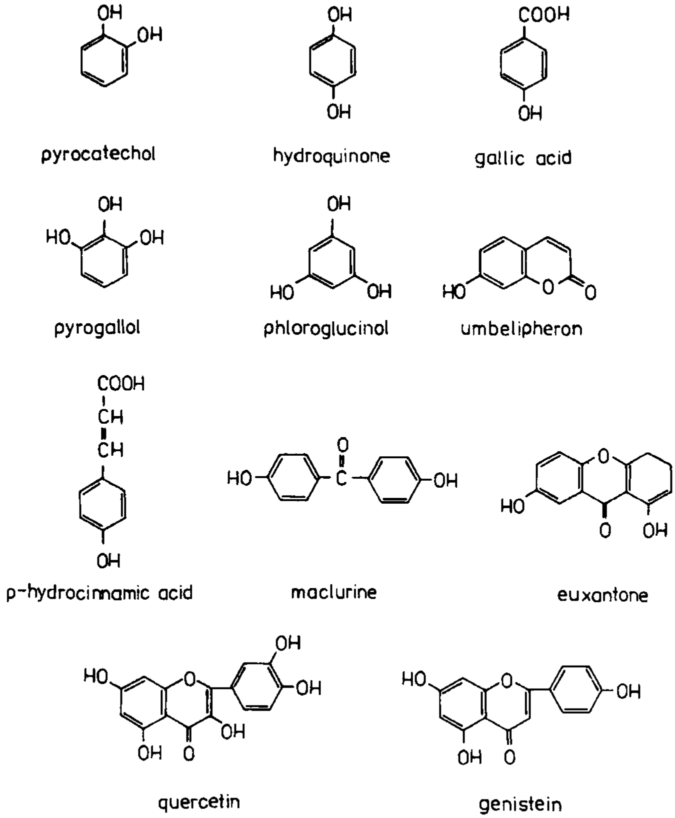


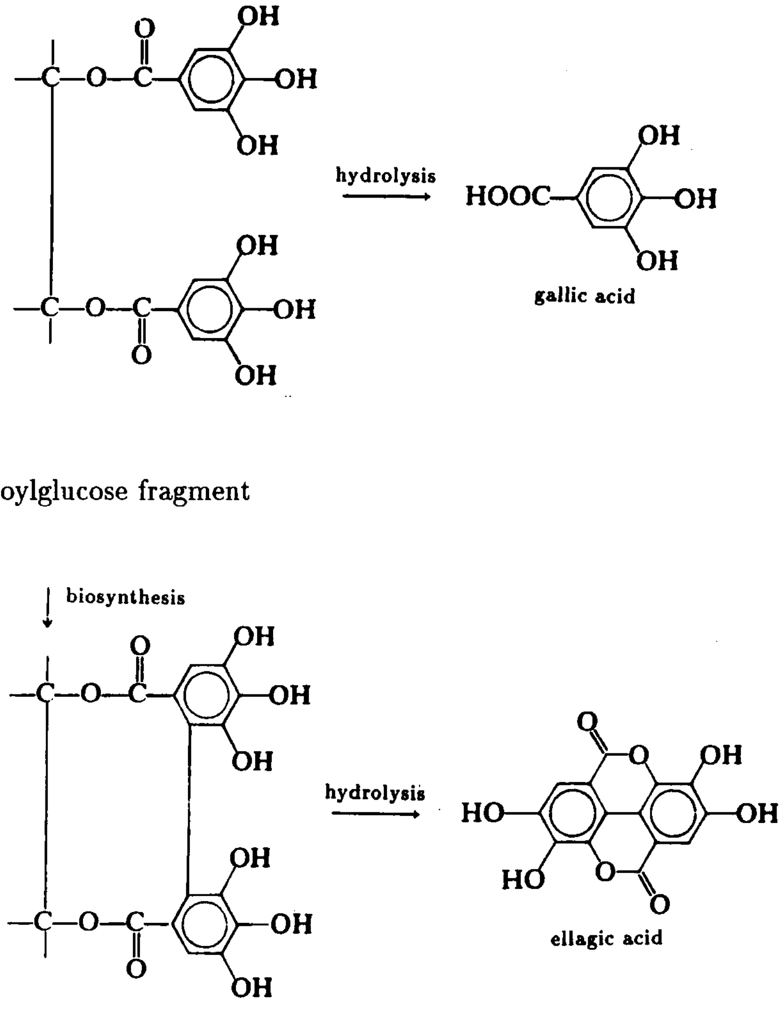
Fig. 3.19. Examples of some simple plant phenols

The tanning materials enter the waters by the natural route as well as from wastewaters of the leather industry, and also after elution of the waste deposits from the preparation of tanning leaches and wastes of the wood-working industry.

All the known tanning materials are polyhydroxyphenols from the viewpoint of chemical structure, with different relative molecular weights. The most important functional groups are phenolic hydroxyls. Many of these compounds provide a multicoloured spectrum of different parts of plants.

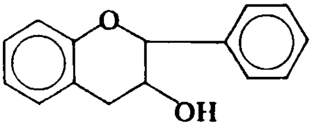
From the chemical viewpoint the tanning materials are classified into *hydrolysable* and *condensed* substances.

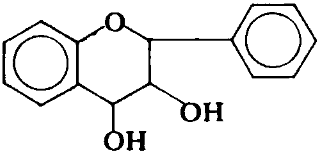
The *hydrolysable* ones have a structure of polyesters with two essential constituents — saccharide and phenolcarboxylic acid. Under the effect of hydrolytic agents (acids, enzymes, alkalies) they split into the original components. Thus, gallotannines provide — in addition to the sucrose component — also gallic acid, and elagitannines provide hexahydroxydiphenyl acids or acids which can be derived from gallic acid by a simple chemical transformation, for example, oxidation or reduction. The mutual affinity of gallitannines and elagitannines is illustrated in the following scheme:



(3.101)

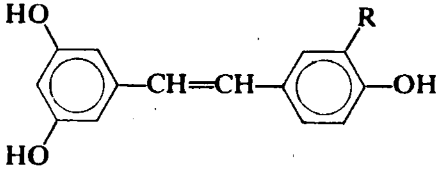
From the chemical viewpoint *condensed* tanning materials belong to the group of flavonoides whose monomers are precursors of the origin of condensed tanning materials by polycondensation. The most important types are as follows:


flavan-3-ol


flavan-3,4-diol

(3.102)

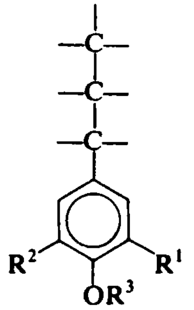
The group of condensed tanning materials also includes polycondensates based on hydroxystilbenes as their precursors. These substances were found in the bast of the spruce bark (*Picea excelsa*) and their chemical structure is as follows:


(3.103)

3.4.2.1.3 Lignins

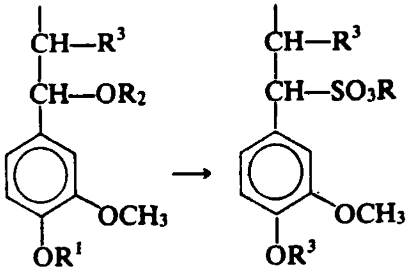
Lignin represents 20–30% of the total mass of wood in the case of higher plants and thus, it is the major component of wood as regards quantity. Wood is the most frequently used and chemically processed raw material.

Lignins are phenolic compounds noted for their insolubility in water. They are highly polymeric substances with a considerable content of methoxyl groups. The chemical structure of lignins is rather complicated with respect to their polymeric character. Studies have shown that the fundamental construction unit has the following arrangement:


R^1 = -OCH_3 or -H
R^2 = -OCH_3, -H, -C
(biphenyl, phenylcoumarone, etc.)
R^3 = -H, alkyl, aryl, acyl, etc.

(3.104)

An important part of the chemical processing of lignin is the preparation of cellulose by soda, sulphate or sulphite processes. The production of cellulose consists in its separation from lignin and other accompanying substances. In the sulphate process lignin transforms into alkali-lignin under the effect of sodium hydroxide and sulphide. In the production of cellulose by the sulphite process lignin changes, by boiling with acid sulphites, into ligninsulphonic water-soluble acids:



R^1 = H, -C
R^2 = H, alkyl, aryl
R^3 = alkyl, aryl, aroxy
R = Na, H

(3.105)

The sulpho group can also be bonded in another site of the lignin macromolecule. Lignin sulphonanes form a biologically difficult-to-degrade and important part of the pollution of wastewaters from the production of sulphite cellulose. Under aerobic and anaerobic conditions they undergo only a very slow biological degradation. In surface waters only 4–15% of lignin was degraded within 30 days and after 20 weeks it still contains 30–70% of lignin. Primarily low molecular weight entities are degraded. Among the intermediates of degradation compounds the following have been identified: coniferyl aldehyde, verulic acid, *p*-coumaric acid, protocatechuic acid, vanillic acid, vanilline, 1-hydroxy-2-methoxybenzene, etc.

The production of cellulose represents 70% of the total pollution of wastewaters from chemical industry on the basis of BOD_5 (biological oxygen demand). Polluted wastewaters from the production of sulphite cellulose cause a brown colour in surface waters, as well as their frothiness due to the surface activity, and they have an unpleasant odour.

3.4.2.1.4 Phenols of artificial origin

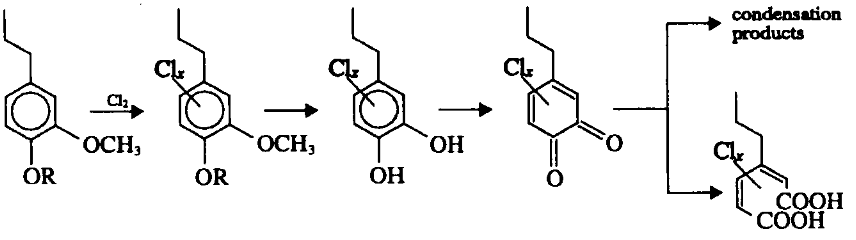
Pollution of wastewaters by phenols of artificial origin is caused particularly by those from the thermal processing of coal, oil refineries, from sulphite woodworking, dyestuff industry, and from the manufacture of pesticides. These wastewaters contain monovalent and multivalent phenols at concentrations of units of g l^{-1}. In the process of biological treatment of phenolic wastewaters different polyphenols are formed which have a similar character to those of natural origin. After biological treatment of phenolic wastewaters the content of polyphenolic substances in the recipient can amount to several tens of mg l^{-1}. The treatment of the phenol containing waters by chlorination to produce drinking water causes many difficulties due to chlorination or oxidation reactions of chlorine. In acid media chlorination preferentially takes place whereas in alkaline media oxidation with opening of the aromatic nucleus is preferred. Chlorination of phenols results in the formation of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol. These products influence primarily the sensory properties of drinking water.

Halogenated phenols are also known as bactericidal and fungicidal substances; they also occur in nature. It is interesting that 2,6-dichlorophenol has effects as a sexual pheromone on the female ticks of *Amblyomma americanum.*

Much work has been carried out on these compounds. For example, in the study [43] an assessment of the impact of the chloroorganic compounds on the hydrosphere is presented, including monochlorophenols and dichlorophenols; in another paper [44] the effect of the quality of sediments on biodegradation of 2,4,6-trichlorophenol in the Delaware River was studied.

The study [45] summarizes the results of photochemistry of chlorinated aromatic substances (including chlorophenol) in aqueous media. Biodegradation of monosubstituted phenols (*m*-cresol, *m*-aminophenol, *p*-chlorophenol) by aquatic bacteria is discussed in the study [46].

An example of the chlorination of water containing organic matter is the reaction of guaiacol alcohol with chlorine (Fig. 3.20), or the oxidation reaction of the phenolic nucleus during chlorination:



(3.106)

R = H or lignin unit, Cl_x = chlorine in unstated position.

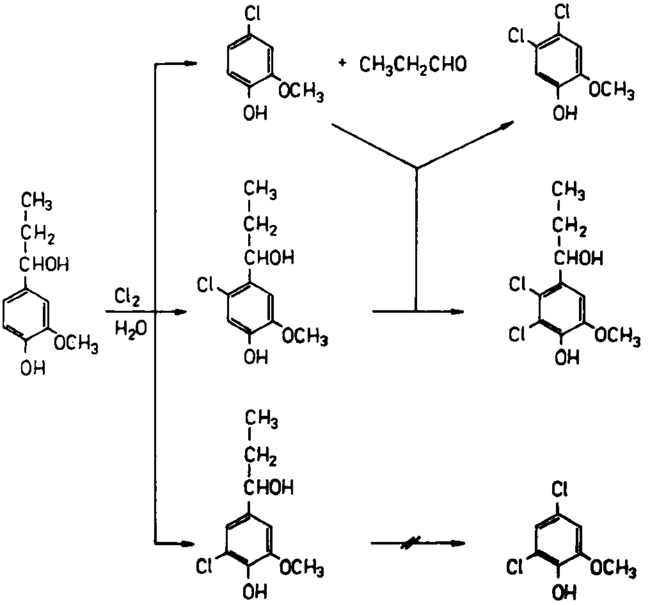


Fig. 3.20. Reactions of guaiacol alcohol with chlorine

Another fairly toxic group of phenolic compounds present in wastewaters is that of the *nitrophenols*. They are toxic when applied perorally, as well as when inhaled or absorbed through the skin. The most toxic is 2,4-dinitrophenol employed in the dyestuff industry (sulphur black). In biochemical reactions, its inhibiting effect on the vital functions of the cell is known. The solubility of some nitrophenols is presented in Table 3.17.

Table 3.17. Solubility of some nitrophenols in water

Compound	Solubility in water (g/100 g of water)
o-Nitrophenol	0.32 g (38°C), 1.08 g (100°C)
m-Nitrophenol	1.35 g (25°C), 13.30 g (90°C)
p-Nitrophenol	0.80 g (15°C), 1.60 g (25°C), 29.1 g (90°C)
2,4-Dinitrophenol	0.02 g (12°C), 1.32 g (100°C)
2,6-Dinitrophenol	slightly soluble in cool water
2,4,6-Trinitroresorcinol	0.45 g (15°C), 0.57 g (20°C), 0.68 g (25°C)

In the water treatment to produce drinking water phenols play an important role from the viewpoint of their negative sensory properties which are even more marked in their chlorinated derivatives, from the point of view of odour. In water treatment, excess of chlorine must be used so that phenols are degraded via oxidation reactions.

It is clear from these facts, that in addition to the general removal of organic substances, the removal of phenols is of essential importance for water treatment. Various emergency situations which have arisen in supplying large industrial towns with drinking water, causing problems by drinking water polluted with phenols, are sufficient warning.

3.4.2.2 Humic substances

Decayed plant and animal organic substances are degraded biologically and form the organic component of the soil, i.e. humus [47–50]. The degradation and synthetic processes by which humic substances are formed from the primary organic matter are called humification processes. Depending on the composition of the primary organic substances and biological conditions in soil the composition of humus differs both qualitatively and quantitatively. About half of the primary organic matter is humified and the residue is mineralized.

Humic substances represent a broad spectrum of different compounds. In the formation of humic substances saccharides, pectins, lignin, proteins, fats, waxes, resins, tannins, etc. participate. During humification, biochemical and chemical processes take place. Of these, the polymerization and condensation reactions of the products of the degradation of primary organic matter into products which are the result of the humification process are important.

Humic substances are high-molecular cyclic compounds representing a complex of organic substances as products of condensation of phenol-type aromatic substances with amino acids and proteins. The amount of humic substances in soil ranges from 0 to 5%, and in peat from 40 to 55%.

Humic substances are classified according to physico-chemical and chemical properties into

- humic acids
    - humic acids,
    - fulvic acids,
    - hymatomellanic acids;
- humines;
- humic coal.

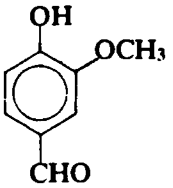
The classification is based on differing solubility in acid and alkaline media as well as in alcohol. There is no general agreement over the classification into individual groups.

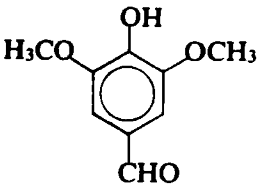
3.4.2.2.1 Humic acids

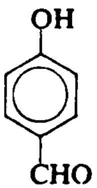
Humic acids are slightly dissociated polyhydric organic acids. The values of dissociation constants range from 10^{-4} to 10^{-5}. The pH values of their solutions are about 3.5 depending on the concentration. In solutions they behave as micellar colloids. The colloid particles have a negative charge and their isoelectric point is in the acid region. They form mostly true solutions in strongly alkaline media. They can also be obtained via extraction using alkaline solutions and precipitation in acid media.

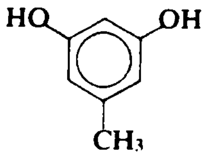
Up to the present the structure of humic acids has not been deduced in detail. As the basic structural unit of humic acids, cyclic compounds, most frequently aromatic ones with side-chains and hydrophilic groups, can be considered which are bonded to the nucleus also in the side-chains. Quinoid structures have also been found. Heterocyclic compounds are present as well, such as derivatives of furan, pyridine, indole, purine and pyrimidine. There are built-up or bridge-type systems. Humic acids of different origin have also a different pattern of functional groups and side chains. One would expect that these are formed in different stages of microbial degradation and thus the determination of the structure of particular components of humic acids is rather complicated. A general and characteristic feature of these substances is the presence of carboxyl and hydroxyl groups — both phenolic and alcoholic ones, as well as of the methoxyl group. The carboxylic and hydroxyl groups cause acid reactions, sorption and exchange capacity of humic acids which differ in dependence on the nature of the cation. Humic acids usually contain three or four carboxylic groups and three to seven hydroxyl (phenolic) groups. At present, the opinions and theories of the structure of humic acids are often contradictory, particularly due to disagreement over the origin of humic acids. Difficulties appear also from the viewpoint of the study of humic acids based on the data of elementary analysis. The contents of C, H, O, N, S are common to all humic acids. Therefore, original structures can be deduced only after the fractional analysis of humic acids. This analysis is important for the determination of the structure of specific sub-units and the character of the functional groups involved, as well as for the determination of their mutual link in a macromolecule. Some organic compounds obtained by hydrolysis, oxidation or reduction of humic acids are schematically illustrated as follows:

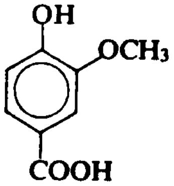
(a) acid or alkaline hydrolysis,

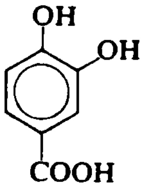

vanillin

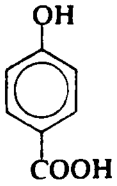

syringaldehyde


p-hydroxybenzaldehyde


orcinol

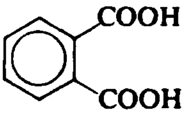

vanillic acid

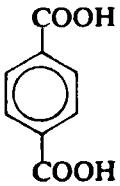

protocatecholic acid

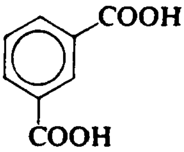

p-hydroxybenzoic acid

(3.107)

(b) HNO_3 oxidation,


phthalic acid

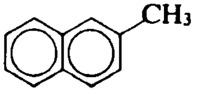

terephthalic acid


isophthalic acid

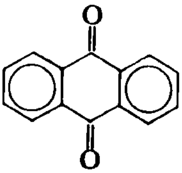
(3.108)

(c) oxidation by nitrobenzene resulting in the formation of syringaldehyde, vanillin, *p*-hydroxybenzaldehyde, syringic acid, vanillic acid and *p*-hydroxybenzoic acid,

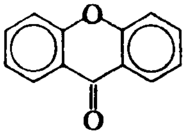
(d) oxidation by $KMn0_4$:



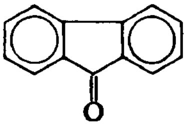
2-methylnaphthalene



anthraquinone



xanthone

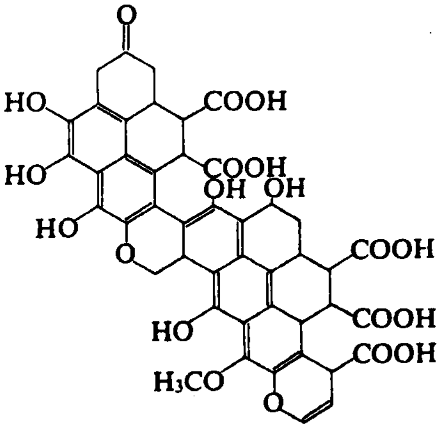


fluorenone

(3.109)

(e) oxidation by chlorine resulting in the formation of aliphatic aldehydes, ketones, alcohols as well as chloroform.

By acid hydrolysis with HCl, ten amino acids were obtained from the peat humic acids: cystine, lysine, hystidine, arginine, aspartic acid, serine, glycine, glutamic acid, threonine and alanine. Proposals for the structure of humic acids have also been published; of these, the structure of the humic acid according to Ludmila (1936) [51] is presented:



(3.110)

A comparison of the functional groups in lignin and humic acids is shown in Table 3.18.

Table 3.18. Comparison of functional groups in lignin and humic acids

Group	Lignin[a]	Humic acids[a]
$-OCH_3$	5.1	0.2
-OH (total)	6.2	5.1
-OH (phenolic)	1.6	2.9
-OH (alcoholic)	4.6	2.2
$>C{=}O$	1.0	5.5
-COOH	Traces	8.6

[a] mmol mol^{-1}

3.4.2.2.2 Fulvic acids

Fulvic acids are organic substances which remain in the solution after acid precipitation of humic and hymatomelanic acids from the extract of humic acids. The chemical structure and physico-chemical properties of these substances are similar to those in humic acids. The aromatic character of the molecule is less distinct, and side chains predominate. They also differ from humic acids in their lower molecular weight, yellow to light-brown colour, better solubility in water and easier hydrolysis in acid media. They are easily eluted from soils and peat. They are more acid than humic acids (pH of solution with $c = 0.01$ mol l^{-1} is about 2.6). They manifest complex-forming properties and exchange capacity.

3.4.2.2.3 Hymatomelanic acids

These differ from humic acids by solubility in alcohol. The free acids are difficult to dissolve in water. In their elementary composition they differ only very little from humic acids (Table 3.19).

Table 3.19. Comparison of functional groups in hymatomelanic acids and humic acids

Fundamental structure	Hymatomelanic acids	Humic acid
	$C_{42}H_{47}O_4$	$C_{68}H_{53}O_4$
$-OCH_3$	1	1
-OH	2	2
-COOH	2	4

3.4.2.2.4 Humins and humus coal

Humins and humus coal are water insoluble and non-hydrolysable, and therefore, they are of no importance from the hydrochemical viewpoint.

3.4.2.2.5 Occurrence of humic substances in waters

Humic matters are present in almost all natural waters. They are extracted from soil and peat. The solubility of the constituents of the soil humus depends on the type of soil, period of contact with water, pH of the water and its composition, and depending on such factors, the humic materials are present as either true or colloid solutions. In waters from peat moors the concentration of humic matters is usually tens of mg l^{-1}. In some stationary waters as much as 500 mg l^{-1} can be found. In waters from peat moors a low pH is typical (it can be lower than 4), high oxidation potential and the presence of iron, manganese and ammonia nitrogen (anaerobic processes). Iron and other metals are present in an organic complex form and they are difficult to remove [52, 53].

Humic matters cause a deterioration of the sensory properties of water, giving rise to a yellow to brown colour of the water and an unpleasant odour. The intensity of colour increases with increasing pH.

The presence of humic matters in drinking, service and industrial waters is undesirable on account of these properties. Their colour, for example, can impair the quality of some products, e.g. of textil and paper industries.

They are of small detrimental significance from the viewpoint of hygiene. The toxicity limit for warm-blooded animals is about 100 mg l^{-1} in drinking water.

With regard to chlorination, the lowest possible content of humic matters in waters intended for drinking is desirable for water treatment. Many papers currently deal with the study of the structure of humic matters. For example, the authors of the study [54] have characterized the humins of sediments on the basis of their alkaline hydrolysis whose products were separated via gas chromatography or GC-MS technique. Another study [55] deals with the distribution of fulvic and humic acids of different molar weights determined by gel permeation chromatography (GPC). In the study [56] structural analysis of aquatic humic matters was carried out using NMR spectroscopy. By means of the ^{13}C NMR spectroscopy the relationship between the structure of sea humic matters in sediments and in the sediments in the estuaries has been studied [57]. In another study [58] humic and fulvic acids in the sediments of the Baltic Sea are characterized, employing ^{1}H NMR and ^{13}NMR spectroscopy. The role of free radicals in the formation of humus has been emphasized elsewhere [59]. Other possibilities for the use of NMR spectroscopy use for the determination of the structure of humic compounds are presented in the study [60]. Its author discusses the possibility of the application of the CP-MAS (cross-polarization magic-angle spinning) technique for the determination of structural differences of soil and aquatic humic acids.

3.4.2.3 Pesticides

Increasing requirements for nutrition of the global population of our planet has led to an extreme situation in the case of the application of pesticides [24, 61–66]. Although the negative effects of these materials on the environment are well known, pesticides will certainly continue to be used into the near future.

Pesticides are classified from different standpoints. The classification according to the type of harmful agents against which they are used is as follows:

— *fungicides* — against diseases caused by fungi,
— *insecticides* and *acaricides* — against insects and mites,
— *herbicides* — against weeds,
— *rodenticides* — against rodents,
— *other agents* — special application for plant protection.

Although it is rather difficult to evaluate the positive effects of pesticides for the period of their application, it is even more complicated to evaluate their negative effects on the environment. The beneficial effects are well documented. In the case of the most frequently discussed preparation, DDT (for the discovery of biological application of DDT P. H. Müller was awarded the Nobel Prize for physiology and medicine in 1948), it is estimated today that in the first 10 years of its application, DDT saved lives of millions of people. Furthermore, hundreds of millions of people have been protected from malaria, typhoid fever, dysentery and more than twenty million people from diseases caused by insects and arthropods.

The worldwide production of pesticides has an increasing tendency and the pattern of use continually changes. It is estimated that there are 400–500 pesticide preparations available, of which — depending on the mechanism of the effect — 68 influence respiration, 74 photosynthesis, 148 the nervous system, 44 biosynthesis, 47 growth of plants, 31 have non-specific effects and 67 are with unknown mechanisms of effects. In Czechoslovakia (1979), for example, about 470 different preparations have been permitted

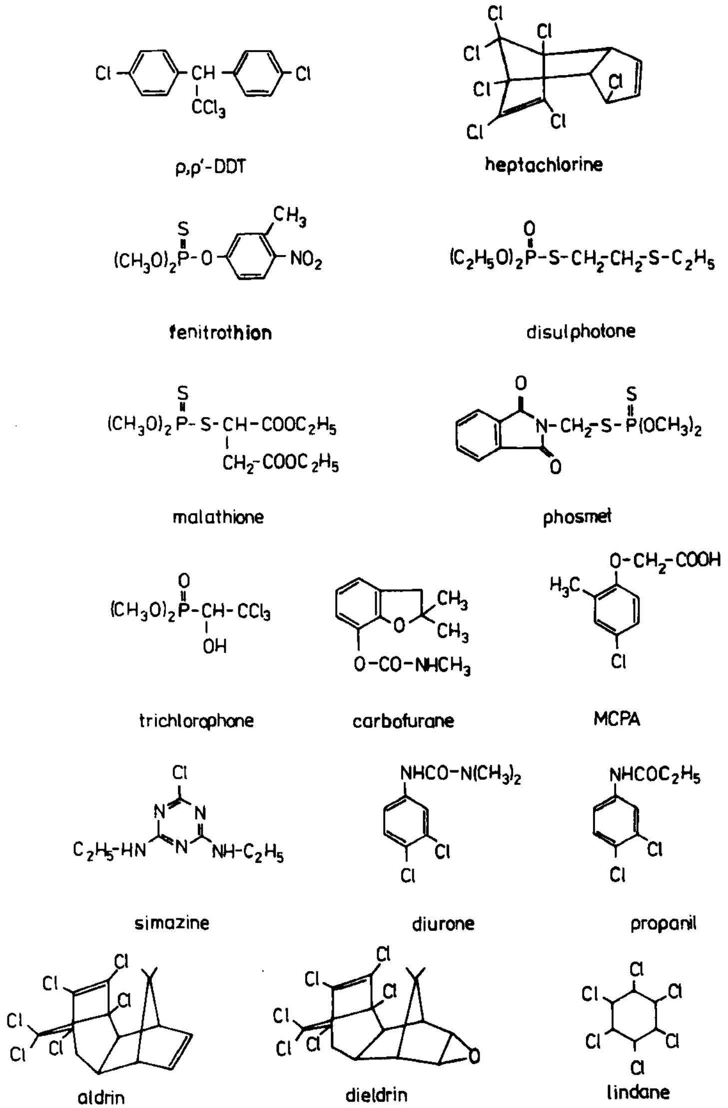


Fig. 3.21. Examples of some types of pesticides

of which 153 are herbicides, 135 insecticides and acaricides and 80 fungicides. On the worldwide scale the production of chlorinated insecticides has decreased by more than 60%. At present, the global consumption of pesticides is about 2 million tons which is approximately 0.5 kg per capita. Of this amount 34% is applied in the USA, 45% in Europe and 21% in other parts of the world. The estimated consumption of pesticides in the year 2000 is about 3 million tons. In Czechoslovakia, for example, about 25,000 tons of pesticides per year is used in agriculture.

It is evident from the scheme shown in Fig. 3.21 that the chemical structures of pesticides are quite diverse; they undergo various physico-chemical effects in the environment after application (solar radiation, heat, air, soil, water) as well as being subjected to various metabolic transformations in plants, microorganisms, insect and animals. Common metabolic transformations are schematically surveyed in Table 3.20, which shows that primarily oxidation, hydrogenation, reduction and hydrolytic reactions are concerned. Also among the individual chemical compounds mutual chemical reactions take place. Some examples of photochemical reactions of pesticides in water are presented in Figs 3.22 to 3.26. Biochemical reactions of DDT and DDE are shown in Fig. 3.27. The number of individual chemical species is hence significantly multiplied in the hydrosphere due

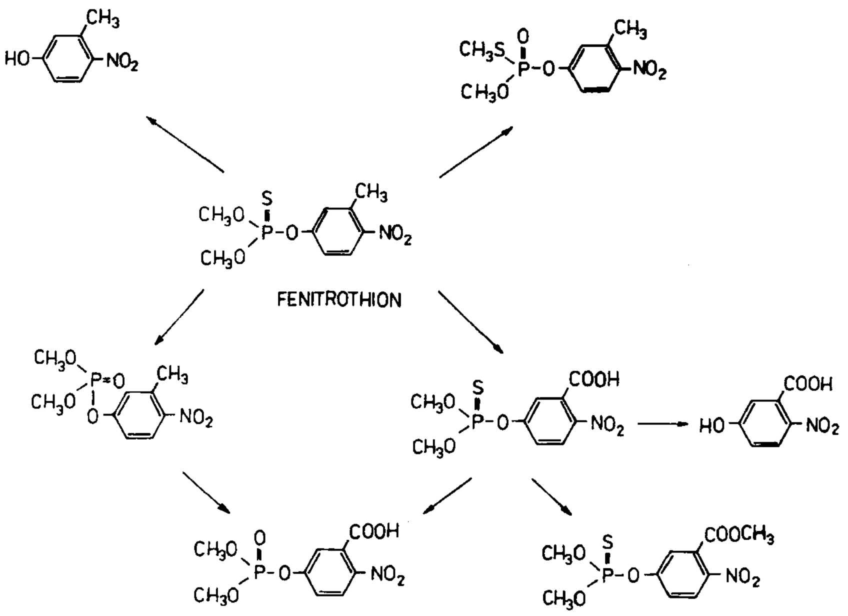


Fig. 3.22. Photochemical reactions of fenitrothion in water [67]

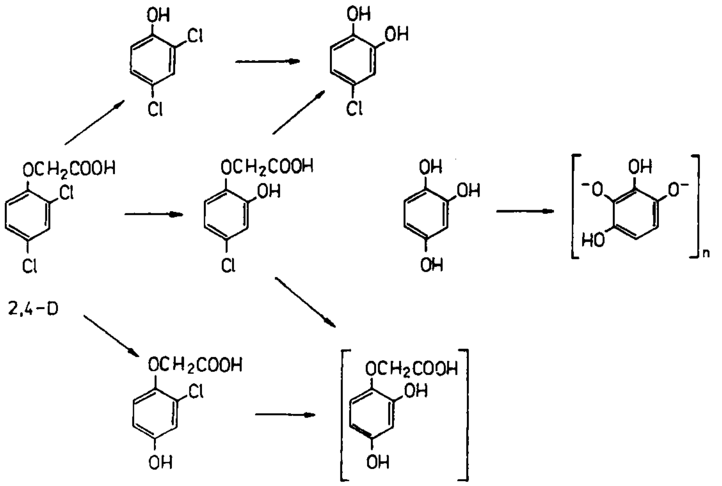


Fig. 3.23. Photochemical reactions of 2,4-D in water [68]

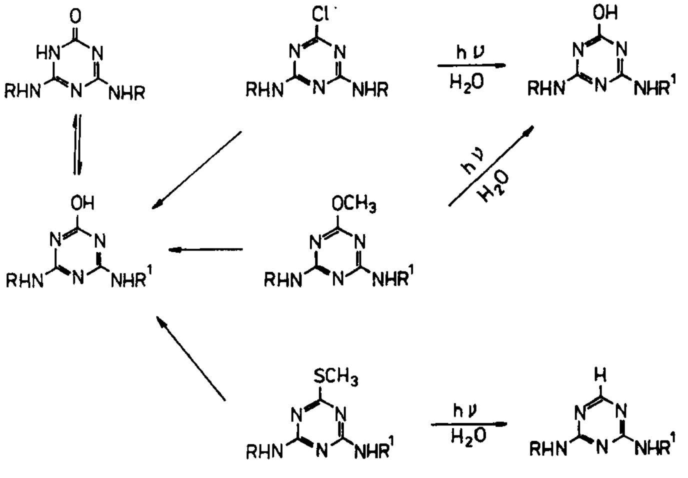


Fig. 3.24. Photochemical reactions of *s*-triazines in water [69, 70]

to secondary reactions. The increasing worries concerning the omnipresent residues of these chemicals in abiotic and biotic environments is thus fully justified.

Table 3.20. Some general metabolic reactions of pesticides

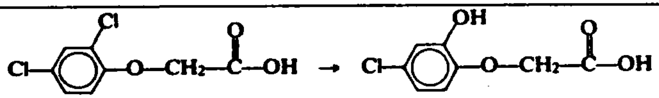
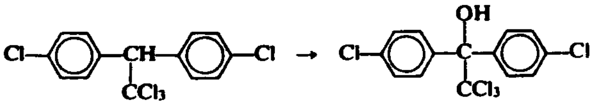
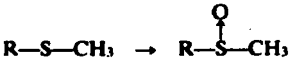
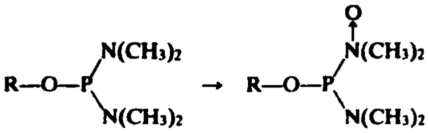
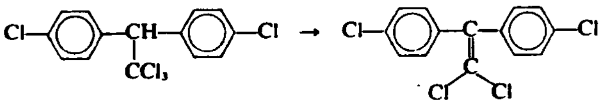
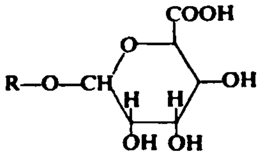
Chemical reactions	Schematic representation	Pesticide undergoing this reaction
(1) Oxidation (a) hydroxylation		2,4-D
(b) side chain oxidation		DDT
(c) splitting of ether		2,4-D
(d) formation of sulphoxides	 $R{-}S{-}CH_3 \rightarrow R{-}\overset{O}{\overset{\uparrow}{S}}{-}CH_3$	Phorate
(e) formation of *N*-oxides		Schraden
(2) Dehydrogenation and dehydrohalogenation		DDT
(3) Reduction	$R\text{-}NO_2 \rightarrow R\text{-}NH_2$	DNOC

Table 3.20 (continued)

Chemical reactions	Schematic representation	Pesticide undergoing this reaction
(4) Conjugation (a) formation of amides	$R\text{-}NH_2 + R'\text{-}COOH \rightarrow R\text{-}NH\text{-}CO\text{-}R^-$	Amitrole
(b) metal complexes	$R_2\text{-}N + MeX \rightarrow (R_2N\text{-}Me)X$	Amitrole
(c) glucosides and glucuronic acid	R–OH + glucuronic acid → 	Barthrin
(d) sulphates	$R\text{-}OH + SO_4^{2-} \rightarrow R\text{-}O\text{-}SO_3^-$	Biphenyl
(5) Hydrolysis of (a) esters	$R\text{-}CO\text{-}OR' \rightarrow R\text{-}CO\text{-}OH + HO\text{-}R$	Malathion
(b) amides	$R\text{-}CO\text{-}NH\text{-}R' \rightarrow R\text{-}CO\text{-}OH + R'\text{-}NH_2$	Dimethoate
(6) Exchange reactions		Parathion
(7) Isomerization		

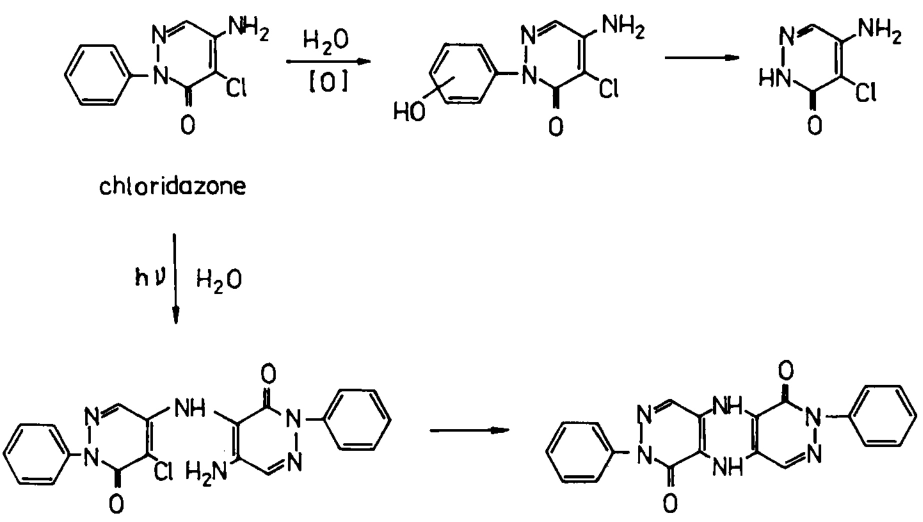


Fig. 3.25. Chemical and photochemical reactions of chloridazone in water [71, 72]

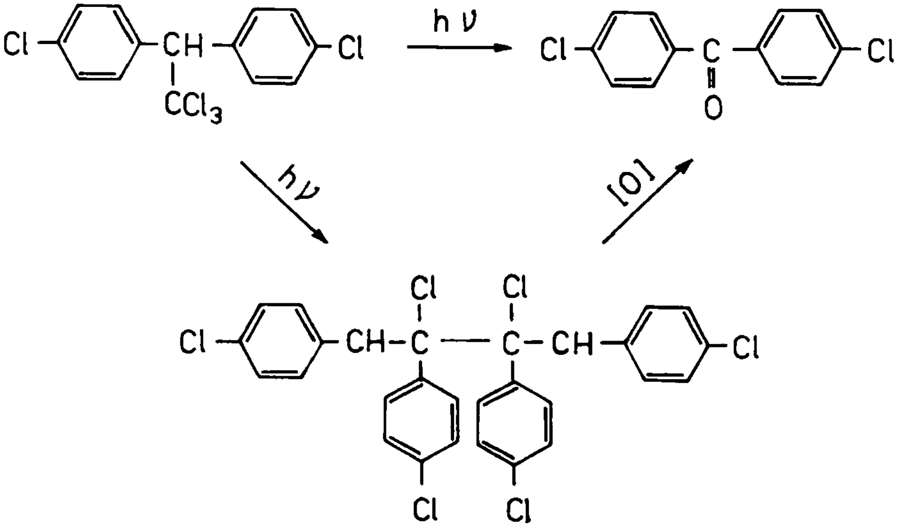


Fig. 3.26. Photochemical reactions of DDT

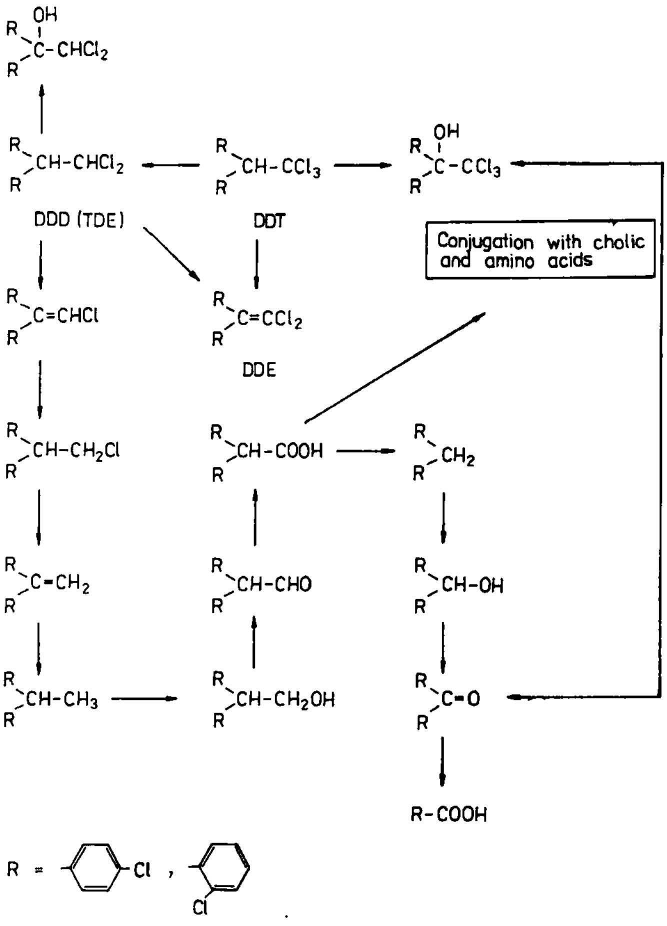


Fig. 3.27. Biochemical reactions of DDT and DDE [27]

Among the main sources of the pollution of ecological systems, conventional use of pesticides in agriculture, forestry and water systems, and public health care and hygiene, should be considered. This concerns particularly aerial large-scale spraying of fields and forests, and the frequent application of pesticides to waters to control the carriers of diseases or aquatic plants in irrigation systems.

Other important sources of direct pollution of rivers are the wastes from the industrial production plants for pesticides, wastes from households, and from the cleaning of application machinery and auxiliary equipment. Particularly harmful is aerial spraying, in which 50–75% of pesticides can fall outside the target zone.

Pesticides of atmospheric origin are the most serious source of the pollution of the oceans. The fall-out of aerosols and washing out of pesticides

Table 3.21. Solubility of some pesticides in water [24]

General name of pesticide	Temperature of measurement (°C)	Solubility in water (mg l^{-1})
Insecticides:		
Aldrin	20–30	0.027
Camphechlor	20–30	3.0
DDT	25	0.0012
Dieldrin	20–30	0.186
Endrin	25	0.23
Heptachlor	20–30	0.06
Lindane	20	10.0
Acephate	20	700×10^{-3}
Diazinon	Room	40
Dichlorvos	Room	1×10^{-4}
Dimethoate	Room	25×10^{-3}
Disulphoton	25	66.0
Metathion	25	145
Mevinphos	—	Soluble
Parathion-methyl	25	55–60
Thiometon	20	200
Trichlorophon	25	154
Carbaryl	30	40.0
Carbofuran	25	250–700
Pirimicarb	25	2.7×10^{-3}
Propoxur	20	2×10^{-3}
Herbicides:		
Atrazine	20–27	70.0
Chloridazone	20	300–400
Chlorophenprop-methol	20	690
Chlorotoluron	20	70
2,4-D	25	890
2,4-D butylester	25	890
Dinoseb-acetate	20	2.22×10^{-3}
EPTC	20	375
Isoproturon	25	170
MCPA	25	$1.5–1.6\times10^{-3}$
Mecoprop	20	620
Picloram	25	430
Simazine	20	5
2,4,5-T	25	280
2,4,5-T butylester	25	280
Terbutryn	20	58
Terbutylazine	20	8.5
Trifluralin	20	1

Table 3.21 (continued)

General name of pesticide	Temperature of measurement (°C)	Solubility in water (mg l^{-1})
Fungicides:		
Captan	25	0.5
HCB	25	Insoluble
Triforine	Room	30
Tridemorph	20	100

from the atmosphere by rain increase the quantity of pesticides entering oceans via rivers (see Table 3.24).

The hydrosphere coexists in a dynamic equilibrium with other spheres. However, only a small fraction of persisting pesticides is present in true solutions due to their low solubility (Table 3.21). The highest quantity is concentrated in the sediments on the bottom of rivers, lakes and oceans. However, on account of the cumulative ability of the living organisms in water, even the low concentration of pesticides becomes very dangerous. As shown in Table 3.22, DDT present in water is considerably accumulated in living aquatic organisms. This accumulation in fish and birds is even more multiplied due to the DDT residue accumulation in extensive reserves of fat in the body (in animals, also in the milk). DDT and other chlorinated insecticides interfere with the metabolism of steroid hormones (this is true for mammals as well) and influence the reproductive ability of whole populations. And thus, very low doses which are not lethal for individuals become lethal for populations. Of course, this problem also concerns man,

Table 3.22. An example of DDT concentration increase in the food chain [73]

Links in the food chain	DDT residua (ppm)
Water	0.00005
Plankton	0.04
Fish of the *Atherinidae* family	0.23
Fish *Cyprinodon variegatus*	0.94
Pike-like fish (predators)	2.33
Fish *Scomberesox scaurus* (predators)	2.07
Heroms (feeding small animals)	3.57
Gannets (feeding small animals)	3.91
Lapwings (feeding small animals)	6.00
Eggs of osprey	13.80
Cormorants (feeding bigger fish)	26.40

and biological impacts cannot yet be predicted. One example which has been studied is the loss-rate of pelicans on American lakes where Toxafen was applied (Table 3.23).

Table 3.23. Occurrence of Toxafen in the lakes of the USA

	Toxafen residua (ppm)
Lake water	0.2
Plankton	77.0
Fish	200.0
Pelican (lethal dose)	1700.0

In addition to the above biological effects, pesticides negatively influence the self-cleaning ability of water, deteriorate its sensory properties and influence the operation of biological wastewater treatment plants. There is also the possibility of deterioration of underground waters by pesticides or their residues. To illustrate this, Table 3.24 lists concentrations of some chlorinated insecticides in rain water, and Table 3.25, in surface waters. The maximum allowable concentrations from the viewpoint of sensory properties are, however, lower than the concentrations with toxic effects. The World Health Organization has defined the permissible daily dose of pesticides which is without evident risk for man. When treating water for drinking purposes many pesticides cannot be eliminated by common technological processes, such as clarification, chlorination or ozonization. Some values of the pesticide concentration in drinking water are listed in Table 3.26.

Table 3.24. Concentrations of some chloroorganic insecticides in rain waters ($\mu g\ l^{-1}$) ng l^{-1}

Geographic region	α-BHC	γ-BHC	Dieldrin	DDE	DDT	DDD
Antarctica (snow)	–	–	–	–	40	–
England (1966–1967):						
London	29	59	16	25	61	7
Camborne	5	43	6	28	53	34
Lerwick (isle)	24	121	11	20	46	7
Hawaii (1970–1972)	–	1–9	1–97	–	1–14	–
GDR (1970–1972)	–	80	–	50	190	20

Table 3.25. Concentration of chloroorganic pesticides in surface waters ($\mu g\ l^{-1}$) $ng\ l^{-1}$

Locality	No. of with-	DDT		BHC	
Type of water	drawals	max.	med.	max.	med.
England					
rivers	76	—	—	118	25.82
rivers	15	43	8.67	214	53.6
household waste	21	800	130.9	390	92.5
GDR					
Havel	—	3200	650	670	240
FRG					
the Elbe (Hamburg)	—	—	—	430	252
the Rhine	—	—	—	535	211
main rivers	51	300	18.9	1700	138
Switzerland					
the Rhine (Kembser)	—	—	—	86	—
USA					
main rivers	11	120	10.3	20	2.8
Mississippi-delta	10	720	112	120	28
Canada					
water surfaces	4	397	64	—	—
Czechoslovakia					
the Danube (Devín–Komárno)	185	165	—	197	—
the Danube (mud)	10	1120	0.7	0.045	0.01

Table 3.26. Concentration of chloroorganic pesticides in drinking water ($\mu g\ l^{-1}$) $ng\ l^{-1}$

Locality	DDT	DDE	Lindane	BHC	Dieldrin	Endrin	Camphechlor
Hawaii	44.0	—	—	1.6	9.4	—	—
GDR	100.0	60.0	50.0	—	—	—	—
Slovakia	42.0	22.0	69.0	—	—	—	—
Sweden (Lovö)	0.2	0.07	0.07	0.015	—	—	—
USA	—	—	—	7–1000	160.0	160.0	7–140

Mutual synergistic effects of various pesticides and combined effects of pesticides with other toxic substances are so far only little known.

As it is impossible to stop the use of pesticides at present, it is necessary to look for new types of chemicals, such as attractants, hormonal preparations, sterilenes, which could be substituted for the highly toxic and persistent pesticides used till now. Only the future will show to what extent this problem will be successfully managed by mankind, and current trends confirm that efforts are being made in this direction. The basic requirement is a knowledge of the behaviour of pesticides in the environment, e.g. it is necessary to know their chemical and biological transformations and effects of intermediates formed in this way; we now give some examples to illustrate the varied directions of this research.

In addition to the above-mentioned photochemical transformations of some pesticides another study of photodegradation of Basagran (Bentazon) herbicide has been carried out both under natural conditions (solar radiation) and model conditions [74]. The study also deals with the photodegradation of Basagran in aqueous solutions.

The photodegradation of Bromobutid herbicide has been described [75]. The authors present expected routes for its photodegradation. Their assumptions result from detailed ESR-analysis of model reactions of Bromobutin with different additives, reaction with the OH radical and the reaction with singlet oxygen. The papers dealing with the photooxidation of Bromacil [76, 77] and Terbacil [78] in water, or photodegradation reactions of diphenylether herbicides in water and other solvents cyclohexane, methanol are of a similar character. One study [79] can serve as an example of research into the secondary generation of nitrophenols into the environment.

A promising group of intensively studied derivatives at present is represented by insecticides known as pyrethroids [61, 80]. These originally natural compounds are now produced by synthetic processes [80]. A detailed study of their photochemical and hydrolytic reactions has been carried out by a group of Japanese scientists [81–85].

It is of great importance to know the biological degradability of pesticides [86], as studied, for instance, in the biotransformation reactions of pentachlorobenzene-based fungicides. In another study [87], the biotransformation reactions of pentachloronitrobenzene with hexachlorobenzene are compared. The mechanism of reduction denitrification is discussed by the same authors elsewhere [88]. Similar studies are presented in the papers [89, 90].

The omnipresence of pesticides and their residues [91–94] accentuates the need for reliable analysis [95–98] and sensitive detection of the hydrosphere pollution by these substances [99].

3.4.2.4 Carcinogenic compounds

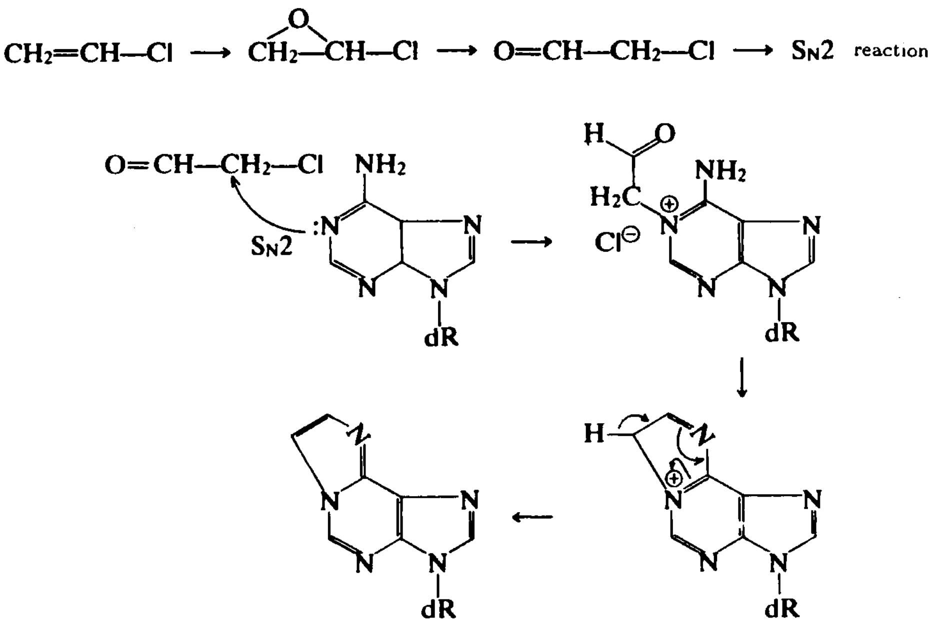
The occurrence of carcinogenic substances in the environment and thus in the hydrosphere as well is a vitally urgent problem [100–110]. The curve of the occurrence of cancer-related diseases has such an increasing tendency that, in parallel with the heart disease, it represents at present one of the most frequent causes of death, especially in view of the fact that these diseases occur in man regardless of age.

The urgent problem of the study of carcinogenic substances in the environment seems to be becoming ever more complex at present. The situation is well documented by the development of opinions on the carcinogenic effects of polyaromatic hydrocarbons (PAH), particularly benzo[*a*]pyrene. The number of studies dealing with this problem, differences in opinions as to the main point as well as the determination of which intermediates, or which activation causes the generation of the ultimate cancer, underline the view that our knowledge is only partial and that the mechanism in some cases is more suspected than actually known. Considerable progress in this field has been achieved primarily due to new ESR techniques and other spectral methods (e.g. spin trapping) which make it possible to measure or to indentify even very low concentrations of intermediates possessing the decisive role in chemocarcinogenesis [111–114].

The problem is also complicated by the fact that several substances frequently interact. Their mutual activity can have procarcinogenic effects. Thus, the field of co-carcinogenesis is entered, which even further complicates the situation.

In the following paragraphs, only *chemical carcinogens* will be discussed. Of the extensive groups of carcinogenic substances which occur or are regularly applied into the environment one should mention, for example, pesticides, widespread detergents which either have carcinogenic effects or their presence in water results in increased solubility of other dangerous carcinogens involving some heavy metals which occur most frequently in the form of organic complexes. Other examples are nitrosoamines, nitro compounds, halogen derivatives, and some aromatic as well as aliphatic amines.

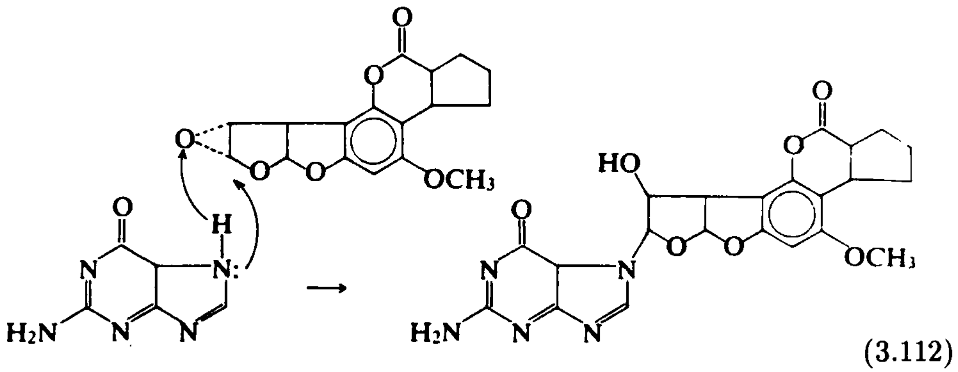
However, with regard to widespread and high carcinogenic activity the most dangerous for man are the polyaromatic hydrocarbons as well as some heterocyclic compounds, nitroheteroaromates, nitroaromates, and polycyclic carbonyl compounds. These substances have the character of procarcinogens and can be frequently activated up to the level of direct carcinogens via metabolic transformations in the biosystem. For the ultimate carcinogens, Miller postulated that the final entity must have an electrophilic character [104, 105]. This precondition is satisfied by the experimentally found details of typical activation reactions of some derivatives (Table 3.27). The reactions of the ultimate chemical carcinogens can be illustrated by examples of the reactions of vinylchloride and aflatoxin B_1 with nucleic acids: (a) reaction of vinylchloride with DNA



$$CH_2{=}CH{-}Cl \longrightarrow \overset{O}{CH_2{-}CH}{-}Cl \longrightarrow O{=}CH{-}CH_2{-}Cl \longrightarrow S_N2 \text{ reaction}$$

(3.111)

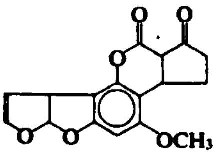
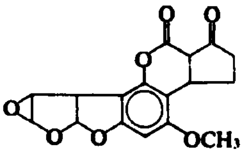
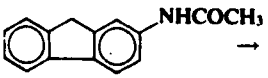
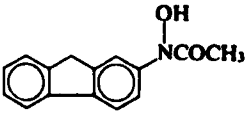
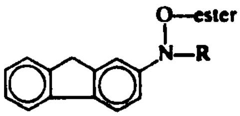
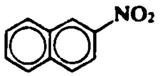
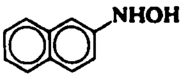
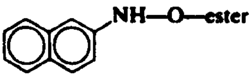
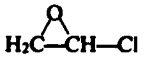
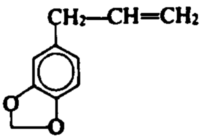
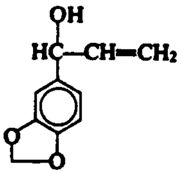
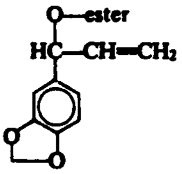
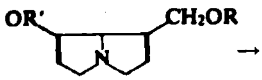
(b) reaction of aflatoxin B_1 with DNA



(3.112)

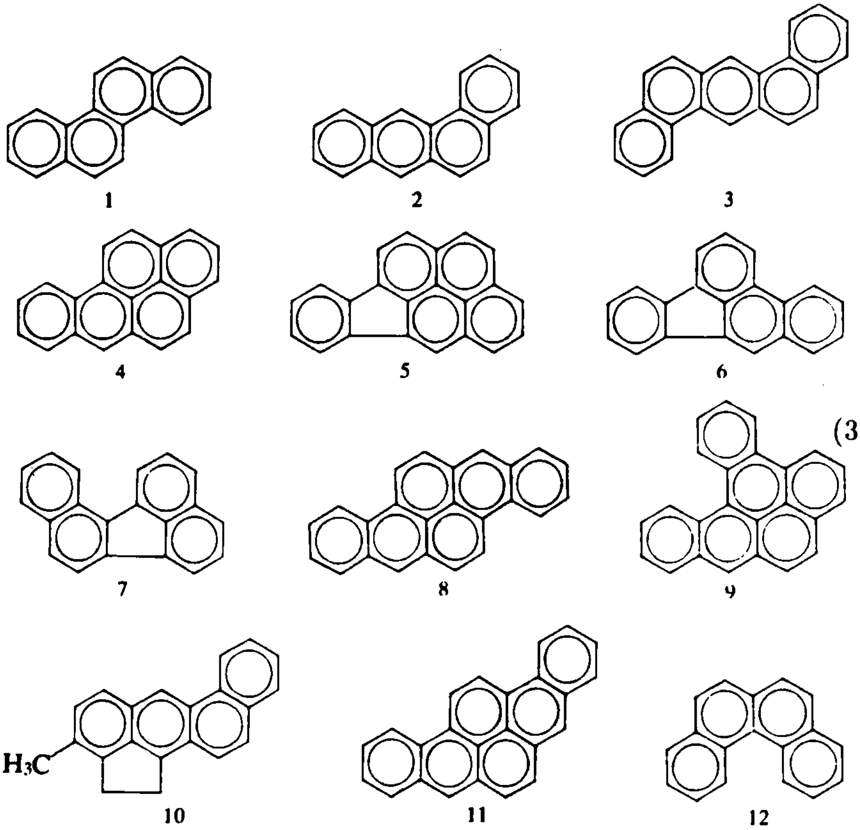
Carcinogenic polycyclic hydrocarbons occur in water either in the dissolved form (Table 3.28) or adsorbed on various particles. The content

Table 3.27. Examples of some carcinogen activation reactions

Procarcinogen	→	Direct carcinogen	→	Ultimate carcinogen
 aflatoxine B_1	→			
 2-acetylaminofluorene	→		→	
 2-nitronaphthalene	→		→	
$H_2C{=}CH{-}Cl$ vinylchloride	→			
 safrol	→		→	
 pyrrolizidine (alkaloid)	→		→	

of these corpuscular carcinogens in natural waters ranges from 0.004 to 0.5 mg kg^{-1} of dry matter with a simultaneous content of dissolved carcinogens of 0.002–0.008 mg m^{-3}.

Some carcinogenic polyaromatic hydrocarbons which have been identified and which occur in the environment of man are the following:



(3.113)

1 — chrysene, 2 — benzo[*a*]anthracene, 3 — dibenzo[*a*, *h*]anthracene, 4 — benzo[*a*]pyrene, 5 — indeno[1, 2, 3 – *cd*]pyrene, 6 — benzo[*b*]fluoranthene, 7 — benzo[*j*]fluoranthene, 8 — dibenzo[*a*, *h*]pyrene, 9 — dibenzo[*a*, *l*]pyrene, 10 — 3-methylcholanthrene, 11 — dibenzo[*a*, *i*]pyrene, 12 — benzo[*c*]phenanthrene. The most dangerous of these is benzo[*a*]pyrene.

With regard to the serious pollution of our rivers with these substances and their sensitivity to light, oxygen, ozone or other oxidation agents, one can expect quite a fast transformation from the stage of procarcinogens into

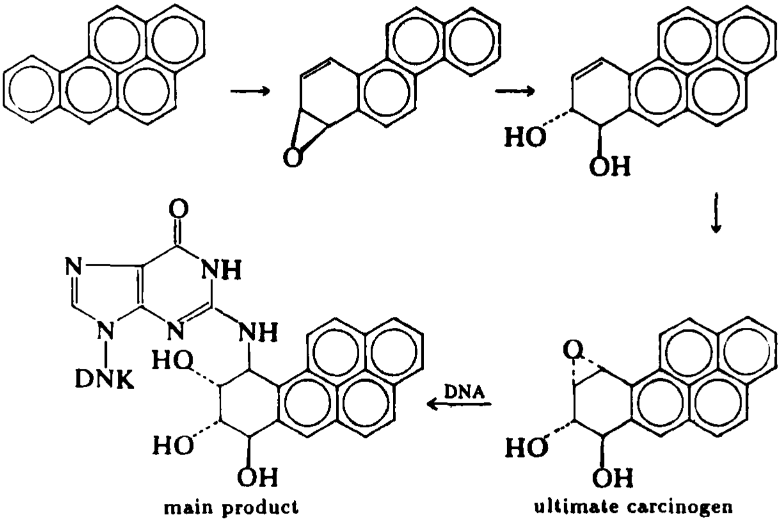
Table 3.28. Solubility of some polycyclic hydrocarbons in water

Hydrocarbon	Solubility (mg m^{-3})[a]
Benzo[*a*]pyrene	4–60
Anthracene	75
Benzo[*a*]anthracene	10–11
9,10-Dimethylbenzo[*a*]anthracene	550[b]
Dibenzo[*a*, *h*]anthracene	0.5–0.6
Phenanthrene	1600
Chrysene	1.5–6.0
Pyrene	165–175
Fluoranthene	240–265
Perylene	0.5
3-Methylcholanthrene	1.5

[a] Values from different sources are often controversial for the given temperature. Temperatures of measurement were 25 and 27°C.

[b] 0.5% of caffeine.

direct carcinogens. This fact is illustrated by the scheme for the metabolic activation of benzo[*a*]pyrene



(3.114)

Its stability and thus also the transformation into direct carcinogen in water is characterized by the loss from the original content of 2.0 to

1.74 mg m^{-3} after 5 days, and 0.094 mg m^{-3} after 35 days. Only after 45 days was no residual concentration observed.

Man is endangered by carcinogenic substances from many sources. The problems of hygienic prophylaxy of malign tumours will not be satisfactory solved until the problems of the environmental pollution by these substances are solved separately. As surface waters are ever more used in water treatment practice, it is in the common interest to protect the hydrosphere against further pollution by carcinogenic organic materials.

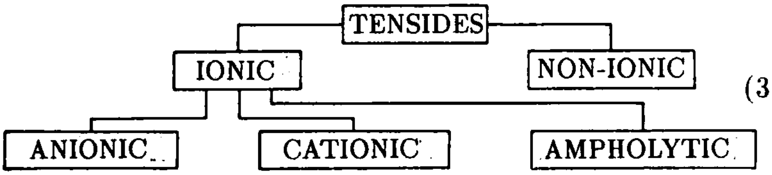
3.4.2.5 Tensides and detergents

Another large group of organic substances polluting the hydrosphere are the preparations known as tensides and detergents [115, 116].

Tensides are surface active substances with a capability to reduce the surface tension at an interface. In aqueous solutions they have cleansing, wetting, emulsifying, dispersing, stabilizing and frothing effects.

The term *detergent* denotes washing and cleaning preparations which contain, in addition to tensides, also other additives to increase the washing and cleaning properties of the preparation.

A molecule of tensides consists of hydrophilic and hydrophobic parts. The polar parts of the molecule are formed particularly by the sulphone, sulphonate groups or cumulated hydroxyl or etheric groups, which are all hydrophilic. The hydrophobic part is formed by aliphatic or aromatic carbon, frequently branched and substituted. From the viewpoint of dissociation capability of the polar hydrophilic group, tensides are classified into ionic and non-ionic categories:



(3.115)

Ionic tensides dissociate in aqueous media to generate positively or negatively charged ions. *Non-ionic tensides* contain a polar non-dissociated group, such as –OH, or –O–.

Ampholytic tensides contain functional groups which are alkaline or acid depending on pH. Examples of some tensides are listed in Table 3.29.

Table 3.29. General examples of some tensides

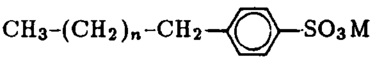
(a) Anionic tensides

CH_3-$(CH_2)_n$-CH_2-COOM

soaps $n = 6$–10

CH_3-$(CH_2)_n$-CH_2-OSO_3M

sulphates of higher fatty acids

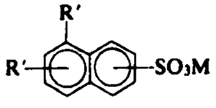


alkylarylsulphonanes

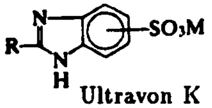
R-X-CH_2-COOM

X-non-dissociated polar group

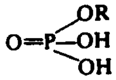
-SO_2NH-,-O-,-SO_2-,-S-,-CONH-



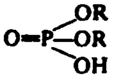
Neokal



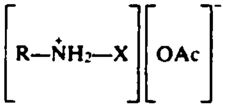
Ultravon K



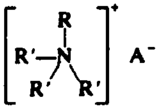
Hopstaphat KW 200



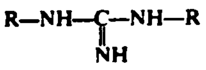
(b) Cationic tensides



Armac



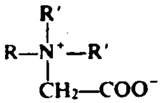
quaternary amonium salts



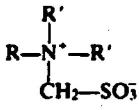
$$R{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}R$$

dialkylguanidines

(c) Ampholytic tensides



$$R{-}\overset{\overset{R'}{|}}{\underset{\underset{CH_2-COO^-}{|}}{N^+}}{-}R'$$



$$R{-}\overset{\overset{R'}{|}}{\underset{\underset{CH_2-SO_3^-}{|}}{N^+}}{-}R'$$

(d) Non-ionic tensides

R-O-$(C_2H_4O)_nH$

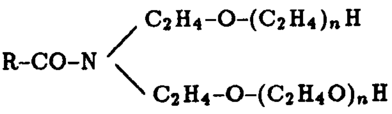
alkylpolyglycolethers

R-Ar-O-$(C_2H_4O)_nH$

alkylarylpolyglycolethers

R-CO-O$(C_2H_4O)_nH$

acylpolyglycolethers



$$R\text{-}CO\text{-}N\begin{cases}C_2H_4\text{-}O\text{-}(C_2H_4)_nH\\ C_2H_4\text{-}O\text{-}(C_2H_4O)_nH\end{cases}$$

acylated alkanoamino polyglycol ethers

M = monovalent metallic cation,

R = higher alkyl or alkylaryl,

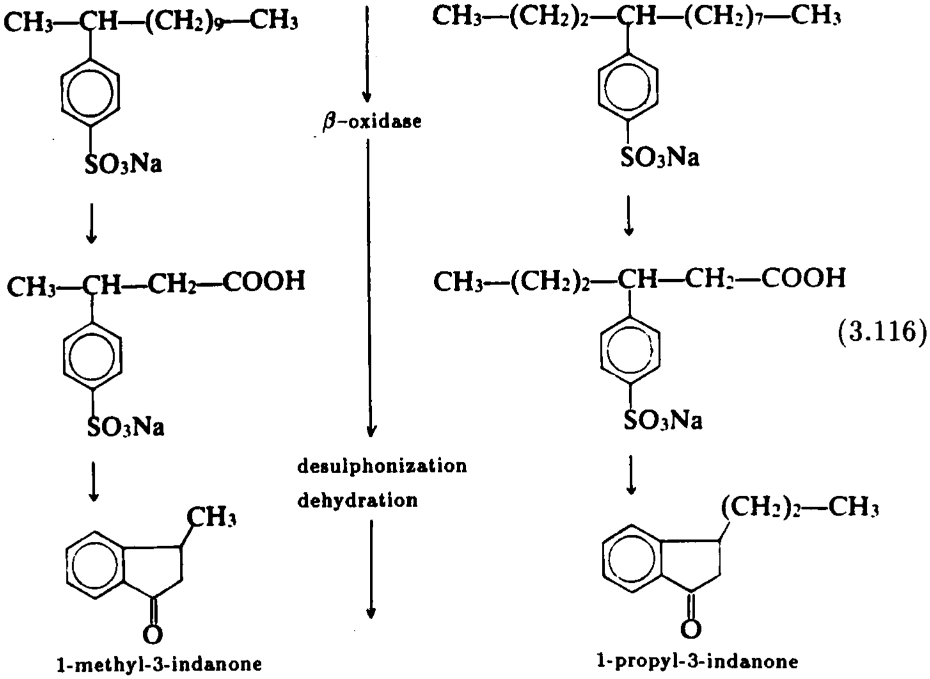
R′ = lower alkyl.

Tensides have a wide range of practical applications particularly in the textile industry, and in the production and processing of plastics. They are also extensively used in the oil industry, in pulp and paper making, in foodstuff and leather industries, as well as in agriculture.

Their occurrence in waters causes a higher solubility of other organic low-soluble compounds. Due to their effects the oxygen balance of rivers is considerably reduced. In water treatment they cause serious difficulties with regard to their physical and chemical properties. Quite frequently they are biologically difficult-to-degrade and their biodegradability is thus an important factor which becomes a criterion for the practical use of tensides.

In Tables 3.30 and 3.31 examples of the biological degradability of some tensides are presented.

In the scheme below an example of metabolic degradation of 2-(4-sulphophenyl)dodecane and 4-(4-sulphophenyl)dodecane is illustrated:



(3.116)

The scheme shows that here too, β-oxidation scission with subsequent desulphonization and cyclization dehydration occur.

Tensides cause many difficulties in water treatment. The treatment process of surface waters into drinking water removes tensides only partially and a population supplied with such water permanently ingests tensides.

Table 3.30. Degradability of thiosuccinic acid diesters in rivers according to the reaction with Methylene Blue

Alkyl ester groups	Time of degradation (d)
Benzyl-	5
n-Octyl-	6
2-Ethylhexyl-	11
3,5,5-Trimethylhexyl-	11
Isobutyl-	24
1,3-Dimethylbutyl-	No degradation after 28 days
Cyclohexyl-	No degradation after 28 days

Table 3.31. Biological degradability of α-sulphonated esters of aliphatic acids according to the reaction with Methylene Blue

Name	Avarage times for 80% degradation (h)
2-Sulphohexadecanoic acid	125
2-Sulphooctadecanoic acid	180
9,10-Dichloro-2-sulphooctadecanoic acid	186
9,10-Dihydroxy-2-sulphooctadecanoic acid	89
Hexylester of 2-sulphononanoic acid	239
Methylester of 2-sulphohexadecanoic acid	103
Isopropylester of 2-sulphohexadecanoic acid	120
Butylester of 2-sulphohexadecanoic acid	165
N-Hydroxyethylamide of 2-sulphooctadecanoic acid	113
X-Phenyl-2-sulphooctadecanoic acid	335
Sodium *n*-dodecylhydrogenosulphate	39
Sulphated hexadecyltriethylene glycolether	48
n-Dodecylsulphonate	94
Sodium *n*-hexadecylsulphonate	103
Sodium *n*-heptadecylsulphonate	117

In contrast to tensides, soaps form insoluble surface-inactive compounds with Ca^{2+} and Mg^{2+} ions present in water. Their residues easily undergo biological degradation.

Maximum permitted concentrations of tensides in surface biologically treated waters depend on the type of the tenside and its biological degradability. The standard refers to aesthetic rather than physiological aspects, as anion-active tensides at concentrations upwards from 0.5 to 1.0 mg l^{-1} begin to froth. This concentration is sufficient to increase the intake of harmful substances into the organism (pesticides, carcinogenic substances, etc.). Therefore, the fundamental requirement, worldwide, is the need to produce biologically easily degradable tensides. Many emergency situations in the rivers of the FRG and other countries have called for the legal imposition of this requirement for tensides and detergents. This is the only way of achieving reduction or entire elimination of these preparations from surface and drinking waters.

3.4.2.6 Petroleum components

From the viewpoint of the possibilities of environmental pollution by petroleum components the hydrosphere is the most seriously affected [117–119]. Although the compounds present in oil have a low solubility in water, they form a continuous film on the water surface which has very negative impacts on the oxygen balance of, for example, a river. Futhermore, hydrophobic organic substances, such as pesticides, are more readily dissolved in this surface film.

Petroleum is an inflammable liquid consisting largely of hydrocarbons. It is usually lighter than water, and has a light to almost black colour, with a characteristic smell. It contains all groups of hydrocarbons except monoenes and polyenes. *n*-Alkanes are present in all fractions of the oil. It also contains isoalkanes, cycloalkanes, condensed hydrocarbons, aromatic hydrocarbons and polycondensed hydrocarbons. Oxygen, sulphur and nitrogen substances are also present, for example, cycloalkane acids, hydrogen sulphide, mercaptans, acyclic and cyclic sulphides, thiophenes, and the heavier fractions contain derivatives of benzothiophenes. In the case of nitrogen derivatives there are pyridines, quinolines, carbazoles and their hydrogenated analogues. Petroleum also contains some oil-soluble metallic compounds. These substances are accumulated in the heaviest asphaltic fractions. The most important metals are V, Ni, Na, followed by Al, Si, Ca, Mo, Cu, Mg, Pb, Ag, Cr and Mn. Such a vast heterogeneous composition of petroleum has considerable impacts on the environment.

The source of the pollution of the hydrosphere by constituents of the oil are of different origin. They begin at the site of petroleum exploitation itself (on land as well as in the sea), then during transport, when the water of oceans is polluted by fairly frequent breakdowns and occasional ship-wrecks. For example, in the wreck of the oil-tanker Torrey Canyon in 1967, 118,000 t of oil was spread on the surface of the English Channel. Within this ecological disaster 25,000 sea birds died. The use of cleaning preparations turned out to be even more harmful for the sea life than the oil itself. At the present rate of shipwrecks of tankers, some 5–10 million tons of petroleum per year get into the seas.

Petroleum and petroleum products ever more pollute surface and underground waters (e.g. in Bratislava). The source of the pollution of these waters is primarily the petrochemical industry, followed by mechanical and metallurgical industries, motor-car repair shops and service stations.

Some oil products are biologically quite easily metabolized, such as alkanes, alkenes, cycloalkanes and aromates. Products of this activity are differently oxidized oxygen derivatives (peroxides, alcohols, phenols, aldehydes, acids, etc.). In this way microorganisms enable self-cleaning processes in soil and rivers. The rate of these degradation reactions depends on sufficient access of oxygen from the air.

The physiological properties of oil and oil products are diverse. In contrast to their few positive merits in medical treatment (reumatism, eczema, burns, gynaecological diseases, etc.) the negative effects from petrochemical and related operations are of very great significance.

From the viewpoint of water treatment, petroleum components particularly affect the sensory qualities of water (even at low concentrations, of the order of 10^{-6} to 10^{-7} g l^{-1}, they cause an unpleasant odour or aftertaste of the water) which cannot be entirely eliminated by the treatment processes.

On account of the known toxic or carcinogenic effects (see Section 3.4.2.4) of some hydrocarbons in petroleum or in its products, the initial preventive removal of the sources polluting the hydrosphere is especially desirable, as cleaning of surface and groundwaters already polluted by these substances is complicated.

Organic pollutants of the hydrosphere are regularly analysed and the results are published systematically [120–125]. The immense quantity of papers dealing with identification of organic pollutants of the hydrosphere, e.g. [126–130], shows the considerable development of analytic methods in this field. A good example of the progress in this interdisciplinary field is the monograph [120].

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3.5 Natural waters

The origin and development of the hydrosphere is closely connected with the development of other constituents of the Earth. Between the envelope and the earth's crust, between the hydrosphere, atmosphere, lithosphere and biological matter a permanent exchange of water takes place which causes changes in the chemical and isotopic composition of waters.

According to their origin, waters are classified into *juvenile* waters (formed in the primary differentiation of the substances of the earth's envelope) and *recirculated* waters (participating in the hydrologic cycle in the atmosphere). The continuous circulation of water is induced by solar energy and earth's gravity.

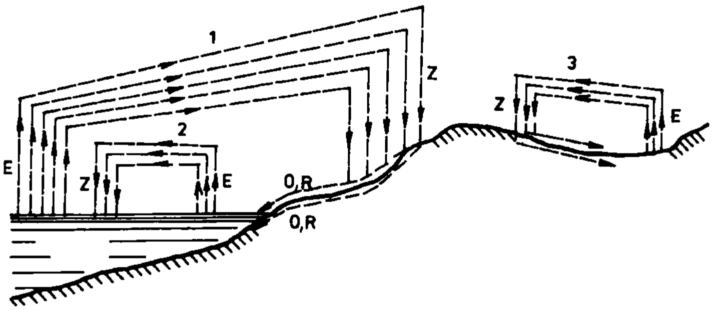

Fig. 3.28. Water cycles in nature. 1 — great cycle, 2 — small cycle, 3 — outflowless area (stagnant water)

The global water cycle operates between ocean and continent (Fig. 3.28); in this case, the complete equation of the hydrological balance is:

$$H_Z = H_O + H_E + H_R \qquad \text{(mm)} \tag{3.117}$$

where H_Z is the average height of the water level from precipitation (mm), H_O — the average height of the run-off water (mm), H_E — the average height of the evaporated water layer (mm), and H_R — the average height of water layer which will increase or decrease the water reserves (retention) (mm).

The small water cycle occurs above the oceans; a shortened balance equation is valid here

$$H_Z = H_E \tag{3.118}$$

A completely separate cycle occurs above zones without an outflow. The complex water transformation in the individual phases of the cycles is shown in the scheme of the hydrosphere (Fig. 3.29) [1].

Recirculated waters can be classified into five groups as follows:

- *magmatic* — separated at magma crystallization,
- *metamorphous*, leaking from rocks at thermal and pressure dehydration of minerals,
- *fossil*, preserved in the pores of sedimentary rocks in which no water exchange takes place,
- *sea*, both ocean and sea waters soaked from seas into the rocks forming continents,
- *meteoric* ones with direct genetic links to the atmospheric circulation, such as atmospheric (precipitation) water, soil water and sub-surface water infiltered from the surface. Meteoric water participates in a com-

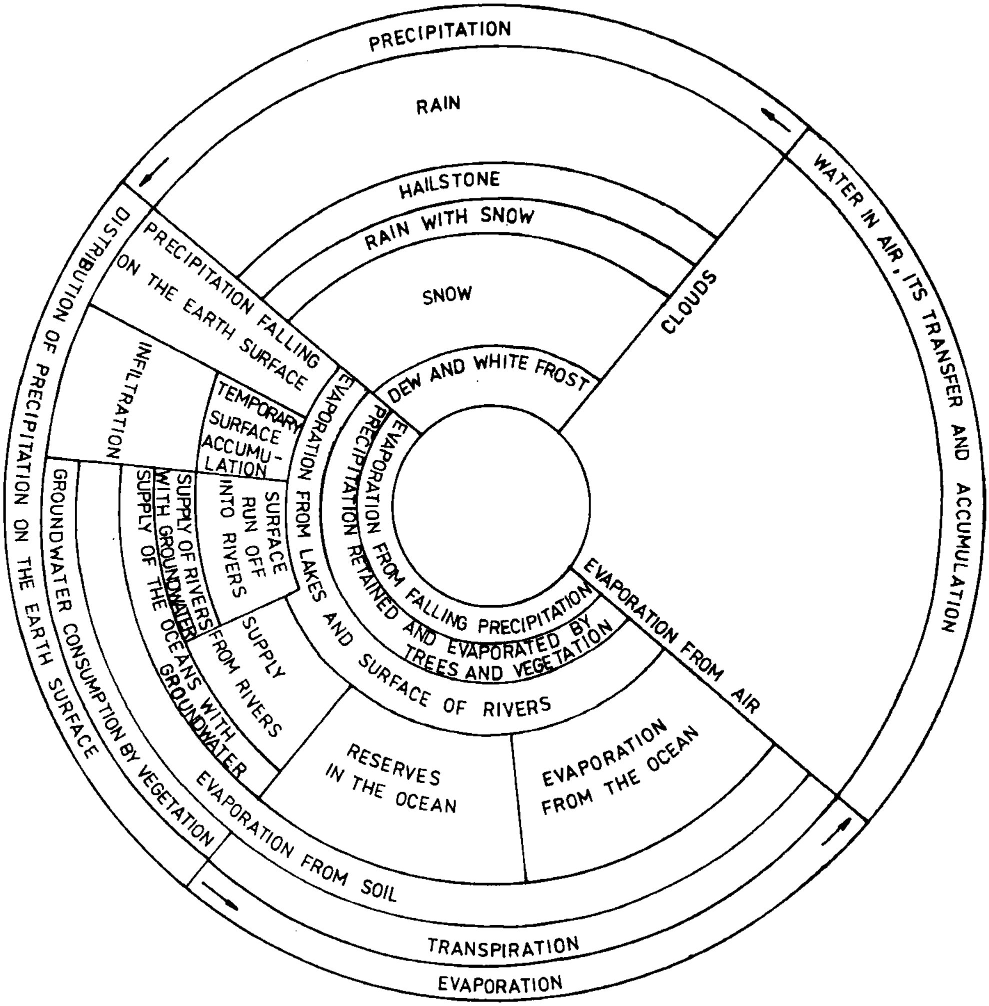

Fig. 3.29. The hydrosphere scheme

plicated biological cycle in the surface layer, with which it forms physicochemical subsystems of the biosphere (Fig. 3.30) [2].

According to their origin the waters occurring in nature are classified as follows:

— *precipitation* (*atmospheric*),

— *surface*,

— *groundwaters*.

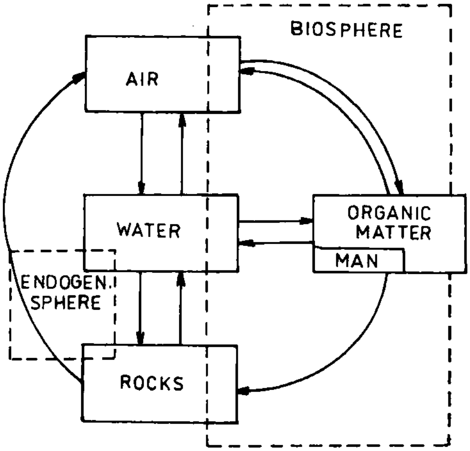

Fig. 3.30. Water circle in the biosphere

Table 3.32. Sources of normal water occurrence on the Earth [3]

Source of occurrence	Percentage of total reserves of normal water
Glaciers and permanent snow coverage	68.65
Groundwaters	30.1
Sub-surface ice	0.86
Lakes	0.26
Soil water	0.05
Atmospheric water	0.04
Swamps and peat moors	0.03
Stream water	0.006
Water in plants and living organisms	0.003

The proportions of fresh water (water with a low content of soluble solid substances, gases or microorganisms, incorrectly called "sweet water") in its various forms are given in Table 3.32 [3].

The processes determining the qualitative and quantitative composition of natural waters are physical, chemical and biochemical. In addition, the character of natural waters is influenced by climatic conditions, the overall features of the landscape, the density and type of its settlement, and other factors.

General classification of water pollutants is given in Table 3.33 [4].

Table 3.33. General classification of water pollutants [4]

Class of pollutant	Significance
Trace elements	Health, aquatic biota
Metal-organic combinations	Metal transport
Inorganic pollutants	Toxicity, aquatic biota
Asbestos	Human health
Algal nutrients	Eutrophication
Radionuclides	Toxicity
Acidity, alkalinity, salinity (pollutants if in excess)	Water quality, aquatic life
Sewage	Water quality, oxygen levels
Biochemical oxygen demand	Water quality, oxygen levels
Trace organic pollutants	Toxicity
Pesticides	Toxicity, aquatic biota, wildlife
Polychlorinated biphenyls	Possible biological effects
Chemical carcinogens	Incidence of cancer
Petroleum wastes	Effect on wildlife, aesthetics
Pathogens	Health effects
Detergents	Eutrophication, wildlife, aesthetics
Sediments	Water quality, aquatic biota, wildlife
Taste, odour, and colour	Aesthetics

3.5.1 Precipitation (atmospheric) water

Water is a permanent constituent of the atmosphere, in which it occurs in three forms:
— water vapour as air humidity,
— drops or granules and crystals forming clouds, and
— atmospheric precipitation falling on the Earth (rainfall).

The term *precipitation (atmospheric) water* denotes water in liquid or solid state which falls from the air onto the earth's surface during water vapour condensation. Depending on the temperature and degree of air saturation with water-vapour it can be either *liquid* (rainfall, dew, mist) or *solid* (snow, hailstones, hoarfrost, ice) precipitation.

Dew is a rain of very slight intensity. It is formed during clear nights due to cooling of the lowest air layers by the earth's surface below the dew point.

Mist consists of minute droplets of water in the range 0.006–0.04 mm in diameter; it is formed by cooling of the ground air below the dew point.

Drizzling rain is formed by mist precipitation.

Hailstones are pieces of ice 5–50 mm in size. They are formed particularly in summer by rapid cooling when very humid air quickly rises to large heights.

Hoarfrost originates from undercooled mist on contact with solid bodies (e.g. with aerial wiring).

Icy surface is formed during rainfall from undercooled droplets which immediately freeze and solidify after reaching the surface of the ground.

Approximately 448,000 km^3 of water is evaporated annually from the seas and oceans, and about 71,000 km^3 from the land. This water returns to the earth's surface in the form of precipitation. Roughly 412,000 km^3 of water fall on the surface of the seas and oceans, and about 108,000 km^3 on the continents. It is evident from this that the same quantity of water which is introduced into the atmosphere due to evaporation returns to the earth's surface in the form of precipitation. Total average precipitation over the whole of central Europe is about 600 mm per year. The average regional annual precipitation on the Earth is shown in Fig. 3.31. The atmospheric precipitation influence both quantitative and qualitative reserves of groundwaters.

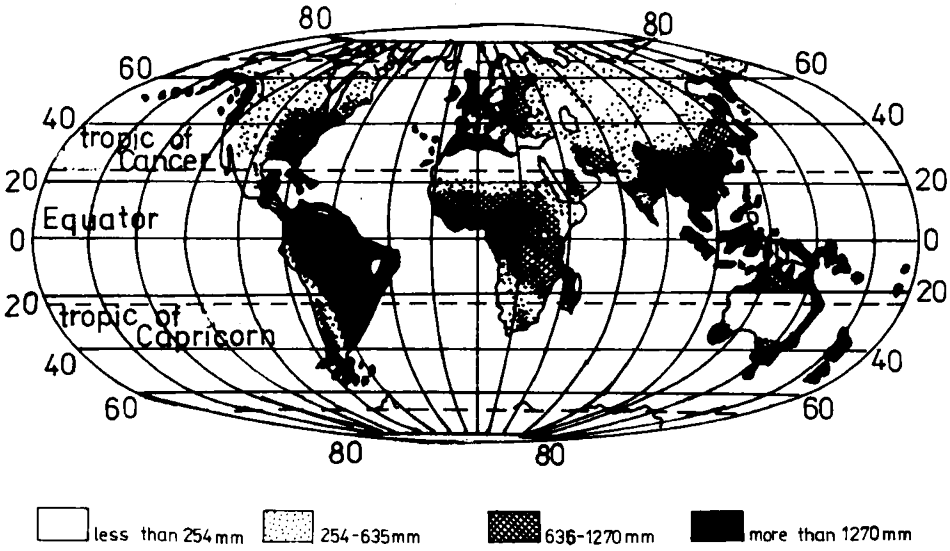

Fig. 3.31. Average annual regional precipitation on the Earth

Atmospheric water is the most abundant form of pure natural water, however, it becomes polluted when passing through the air layers. The greatest influence on the chemical composition of atmospheric waters is that of the layer of the atmosphere at a height of 1000–1500 m from the earth's surface. The rain drops and snow in passing through this layer of atmosphere "wash-out" considerable quantities of aerosols from air whose the most important sources are continental dust, salts carried by wind from the surface of ice, seas, surface rivers, volcanic and anthropogenic activities. Apart from the quantity and composition of aerosols, the chemical composition of atmospheric precipitations depends mostly on water content in clouds, quantity of precipitations, character of the precipitation period, size of aerosol particles, duration of precipitation, size of droplets, etc.

Atmospheric water contains particularly soluble gases which are commonly contained in air (oxygen, nitrogen, carbon dioxide and rare gases) followed by gaseous air pollutants (sulphur dioxide and sulphur trioxide, nitrogen oxides, ammonia, etc.), as well as solid substances (particles of dust, smoke, plants, microorganisms, etc.). The total quantity of inorganic soluble substances (*mineralization*) in atmospheric water ranges from 10 to 100 mg l^{-1} (in industrial or coastal regions these values can be considerably higher — as much as 100 mg l^{-1}). The content of particular anions and cations is usually in units of mg l^{-1}, but more than 10 mg l^{-1} are found only in the case of sulphates and hydrogen carbonates, and sometimes of some cations (Ca^{2+}, Mg^{2+}). In coastal regions atmospheric water can contain as much as 300 mg l^{-1} of chlorides. Inorganic compounds of nitrogen (ammonia, nitrides, nitrates) occur in tenths to units of mg l^{-1}.

Due to the weak mineralization of atmospheric waters and low concentration of hydrogen carbonates their neutralization capacity is very low. The pH value of atmospheric waters ranges from 5 to 6. Due to the absorbed oxides of sulphur and nitrogen (particularly in industrial zones) the pH values of atmospheric waters can be lower than 4.

The chemical mechanism of acid rain formation in the atmosphere [5] is as follows:

(1) Sulphur oxides

$$
\begin{aligned}
S + O_2 &\rightarrow SO_2 \\
SO_2 + H_2O &\rightarrow H_2SO_3 \\
H_2SO_4 + 0.5O_2 &\xrightarrow{\text{catalyst}} H_2SO_4
\end{aligned}
$$

$$2SO_2 + O_2 \xrightarrow{\text{catalyst}} 2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

(2) Nitrogen oxides

$$N_2 + O_2 \rightarrow 2NO$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

Acid atmospheric waters can reduce the pH of surface waters with low neutralization capacity. For example, in Scandinavian lakes and rivers, acidification caused by acid atmospheric precipitations results in the killing of fish species, trout and salmon. Apart from the reduced abundance of fish, acid atmospheric waters also unfavourably affect the soil composition (soil becomes poor in cations, replaced by hydrogen ions), as well as the growth of plants. They also cause significant corrosion of concrete, mortar, iron and other metals. Because of this property, low mineralization and irregularity of precipitation, atmospheric waters are very seldom used directly for water supplies. In some cases atmospheric waters can be an important source of nitrogen compounds for agriculture.

It is rather difficult to give mean values of the composition of atmospheric waters as it varies significantly. However, to illustrate this, Table 3.34 presents some examples of the chemical composition of atmospheric waters

Table 3.34. Examples of chemical composition of atmospheric waters (in mg l^{-1}) [5, 7]

Component	Locality			
	Sweden	Northern Bohemia (CSFR)	High Tatras (CSFR)	Bratislava (CSFR)
pH	3.8–7.7	6.4–6.6	4.3–5.5	4.9–7.5
SO_4^{2-}	6.2–6.5	21–57	7.1–11.4	4.5–5.3
Cl^-	0.1–64.0	—	2.7–12.0	2.1–12.2
NH_4^+	0–8.7	1.8–6.0	0.5–2.5	0–3.3
NO_3^-	0–0.34	4.3–5.4	0.8–1.9	0–1.2
Ca^{2+}	0.2–25.5	0.12–6.0	1.2–4.6	—
Mg^{2+}	0.1–2.9	5.8–16.4	0.1–0.7	—
Na^+	0.6–63	—	0.4–1.6	—
K^+	0–11.2	—	0.2–1.4	—

from different localities [6, 7] and Table 3.35 presents the average chemical composition of atmospheric waters in two very different regions [8].

3.5.2 Surface water

Surface water is run-off water or water retained in natural and artificial reservoirs on the surface. It originates from precipitations, springs of groundwater and melting of icebergs.

The formation receiving water from a certain river basin is called a *water recipient.* It is formed either in a natural way or artificially by man's interference. The water in the recipient may be either moving or stagnant (motionless). Considering this classification the following waters exist:

(1) stagnant:
  - natural (seas and oceans, lakes and swamps),
  - artificial (ponds, dams),

(2) running:
  - natural (brooks, torrents, rivers),
  - artificial (channels).

According to the locality, surface waters are categorized into *continental* and *sea waters.* Based on the measurements within the framework of the International Hydrological Decade (1965–1975) the world oceans contains 1228 million km^3 of water which represents about 96.5% of all water reserves of the Earth. Not quite 3% of the reserves on the Earth is common continental water. The volume of continents emerging above the sea surface is about 125 million km^3. The ratio between the volume of continents above the sea to the volume of the seas is approximately 1:11.

Continental surface waters originate from atmospheric and surface waters. The chemical composition of the continental waters is determined first of all by the reactions between atmospheric water, soil and rocks (from fairly recently, this composition has been and is being significantly influenced by the activity of man). Surface waters supplied by groundwaters are more mineralized, whereas mineralization is more moderate when atmospheric waters predominate. The character of the surface waters is determined by the representation of the above presented sources in the surface waters, climatic effects (precipitations, temperature), structure of geological layers and tributaries.

In Table 3.36 the mean content of chemical elements in surface waters of the Earth is presented. The table shows that sodium chloride prevails in the sea waters, and calcium hydrogen carbonate in common continental waters.

Table 3.35. Average chemical composition of atmospheric water in northern Europe and in southeastern Australia [8]

Locality	Average annual rainfall (mm)	pH	Na ($mg\ l^{-1}$)	K ($mg\ l^{-1}$)	Ca ($mg\ l^{-1}$)	Mg ($mg\ l^{-1}$)	Cl ($mg\ l^{-1}$)	SO_4^{2-} ($mg\ l^{-1}$)	NO_3^- ($mg\ l^{-1}$)	NH_4 ($mg\ l^{-1}$)
Northern Europe (62 stations, 30 month)	560	5.47 3.9–7.7	2.05 0.6–63.2	0.35 0–11.2	1.42 0.20–25.5	0.39 0.12–2.93	3.47 0.06—64.0	2.19 0.18—6.52	0.27 0–1.6	0.41 0–8.7
Southeastern Australia (28 stations, 36 months)	590		2.46 0–82.8	0.37 0.04—6.6	1.20 0–20.0	0.50 0–27.6	4.43 0—138.5	Trace Trace		

Contituents (upper numbers, average; lower numbers, range)

Table 3.36. Mean content of chemical elements (anions and cations) in surface waters of the Earth (wt%) [9]

Elements	Sea water	Common glacier water
Anions		
O	6.29	44.1
Cl	55.30	5.68
S	1.54	4.08
Br	0.19	Traces
C	0.07	7.05
Si	Traces	5.47
N	Traces	0.20
Total	63.39	66.58
Cations		
Na	30.60	5.79
Mg	3.73	3.41
Ca	1.20	20.40
K	1.11	2.12
Fe	Traces	0.94
Al	Traces	0.69
Total	36.64	33.35
Mineralization (%)	3.5	0.027
Anions	Cl>SO_4>CO_3>Br	CO_3>SO_4>Cl
Cations	Na>Mg>Ca>K	Ca>Na>Mg>K

The content of dissolved salts in the sea waters is on average 100-fold higher than the content in the common continental waters [9].

In addition to the above specified compounds also other elements are present whose contents differ and vary over a wider range. The contents of rare elements in the hydrosphere are listed in Table 3.37. Elements whose mean content is not quite certain are shown in brackets. The upward arrow means that it can be higher, the downward arrow signifies the probability of a lower content [9].

Common continental waters differ from the sea waters not only in their mineralization but also by greater differences in their chemical make-up. Therefore, the average composition of common waters can only be determined with much lower accuracy than the average composition of the sea waters. This is also evident from the data in Table 3.38 which shows the considerable differences between the average content of salts of rivers in Europa and Africa. Variations in the composition of individual river waters are even more marked [10].

Table 3.37. Content of rare elements in the hydrosphere [9]

Content in order (g t^{-1})	Elements
10^{-2}	I, Ba, Al, (Mo↓)
10^{-3}	(Fe↑), (Zn↓↑), (As↑), Mn, Sn, Cu, Ti, (Ni↓), (V↓)
10^{-4}	Ne, Kr, Ag, Co, Cs, Bi, Y, (Zr), Cd, Xe, W, Pb, (Sb↓)
10^{-5}	(Se↑), (Hg↑), Ge, Cr, Ga, Nb, (Sc)
10^{-6}	Au, Tl, He, La, Ce
10^{-7}	Be, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu
10^{-8}	
10^{-9}	
10^{-10}	(Ra↓)
10^{-11}	
10^{-15}–10^{-16}	Rn

Other elements are also present in the river waters, in low concentrations. Table 3.39 presents the content of rare elements in river waters. Letters in bold type are elements which occur in higher quantities in the river waters than in the sea waters, the letters in italics denote the elements with the opposite tendency.

The composition of stagnant surface waters (reservoirs) depends particularly on the depth, whereas in the big rivers it changes along the length of its flow and its width. Mineralization of water of the lower flow is many times higher than that of the upper one. Thus, this value varies in different layers of the flow.

For the life of aquatic organisms and self-cleaning capability of the surface waters, the content of dissolved oxygen is of great importance; it is a function of temperature, content of organic substances and intensity of photosynthesis. In summer periods the content of dissolved oxygen usually ranges from 8 to 12 mg l^{-1}, in the winter periods from about 6 to 8 mg l^{-1}. The content of oxygen also varies during the day as well (algae produce oxygen during the day).

The content of free carbon dioxide in surface waters is very low (maximum few mg l^{-1}). It is introduced into the surface waters by solution from air as well as via biological processes during degradation of organic matters in water. The pH of surface waters varies, depending on the CO_2 content. In winter periods the CO_2 content is higher (pH about 6.5–7.7) than in summer (pH as high as 8.8) when vegetation is intensive. In the surface

Table 3.38. Chemical composition of river waters in g t^{-1} [10]

Constituent	Mean value of all rivers	Mean value of European rivers	Mean value of African rivers	Mean value of of the Rio-Grande at Lobatos (Colorado, USA)	The Tuscaravas river at Newcomerstow (Ohio, USA)	The White Nile at Khartoum (Africa)	The Amazon at Obidos (South America)	The Jordan at Jericho (West Asia)
HCO_3^-	58.4	95	43	121	85	149.2	17.9	238
SO_4^{2-}	11.2	24	13.5	84	135	0.44	0.8	175
Cl^-	7.8	6.9	12.1	10	477	8	2.6	473
NO_3^-	1	3.7	0.8	1.5	5.1	0.44		
Ca^{2+}	15	31.1	12.5	39	201	17.4	5.4	80
Mg^{2+}	4.1	5.6	3.8	8.4	16	5.2	0.5	71
Na^+	6.3	5.4	11	29	141	30.7	1.6	253
K^+	2.3	1.7		5.4	4.4	11.8	1.8	14.8
Fe	0.67	0.8	1.3	0.5	0.07		1.9	
SiO_2	13.1	7.5	23.2	32	6.6	25.6	10.6	
Total	120	182	121	331	1072	249	43.1	1310

Table 3.39. Content of elements in river waters [9]

Content by order ($g\ l^{-1}$)	Elements
10^{-1}	*F*, **Al**, **Fe**
10^{-2}	*B*, *Sr*, Ba, **Mn**, **Ni**
10^{-3}	(Cu↑), (Cd), *Br*, *I*, *Li*, *Rb*, Pb, (Ti↑), **Cr**, U, (Co↓)
10^{-4}	Zn, Mo, V, (As), (Cs↓), (Hg↓)
10^{-5}	(Ag↑)
10^{-10}	Ra

waters of peat moor the pH value sometimes drops below 4.0 (depending on the humic matter content).

Surface waters usually contain higher amounts of organic matter. This is, for example, humic substances and other polyphenols, products of the life activity of aquatic organisms (natural sources) as well as organic pollutants of sewage and industrial wastes (artificial sources). Chemical oxygen demands COD(Mn) (see p. 300) in clean waters is usually given in terms of mg l^{-1}, but in the polluted waters it rises to tens of mg l^{-1}. COD(Cr) is usually 3 times higher than COD(Mn). Organic substances in surface waters have a certain degree of complex-forming capacity (usually given in μmol Cu^{2+} or μmol Co^{3+} which can bond organic substances from 1 l of water). This expresses the capability of organic compounds to bond metals into complexes.

In Czechoslovakia, for example, the description and classification of the qualitative properties of continental waters is made according to the indices into 4 groups [11]:

a) oxygen regime indices (particularly dissolved oxygen, BOD_5 (biochemical oxygen demand; see p. 304), COD(Mn), free hydrogen sulphide, biological state),

b) indices of the basic chemical composition (dissolved and non-dissolved substances, calcium, magnesium, sulphates, chlorides),

c) specific indices (pH, ammonia nitrogen, nitrates, iron, manganese cyanides, phenols, tensides, temperature, odour),

d) indices of microbial pollution (number of coliform microbes).

For special needs a set of auxiliary indices is recommended. These are as follows:

— harmful substances (e.g. lead, arsenic, mercury, etc.),

— health toxicological indices (e.g. selenium, fluoride ions, benzene, etc.),

— sensory indices (e.g. carbon disulphide, oil, etc.),
— radioactive substances.

Evaluation is commonly carried out according to chosen indices (dissolved oxygen concentration, BOD_5, COD(Mn), saprobites, dissolved substances, non-dissolved substances, pH, temperature, Coli index). According to the permissible limit values surface waters are categorized into 4 classes (Table 3.40).

Table 3.40. Water purity grades [11]

Indicator	Grade				
	Ia very clean	Ib clean	II polluted	III seriously polluted	IV very seriously polluted
Dissolved oxygen ($mg\ l^{-1}$)	> 7	> 6	> 5	> 3	< 3
BOD_5 ($mg\ l^{-1}$)	< 2	< 5	< 10	< 15	> 15
COD(Mn) ($mg\ l^{-1}$)	< 5	< 10	< 15	< 25	> 25
Biological state	oligo-saprobes	beta-meso-saprobes	beta- to alpha-mesosaprobes	alpha-meso-saprobes	poly-saprobes
Dissolved substances ($mg\ l^{-1}$)	< 300	< 500	< 800	< 1200	> 1200
Non-dissolved substances	< 20	< 20	< 30	< 50	> 50
pH	> 6.5 < 8.5	6.5–8.5	6.0–8.5	5.5–9.0	< 5.5 > 9.0
Temperature (°C)	< 22	< 23	< 24	< 26	> 26
Coli index (germs per 1 l)	$< 10^3$	$< 10^4$	$< 10^5$	$< 10^6$	$> 10^6$

A special case of continental surface waters are *brines* formed by hydrolysis and oxidation of rocks by atmospheric water and evaporation of the resulting solution in runoff-free lakes. In this way salt brine with a predominance of Na^+ and Cl^- ions is formed in the Magadi Lake (Kenya) (total mineralization more than 300 g kg^{-1}).

Of all water on the Earth the *sea water* greatly predominates. The world ocean occupies about two thirds of the earth's surface (Fig. 3.32). Its most

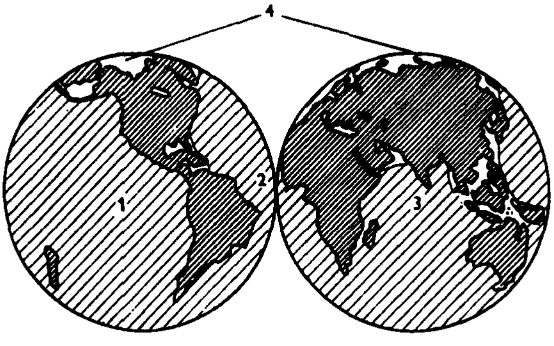

Fig. 3.32. Distribution of oceans on the Earth. 1 — Pacific Ocean, 2 — Atlantic Ocean, 3 — Indian Ocean, 4 — North Sea

Table 3.41. Mean concentrations of constituents in the oceans [12]

Constituent	Concentration ($mg\ l^{-1}$)
Na^+	10,500
K^+	380
Li^+	0.17
NH_4^+	0.5[a]
Ca^{2+}	400
Mg^{2+}	1,350
Fe^{2+}	0.01
Cl^-	19,000
HCO_3^-	142[b]
SO_4^{2-}	2,700
SiO_2	6.4
B	4.6
Total mineralization	34,500 $mg\ l^{-1}$
pH	8.2

[a] Given as total nitrogen ($NH_4^+ + NO_2^- + NO_3^-$).

[b] Given as total CO_2 ($HCO_3^- + CO_3^{2-}$ + free CO_2).

important feature is its quite constant chemical composition. An exception from the view point of the stability of chemical composition are some trace elements and elements participating in biological processes in the sea water (nitrogen and phosphorus) or those which — depending on the conditions — are easily transformed from soluble into insoluble forms, and vice versa (Fe and Mn). Table 3.41 presents the mean concentrations of constituents in the oceans. Sea water has a slightly alkaline reaction (pH 8.0–8.3). In more shallow coastal areas carbon dioxide may be accumulated and thus the pH can drop below this value. The majority of ions is partly complex bonded in sea water [13].

Sea water contains on average 35 g l^{-1} of dissolved solids, however, this amount is not the same everywhere (Table 3.42). The predominating component is sodium chloride. It has been calculated that its reserves in all seas of the world represent 35 x 10^{17} kg. Geographic changes of water mineralization in the oceans are shown in Fig. 3.33. The composition varies with depth down to about 200 m. The temperature of the ocean varies only very little. The temperature of surface layers of the sea water depends on geographic latitude and ranges from freezing point up to about 30°C. In the depths below 3000 m the temperature is constant within the approximate range 0 to 3°C [13–16].

Table 3.42. Mean concentrations of dissolved solids in various seas

Sea	Dissolved solids ($g\,l^{-1}$)
Atlantic Ocean	36
North Sea	32
Mediterranean Sea	38
Indian Ocean	34
Dead Sea	280
Pacific Ocean	35
Baltic Sea	20
Black Sea	11

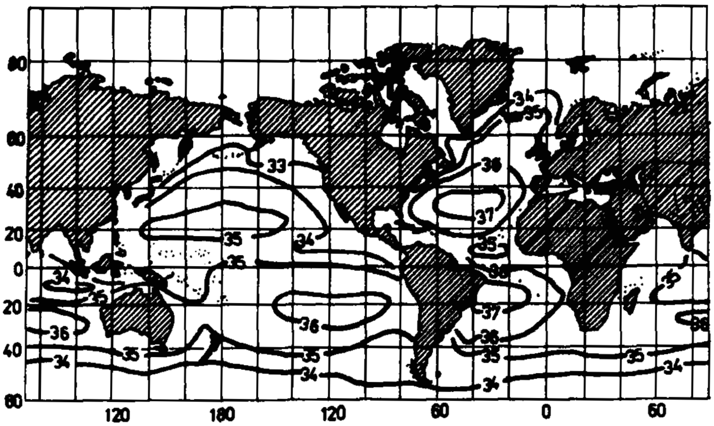

Fig. 3.33. Mineralization of world ocean (the content of dissolved substances in $g\,l^{-1}$) [13]

A general feature of seas and oceans are changes in the content of dissolved salts at a depth of 100–200 m (the so-called *halocline*) and changes in temperature (the *thermocline*). Sea is a specific aquatic environment noted for the sufficient reserves of energy and nutrients, their even distribution as well as stability of conditions. All these aspects are of essential importance for nature and living organisms. It is confidently asserted that these properties of the environment were inevitable for the origin of life on our planet.

3.5.3 Sub-surface water

Sub-surface water occurs under the earth's surface in all forms and states. According to their origin the sub-surface waters are classified as follows:

- *vadose* — these originate by soaking (infiltration) of precipitation and surface waters into the soil and to a small degree also by condensation of water vapours of atmospheric origin under the surface,
- *juvenile* — these are formed by condensation of water vapours escaping from cooling magma in the Earth. They can reach the surface along cracks in the earth's crust and gush out as thermal springs, hot springs or geysers.

The sub-surface water is both chemically and mechanically (physically) bonded in the crustal profile. Chemically bonded water (constitution, crystalline water) is non-utilizable from the hydrological viewpoint. Mechanically bonded water occurs in the zone of saturation as *groundwater* as well as in the zone of aeration as *soil water* (Fig. 3.34).

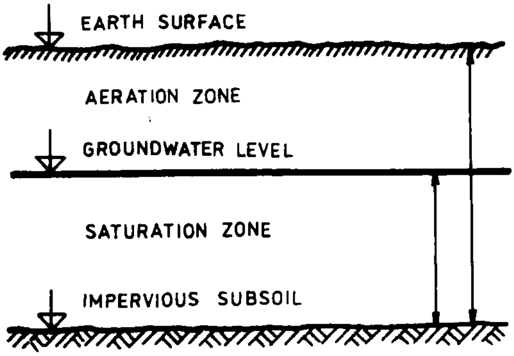

Fig. 3.34. Distribution of sub-surface water

3.5.3.1 Soil water

Soil water is part of the sub-surface water (regardless the state) which does not form a continuous level and does not fill all pores. It occurs in aerated zones where the pores also contain air. According to the predominating forces three types of soil water are recognized (Fig. 3.35).

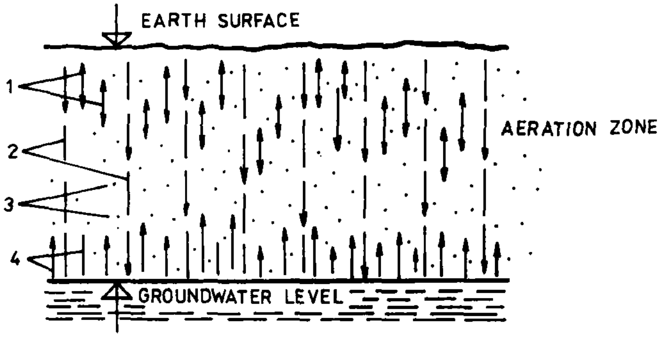

Fig. 3.35. Distribution of soil water. 1 — suspended capillary water, 2 — gravitation water, 3 — adsorption water, 4 — supported capillary water

Gravitation soil water — its motion and effects are due largely to gravitation. It is formed by the soaking of precipitation into the Earth in larger non-capillary pores and flows through the aeration zone into the zone of saturation. It enriches the reserves of groundwaters.

Capillary soil water — its motion and effects are mainly determined by the effects of capillary forces in small pores. It is formed in the soaking of the soil by precipitation, when part of water is trapped in the capillary pores (*suspended capillary water*) as well as by capillary elevation from the groundwater level (*supported capillary water*).

Adsorption soil water — this water is bonded by adsorption forces to soil rock particles. The most strongly bonded is the layer of water molecules which is present immediately on the solid soil particles and provides *hygroscopic water.* The external layer of water molecules bonded to the solid particles of soil by intermolecular forces is called ***envelope water.*** Whereas hygroscopic water moves in the gaseous state only due to different vapour tension the envelope water moves also in the liquid state but only very slowly, and provides soil or rock moisture [1].

3.5.3.2 Groundwater

Groundwater is that fraction of sub-surface water which fills the cavities of water-bearing rocks regardless of whether it provides a continuous surface or not, and the fraction which forms a continuous surface in the soil.

According to mineralization (total amount of dissolved solid substances) and content of gas, the groundwaters are categorized into *normal* and *mineral waters.*

3.5.3.2.1 Normal groundwaters

Normal groundwaters have a low content of dissolved solid substances, gases or microorganisms which do not satisfy any of the criteria for mineral waters. The reserves of groundwater are made up by soaking of atmospheric and surface waters, through permeable layers (infiltration), and also by the condensation of water vapour in the soil and condensation of the vapours from magma.

The groundwaters are the least movable part of the general hydrological cycle on the Earth. Whereas the volume of water in the atmosphere is replaced every nine days, that of oceans and seas on average every 2000 years, the volume of the groundwaters exchanges only every 8000 years, although quite significant differences can be observed here. A similar situation has been recorded in the case of the groundwater flow rate. Groundwaters in the surface zones of the earth's crust usually moves at a rate of 1 to 1000 m per year, whereas those at a depth of 1000 to 2000 m move at a rate of 0.0001 to 0.1 m per year. For comparison, the rate of water exchange in rivers is about 5 km h^{-1}.

Chemical changes of groundwaters are the result of complex processes taking place in the water–rock–atmosphere system. These are physical, chemical and biochemical processes taking place simultaneously or in a close sequence. Dissolution, hydrolysis, adsorption, ion exchange, oxidation and reduction, diffusion and osmosis are of decisive importance in the formation of a given chemical composition.

During infiltration through the soil and rock layers the soluble substances are directly dissolved and leached. In this way sulphates and chlorides of the alkali metals, sulphates of alkaline earths from corresponding minerals, followed by nitrates (from atmospheric waters during storms, from soil fertilized with nitrogen fertilizers, as well as from degraded nitrogen substances), low amounts of fluorides, bromides, iodides, phosphates and other trace elements are introduced into groundwater. However, simple dissolution is not sufficient to produce higher concentrations of dissolved substances in water.

More complicated chemical reactions take place in the presence of carbon dioxide and oxygen. In the presence of CO_2 low-soluble calcium, magnesium, iron, manganese and other carbonates are transformed into more readily soluble hydrogen carbonates, during dissolution of aluminium silicates the Na^+, K^+, Ca^{2+}, Mg^{2+} ions are released being substituted by H^+, Si, Al and Fe. In the degradation of aluminium silicates hydration and hydrolysis are markedly involved.

Many of physico-chemical processes taking place in the system water–rocks–atmosphere have an oxidation or reduction character. Insoluble sulphides are oxidized in the presence of oxygen into sulphates. The rate of oxidation depends on the grain size of the sulphides, the degree of rock protection, conditions of oxygen supply, etc. Thus, the natural waters are enriched by sulphate ions in the chemical erosion of eruptive rocks.

The chemical composition of groundwaters is significantly influenced by ion-exchange reactions. The bearers of the ion-exchange properties in the sedimentary rocks are mostly clays (e.g. kaolinite, montmorillonite, illite, etc.). The exchange of calcium for sodium is of great importance as it can cause a change of the relative quantitative representation between Ca, Mg and Na (the original order $Ca > Mg > Na$ can be changed into $Na > Ca > Mg$).

In sedimentary rocks with a porous structure adsorption processes are involved to a considerable degree. Via the adsorption phenomena, natural water gets rid of many, sometimes undesirable substances, e.g. high-molecular compounds, as well as of some elements (for example, Cu, Pb, Zn, Sr) which enter the waters together with wastewaters.

The transfer of salts by diffusion and the accompanying processes can change the total mineralization of the chemical composition of groundwaters.

The groundwater composition is significantly influenced by biochemical processes. According to the content of dissolved oxygen these processes can have either an oxidation or reduction character. In the upper layers with sufficient access of oxygen, aerobic biological degradation of organic substances takes place, and at greater depths without the presence of oxygen anaerobic processes are observed (particularly reduction of nitrates and sulphates). Via these processes inorganic compounds of nitrogen, hydrogen sulphide and carbon dioxide are introduced into groundwaters.

In addition to the natural sources of contaminants, human activities have also contributed to the build-up of contaminants in groundwaters. Potential sources of groundwater contaminants are shown in Table 3.43 [16].

Table 3.43. Potential sources of groundwater contaminants [16]

Source	Possible contaminants
Accidental spills	Various inorganic and organic chemicals
Acid rain	Oxides of sulphur (SO_x) and nitrogen (NO_x)
Agricultural activities	Fertilizers, pesticides, herbicides, and fumigants
Animal feedlots	Organic matter, nitrogen and phosphorus
De-icing of roads	Chlorides, sodium and calcium
Deep-well injection of wastes	Variety of inorganic and organic compounds, radioactive materials and radionuclides
Hazardous waste disposal sites	Various inorganic compounds (particularly heavy metals) and organic compounds (e.g. pesticides and priority pollutants)
Industrial liquid-waste storage ponds and lagoons	Heavy metals and various cleaning solvents and degreasing compounds
Landfills, industrial	Wide variety of inorganic and organic compounds
Landfills, municipal	Heavy metals, gases, organic compounds and inorganic compounds (e.g. calcium, chlorides and sodium)
Land disposal of liquid and semisolid industrial wastes	Organic compounds, heavy metals and various cleaning solvents and degreasers
Land disposal of municipal wastewater and waste sludges	Organic compounds, inorganic compounds, heavy metals, microbiological contaminants, etc.
Mining	Minerals and acid mine drainage
Rainfall	Chloride, sulphate, organic compounds, etc.
Saltwater intrusion	Inorganic salts
Septic-tank leaching fields or beds (soil absorption areas)	Organic matter, nitrogen, phosphorus, bacteria, etc.
Storage tanks, underground	Organic cleaning and degreasing compounds, petroleum products, and other hazardous wastes

Groundwaters are classified from various viewpoints (according to the degree and character of mineralization, gas content, radioactive substances, trace elements, temperature, etc.). According to the quantity of dissolved substances groundwaters are classified as follows:
— fresh with the content of dissolved substances (up to 1 g l^{-1}),
— slightly mineralized (1-5 g l^{-1}),
— medium mineralized (5–15 g l^{-1}),
— strongly mineralized (over 15 g l^{-1}).

Depending on the main ion constitutents groundwaters are classified as follows:

1st class: bicarbonate waters,
2nd class: sulphate waters,
3rd class: chloride waters.

The specific classes are divided into groups with predominating cation:
1st group — Na^+,
2nd group — Mg^{2+},
3rd group — Ca^{2+}.

From the point of view of treatment criteria (pH, neutralization capacity, dissolved substances, aggressive CO_2, contents of Mn, Fe, F^-, PO_4^{3-}, NH_4^+, NO_3^-, NO_2^-, COD, specific organic compounds) the groundwaters are classified into various quality categories.

Groundwaters are also classified according to the weight or molar ratio between cations and anions. To express the essential data on the water quality, graphic and numerical methods are employed [18–22].

When using the *graphic methods* water composition is represented by a geometric diagram (column, triangle, circle) in which the composition of water is illustrated. The symbols usually express the water composition by their shape, and its mineralization by their size.

The *column graphs* consist either of two columns, one for the cation and another one for the anion, or several columns, each of which is for one ion. Such a graph is shown in Fig. 3.36.

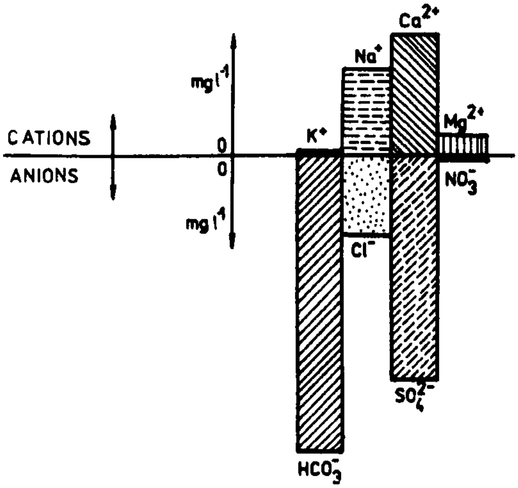

Fig. 3.36. Column graph representing total mineralization

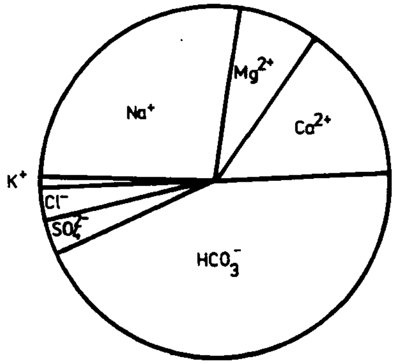

Fig. 3.37. Circular graph

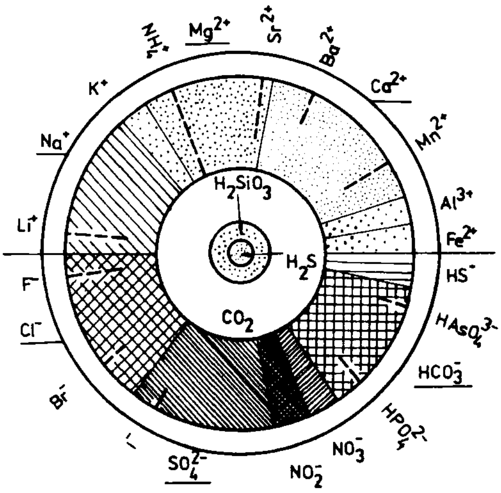

Fig. 3.38. Circular graph according to H.Udluft. Radius $r = 2\pi M$ (M — total mineralization in mg l^{-1}). External circles are determined for temperatures: 1. circle $t < 20°$C, 2. circle $t = 20\text{–}20°$C, 3. circle $t = 40\text{–}60°$C

A vivid means of representation is the *circular graph* (Fig. 3.37). In the lower part of the circle the relative proportions of anions are illustrated, and cations in the upper part. The circle radius is directly proportional to total mineralization. The alternative circle graph by H. Udluft expresses water composition in detail (Fig. 3.38). In addition to the content of main ions, the contents of other ions are also taken into consideration (broken lines). Concentric circles in the centre of the graph illustrate the contents of gases and silicic acid in mg l^{-1}. The outer circles express temperature (each of them represents an increase of 20°C). The area of a circle is proportional to mineralization.

Chemical composition of several waters is illustrated in survey graphs, allowing comparisons to be made.

Good picture of the chemical composition of waters in a given region is provided by maps. Chemical composition of waters in the maps is shown by discontinuous means (using different symbols and graphs) or by continuous means (isoline or surfaces with approximately identical values of the indices studied, or approximately identical water quality).

A typical map of chemical composition of groundwater shows

— the type and mineralization of groundwater of the first significant collector under the surface,

— occurrence of mineral waters with denoted chemical composition, degree of mineralization and temperature,

— localities with waters of anomalous chemical composition indicating supplies from greater depths,

— depth changes of chemical composition of water found by drills,

— polluted waters and waters containing an unsuitable constituent from the viewpoint of its usability for waterworks purposes.

Numerical methods express the chemical composition of water using a digital symbol or formula which, however, does not represent any mathematic relationship. The best known and frequently used method for expressing the chemical composition of water is the *Kurlov formula.* It is a fraction with anions in its numerator and cations in its denominator. The ions are presented according to decreasing contents, the concentration data (g l^{-1}) being written in the form of an subscript. To the left of the fraction total mineralization M (g l^{-1}) is presented together with the contents of predominating gases (g l^{-1}), and temperature T (°C) and capacity Q (l s^{-1}) on the right.

A typical example of water composition would be: 75 mg l^{-1} Ca^{2+}, 29 mg l^{-1} Na^{+}, 24 mg l^{-1} Mg^{2+}, 8 mg l^{-1} K^{+}, 250 mg l^{-1} HCO_3^{-}, 40 mg l^{-1} Cl^{-}, 24 mg l^{-1} SO_4^{2-}, 110 mg l^{-1} CO_2, mineralization 650 mg l^{-1}, temperature 8°C, capacity $Q = 0.2$ l s^{-1}. The Kurlov formula is as follows for this water:

$$CO^{2}_{0.11} M_{0.65} \frac{HCO^{3}_{0.25} Cl_{0.04} SO^{4}_{0.025}}{Ca_{0.075} Na_{0.029} Mg_{0.024} K_{0.008}} T_{8} Q_{0.2} \qquad (3.119)$$

To express *genetic relationships* among groundwaters different coefficients characterizing the ratios between chosen ions are used (particularly $Cl^{-}:Br^{-}$, $Na^{+}:K^{+}$, $HCO_3^{-}:Cl^{-}$).

Table 3.44. Examples of the chemical composition of particular groundwaters

Water, locality	pH	Chemical composition (mg l^{-1})										
		Na^+	K^+	Li^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	SiO_2	Total mineralization
Groundwater of shallower circulation (V. Kámen, The Ore Mountains, CSFR), environment of the circulation — granite	5.25	2.5	2.0	0.02	11.0	0.01		2.1	3.7	30.9	7.6	60
Groundwater of deeper circulation (Moravia, CSFR), environment of the water circulation — troctolite	10.8	25.5	0.7	0.00	12.0	0.61	0.11	5.05	0.00	45.7	3	109

Table 3.44 presents examples of the chemical composition of particular groundwaters.

The groundwater which passes through fine pores of soil layers and changes its composition and properties is usually the top quality drinking water free from organic substances; it is safe from the viewpoint of bacteriology, it has the correct temperature and constant composition.

3.5.3.2.2 Mineral waters

Simple groundwater changes into mineral water after exceeding a certain amount of dissolved solid substances and gases. To distinguish mineral waters from fresh groundwaters no hydrogeological criteria are available, and therefore balneological ones are applied [6]. The first definition of mineral waters dates back to 1907: its authors are Hintz and Grünhut. An extended proposal was adopted in 1912 by the Nauheim Decree. This proposal has become the basis for defining mineral waters all over the world [6]; example are given in Table 3.45.

Mineral waters in the broader sense of the word are waters which differ from normal groundwaters by their chemical composition and physical properties, and they are formed by particular circumstances occurring in the groundwater circulation.

Table 3.45. Characterization of mineral waters

Criterion	Unit	Nauheim Decree (1912)	CSFR (1972)
Temperature	°C	20	25
Dissolved substances	mg l^{-1}	1000	1000
CO_2 (free)	mg l^{-1}	250	1000
H_2S	mg l^{-1}	1.0	1.0
Fe	mg l^{-1}	10.0	10.0
I	mg l^{-1}	1.0	5.0
As	mg l^{-1}	0.7	0.7
Br	mg l^{-1}	5.0	—
B	mg l^{-1}	1.23	—
Rn	Bq l^{-1}	48.1	1369

The following types are recognized [17, 23]:
- natural mineral waters,
- natural curative waters,
- natural mineral table waters.

Natural mineral waters are waters from natural sources which contain more than 1 g l^{-1} of dissolved solid substances, or more than 1 g l^{-1} of dissolved carbon dioxide at the point of emergence.

Natural curative waters are waters from natural sources possessing pharmacodynamic effects due to their chemical composition for therapeutic purposes.

Natural mineral table waters are waters from natural sources without significant pharmacodynamic effects containing 1 g l^{-1} of carbon dioxide minimum and 5 g l^{-1} of dissolved solid substances maximum, and they can be used as refreshing drinks because of their taste properties.

Mineral waters are classified and evaluated according to
- the content of dissolved gases,
- total mineralization,
- predominating cations or anions,
- biologically and pharmacologically important constituents,
- pH value,
- radioactivity,
- temperature at the point of emergence,
- osmotic pressure.

From the viewpoint of content of dissolved gases mineral waters are classified only according to the contents of carbon dioxide and hydrogen sulphide:

(a) *Carbonate waters* called also acidulous waters — waters containing at least 1 g l^{-1} of free CO_2 on emergence.

(b) *Sulphur (hydrogen sulphide) waters* containing at least 1 mg l^{-1} H_2S + HS^- on emergence.

For total mineralization, mineral waters are categorized as

(a) *normal* (contents of dissolved solid substances is lower than 1 g l^{-1}),

(b) *slightly mineralized* (content of dissolved solid substances ranges from 1 to 5 g l^{-1}),

(c) *medium mineralized* (contents of dissolved solid substances ranges from 5 to 15 g l^{-1}),

(d) *strongly mineralized* (content of dissolved solid substances is higher than 15 g l^{-1}).

According to the prevailing ions natural mineral waters are categorized into classes and groups (Tab. 3.46). The first place is occupied by the name of the predominating anion and the second one by the predominating cation. Waters in which other ions reach a concentration of at least 20% of the total number of chemical equivalents in addition to the predominating anion and cation are mixed types of waters. For example, hydrogen carbonate–calcium–magnesium water (HCO_3–Ca–Mg water), sulphate–chloride–sodium water (SO_4–Cl–Na water), etc.

Table 3.46. Classification of natural mineral waters according to the prevailing ions

Class according to prevailing anion	Class according to predominating cation
Hydrogene carbonate and carbonate waters	Sodium
Sulphate waters	Magnesium
Chloride waters	Calcium
Waters with another prevailing anion	With another cation

In the case of biologically and pharmacologically important constituents mineral waters are classified as follows:

(a) *sulphur* — containing at least 1 mg l^{-1} of titratable sulphur at the point of the springing (H_2S, HS^-, $S_2O_3^{2-}$),

(b) *iodine* — containing at least 5 mg l^{-1} of iodides in the spring,

(c) *ferruginous* — containing at least 10 mg l^{-1} of iron (Fe^{2+}) on emergence,

(d) *with increased contents* of arsenic, bromine, fluorine, copper, zinc, cobalt, molybdenum, lithium, strontium, barium, boric acid, silicic acid.

The pH *value* of waters is used as a classification only if the waters are too acid ($\mathrm{pH} < 3.5$) or too alkaline ($\mathrm{pH} > 8.5$).

According to radioactivity, radon waters are those whose acitivity, caused by radon or its isotopes, is at least 1.37 kBq l^{-1}.

Classified by the temperature on emergence those waters with a temperature higher than 25°C are called *thermal waters* and are categorized as follows:

— lukewarm, temperature 25–35°C,
— warm, temperature 35–42°C,
— hot, with temperature over 42°C.

The final grouping concerns osmotic pressure; waters are classified into

— hypotonic,
— isotonic,
— hypertonic.

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3.6 Drinking water

From the viewpoint of life in general and physiology in particular water is of essential importance for humans and animals. It interacts directly or indirectly with their fundamental living processes. Water is necessary for metabolism, and it controls thermal and pressure conditions in organisms. A loss of 10% of the required quantity of water induces serious health disorders in man.

Because of its irreplaceable role in the life of man, drinking water is the most important type of natural waters. It is therefore not surprising that strict qualitative requirements are placed on drinking water.

Drinking water is one of the essential components of human nutrition. It must be safe for humans and it must also have a biological value. It should contain a number of constituents, primarily trace biogenous elements in an amount and ratio such that their optimum utilizability by human organism is secured. These substances can be supplied by drinking water. The most suitable composition of biogenous elements is that of real groundwaters. Waters with a high biological value are called curative mineral waters [1, 2].

The biological value is a very labile property, therefore it is necessary to use a water treatment process which will maintain the natural character of water as much as possible. Whatever chemical treatment of water is used, it usually results in worsening of the physiological properties of water. After the treatment, although the water satisfies the quality requirements given by the Official Standard, its value is considerably lower; it does not contain many of the important biological components. Moreover, its sensory properties make it less pleasant to drink [3–6]. Drinking water, however, is not only used for drinking. It is used also for the preparation of meals, as well as for many other purposes, for example, washing up, washing, bathing, and flushing. In towns, water is used quite extensively for municipal services (grass and flowers, washing of streets), and in smaller industrial plants.

Thus, drinking water also plays the role of utility water, in some cases even the role of service water. Therefore, it is not surprising that the specific demands of water for inhabitants in urban agglomerations are generally higher than that in the countryside, amounting to 300–600 l of drinking and utility water per capita per day.

The process of mechanization, increase of the housing standard and a general increase of the standard of living are manifested in the increasing demands for drinking water under both local and worldwide conditions. By the end of this century the demand for drinking water in developed countries is expected to increase to 1000 l per capita per day.

3.6.1 Drinking water quality standards

Drinking water from any natural source must satisfy health and technological requirements. First of all, water must not contain any organisms or concentrations of substances which have or could have detrimental effects on the health of people after being used over a long period of time.

Drinking water must have an acceptable taste, it should have good appearance, it should be free from unpleasant odour and it should also have an appropriate temperature so that it is refreshing. Drinking water distribution through pipelines should not worsen its quality. The requirements for a sufficient quantity of drinking water result from the aspects of hygiene [7–12].

Standards for drinking water have evolved over the years as knowledge of the nature and effects of various contaminants has grown. Such standards require that the water be free of suspended solids and turbidity, that it is tasteless and odourless, that dissolved inorganic solids are in moderate quantities, and that organics, toxic substances and pathogens are absent. As more is learned about the constituents of water, additional requirements will probably be added to this list, making drinking water requirements even more stringent.

The World Health Organization has established minimum criteria for drinking water that all nations are urged to meet. These standards are listed in Table 3.47. Countries with more advanced technology generally have standards that exceed this quality.

The maximum contaminant level (MCL) of inorganic and organic chemicals and microbiological contaminants are shown in Tables 3.48 through 3.50 [13–22]. These standards were established by the U.S. Environmental Protection Agency and were published in 1975 under the title "National Interim Primary Drinking Water Regulations", Federal Register, Part IV.

Table 3.47. Drinking-water standards of the World Health Organization

Chemical constituent	Concentration (mg l^{-1})				
	WHO International (1958)			WHO European (1961)	
	Permissible limit	Excessive limit	Maximum limit	Recommended limit	Tolerance limit
Ammonia (NH_4)	—	—	—	0.5	—
Arsenic	—	—	0.2	—	0.2
Cadmium	—	—	—	—	0.05
Calcium	75	200	—	—	—
Chloride	200	600	—	350	—
Chromium (hexavalent)	—	—	0.05	—	0.05
Copper	1.0	1.5	—	3.0[a]	—
Cyanide	—	—	0.01	—	0.01
Fluoride	—	—	—	1.5	—
Iron	0.3	1.0	—	0.1	—
Lead	—	—	0.1	—	0.1
Magnesium	50	150	—	125[b]	—
Magnesium+sodium sulphates	500	1000	—	—	—
Manganese	0.1	0.5	—	0.1	—
Nitrate (as NO_3)	—	—	—	50	—
Oxygen, dissolved (minimum)	—	—	—	5.0	—
Phenolic compounds (as phenols)	0.001	0.002	—	0.001	—
Selenium	—	—	0.05	—	0.05
Sulphate	200	400	—	250	—
Total solids	500	1500	—	—	—
Zinc	5.0	15	—	5.0	—

[a] After 16 h contact with new pipes; but water entering a distribution system should have less than 0.05 mg l^{-1} of copper.

[b] If there is 250 mg l^{-1} of sulphate present, magnesium should not exceed 30 mg l^{-1}.

As an example of a national standard for drinking water quality based on the above specified requirements of the World Health Organization which considers specific conditions of a given country, the Czechoslovak Standard can be presented.

The requirements for drinking water quality are specified in CSN 83 0611 — Drinking Water. This Standard presents permissible concentrations of elements, compounds and microorganisms which must not be exceeded, for the safeguard of man's health, or to avoid other damage resulting from its use. The Standard also includes some other properties concerned with

Table 3.48. Primary drinking-water standards: maximum contaminant levels for inorganic chemicals

Contaminant	Level (mg l^{-1})
Arsenic	0.05
Barium	1.00
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10.00
Selenium	0.01
Silver	0.05

Table 3.49. Primary drinking-water standards: maximum contaminant levels for organic chemicals

Chemical	Maximum contaminant level (mg l^{-1})
Chlorinated hydrocarbons:	
Endrin	0.0002
Lindane	0.004
Methoxychlor	0.1
Toxaphene	0.005
Chlorophenoxys:	
2,4-D	0.1
2,4,5-TP silvex	0.01

the deterioration or aesthetic impairment of drinking water quality, for example, colour, turbidity, odour, etc. The Standard is based on recommendations of the World Health Organization, and is in agreement with similar standards of other countries. It is permanently updated, taking into account the latest scientific results.

The Standard presents two groups of requirements for drinking water quality: bacteriological and biological, and chemical and physical requirements. They are classified into permissible and rated indicators.

The permissible indicator is a limit value of a property or constituent which must be maintained, otherwise the water is unsuitable for drinking.

The rated indicator is a limit value of property or constituent which must be observed in a general way. However, under certain circumstances this value can be higher, for example, if there are reasons which do not allow

Table 3.50. Primary drinking-water standards: maximum contaminant level for microbiological contaminants

Test method used	Monthly basis	Individual sample basis	
		Fewer than 20 samples/mo	More than 20 samples/mo
		Number of coliform bacteria shall not exceed	
Membrane filter technique	1/100 ml average density	4/100 ml in more than one sample	4/100 ml in more than 5% of samples
		Coliform bacteria shall not be present in:	
Fermentation tube method			
10-ml standard portions	More than 10% of the portions	Three or more portions in more than one sample	Three or more portions in more than 5% of samples
100-ml standard portions	More than 60% of the portions	Five portions in more than one sample	Five portions in more than 20% of samples

its achievement. The excess limit must be approved by responsible hygiene authorities.

From the viewpoint of bacteriological and biological requirements the permissible indicators involve the quantity of coliform and mesophile bacteria. Of course, drinking water must not contain any pathogens, microscopic and macroscopic organisms which come from waste- or surface waters. The Standard limits the number of infusoria and colourless flagellata. The rated indicators also include the amounts of psychrophile bacteria and enterococci.

From the viewpoint of chemical and physical requirements the *permissible indicators* involve a number of criteria; mercury, selenium, cadmium, vanadium, chromium, arsenic, silver, lead, barium, cyanides, hydrogen sulphide, fluorides, phenols, oil and oil substances, COD(Mn), colour, odour, taste and turbidity. The most stringent criterion concerns the content of mercury, followed by selenium, cadmium, vanadium, cyanides, oil and oil substances. Another important indicator is the content of organic matters characterized by COD(Mn).

The rated indicators, on the other hand, include the content of dissolved oxygen, active chlorine, ammonia and ammonia ions, iron, manganese, aluminium, zinc, magnesium, calcium, phosphates, nitrites, nitrates, chlorides, sulphates, humin substances, all dissolved constituents, anions of tensides, copper, hydrogen carbonates and pH value. This category also includes radioactivity characterized by total volume alpha-activity, and in surface waters also by total volume beta-activity.

Drinking water quality is governed by physical, chemical, biological and bacteriological properties. Of the physical properties of drinking water, its appearance is evaluated (turbidity, colour), and also taste, odour and temperature [13–22].

The maximum permissible concentrations of the most important elements and compounds in drinking water as well as the requirements for physical properties of drinking water are listed in Table 3.51.

From the viewpoint of *biological and bacteriological properties* of drinking water there is a requirement in the Standard that drinking water must not contain any pathogenic organisms. Permissible quantities of mesophile and coliform germs are limited as follows:

In 1 ml of drinking water for local supply the maximum permissible count of mesophile germs (at 37°C) is 100, that of psychrophile (at 20°C), 500. Indicators of faecal pollution must be negative in 50 ml.

Table 3.51. Requirements for physical and chemical properties of drinking water according to CSN 83 0611

Permissible indicators (maximum permissible concentration)		Rated indicators	
	(mg l^{-1})		(mg l^{-1})
Mercury	0.001	Dissolved oxygen	min. 50%
Selenium	0.01	Active chlorine	min. 0.05; max. 0.3
Cadmiun	0.01	Ammonia and NH_4^+	max. 0.5
Vanadium	0.01	Iron — collec. res.	max. 0.3
Chromium	0.05	— individ. res.	max. 0.5
Arsenic	0.05	Manganese — collect. res.	max. 0.1
Silver	0.05	— individ. res.	max. 0.3
Lead	0.05	Aluminium	max. 0.3
Copper	0.05	Zinc	max. 5
Barium	1.5	Magnesium	max. 125
Cyanides	0.01	Total calcium and magnesium	min. 0.375 mmol l^{-1}
Hydrogen sulphide	0.01		
Fluorides	1.5	Alkalinity (Methyl Orange)	min. 0.375 mmol l^{-1}
Phenols (monovalent)	0.05	pH	6–8
Oil and oil products	0.01	Phosphates	max. 1.0
COD(Mn)	3.0	Nitrites	max. 0.1
Colour	20 (Pt)	Nitrates	max. 50
Turbidity	5 ZF	Chlorides	max. 100
Radioactivity		Sulphates	max. 250
total alpha-activity	0.1 Bq l^{-1}	Tensides (anionic)	max. 0.2
total beta-activity	1 Bq l^{-1}	Huminous matters	max. 2.5
		Extractable substances	max. 0.2
		All dissolved substances	max. 1000

The number of mesophile germs in drinking water for public consumption must not be higher than 20 per ml and that of psychrophile germs, 100 per ml.

Bacteriological analysis must be carried out immediately after sampling, or the sample of water must be suitably preserved.

3.6.2 Indicators of faecal contamination of drinking water

The most important requirement for drinking water is its health safety. The health of man can be endangered by germs of infectious and parasitic diseases, as well as by substances of toxic character.

The most frequent sources of germs causing infections and parasitic diseases are animal wastes. Therefore, when evaluating water quality it is important to determine if the water is contaminated by faeces. If so, it is possible to determine various microorganisms from the gastrointestinal tract of animals or man, as well as various organic and inorganic substances present in faeces, or products of their biochemical transformations [23–26].

Some of these microorganisms or characteristic substances can be determined by microbiological or chemical analysis. The most convenient ones can be used as *indicators of faecal contamination.*

This concerns the following determinations:

— counts of psychrophile microbes (20°C) which characterize total bacterial water contamination,

— counts of mesophile microbes (37°C) which indicate contamination of water by microbes from warm-blooded animals,

— microbes of the Enterobacteriaceae family, the *Escherichia* genus, which are residents of the intestinal tract.

Faecal water pollution is characterized bacteriologically by the determination of coliform microbes. It is expressed either in counts of microbes per ml of water, or the minimum quantity of water in which the above specified microbes are still present.

The importance of microbiological indicators varies. The most important is the determination of microbes from the Enterobacteriaceae family and faecal streptococci.

Chemical indicators of faecal water contamination are as follows:

— degradation products of organic substances of animal origin and their transformation products (e.g. ammonia nitrogen, nitrites, phosphates, hydrogen sulphide and its ionic forms),

— inorganic substances accompanying the organic substances of animal origin (e.g. chlorides from urine),

— specific organic substances occurring in animal wastes (e.g. steroids, uric acid, urochromium and others).

Ammonia nitrogen is released primarily during biological degradation of organic nitrogen substances. Its presence in groundwater indicates fresh contamination with animal waste. Moreover, NH_4^+ ions are intensively adsorbed by soil and they also undergo ion exchange. These facts even increase the indicator value of ammonia nitrogen. However, in some cases it does not necessarily originate from faecal contamination. It can be generated by decomposition of plant organisms, reduction from nitrogen substances with a higher oxidation number of nitrogen, or its source can be the washings from fields to which nitrogen fertilizers were applied.

Nitrites formed by nitrification from ammonia nitrogen also have a high indicator value; they too are considerably adsorbed in soil. However, the source of their occurrence is not limited to faecal contamination.

Nitrates as the final products of nitrification are usually not used as indicators of faecal contamination as they are only little adsorbed by soil and penetrate to remarkable distances.

Chlorides have a low indicator value because they are common components of natural waters and adsorbed very little in soil, thus they easily penetrate it, like nitrates.

Phosphates — if of organic origin — have an important indicator value as the soil complex retains them strongly by both sorption processes and chemical reactions. Phosphates of inorganic origin (e.g. industrial fertilizers, corrosion inhibitors), or those which were formed by plant degradation are not significant as indicators of faecal contamination [27–32].

3.6.3 Drinking water resources

Drinking water is obtained from a number of different natural sources. According to the origin it can be *ground-*, *surface* or *precipitation* water.

Groundwater with its advantageous properties and composition is the most suitable source of drinking water. From groundwater sources it is possible to get water with a high biological value and favourable physical and bacteriological properties. Usually, no special treatment is required, except that which concerns its health aspects, e.g. by disinfection with chlorine. Only in some cases is some treatment required, for example, removal of iron, manganese, or carbon dioxide.

According to its origin the groundwater can be categorized into *porous* or *crack* (*crast*) waters. Only water filling soil pores is optimally mineralized. In passing through the soil layers, bacteriological or chemical contaminants are removed and the water has a constant and convenient temperature. The properties and composition of crack or crack water are not as good as those of porous water. The search for and extraction of groundwater involves lower financial costs and a shorter time period in comparison with the construction of water reservoirs.

In areas poor in groundwater it is possible, under certain conditions, to obtain water with similar properties to those of groundwater. For this purpose artificial infiltration of surface water from a stream or reservoir is used.

Surface water with its properties and composition does not reach groundwater quality. In view of the limited sources of natural water and increasing demands for drinking water the importance of surface waters for public supply is ever increasing under the conditions both in Europe and all over the world.

In surface water the instability of composition, variations in temperature, lack of biogenous elements and particularly its ever growing contamination have negative effects, making surface water treatment a demanding and expensive technological process. In spite of the continuing improvement of the technology of treatment, the current functioning of water works cannot eliminate some resistant substances from surface waters, and often such waters reach the consumer. This concerns particularly residues of pesticides, oil products, phenols, tensides and nitrates.

The major part of the requirements of water for public consumption is obtained by water diversion from streams or water reservoirs. The water diversion from reservoirs is more suitable because of more stable physical properties and composition of such water.

At the beginning of the next millenium the average daily requirement for drinking water is expected to exceed 500 l per capita, underlining the importance of surface water for public supply. Its protection against further contamination is thus becoming ever more important [33–39].

Precipitation water is not significant for public supply of drinking water on regional or national scales.

With regard to the immense reserves of salty water on the Earth, particularly of sea water, seas will become important worldwide sources of drinking water in the future, and many countries already operate large-scale desalination plants for this purpose.

Another potential source of drinking water in the long term is the water from Arctic and Antarctic icebergs and ice fields in which the major part of normal non-mineralized water on the Earth is accumulated.

3.6.4 Requirements for raw water quality

The quality of drinking water depends considerably on the quality of the raw water from the water source. Its quality is influenced by meteorological and hydrological factors, and it varies according to the seasons, etc.

In the search for suitable sources of drinking water for public supply, long-term observations of the water source capacity and water quality are carried out. Water sources with permanent contamination from harmful substances are ruled out. It is also necessary to take into consideration the hydrological balance of the water source, as well as many other factors.

Because of the seriousness of the problems concerning the drinking water, these matters are supervised by the World Health Organization (WHO) with offices in Geneva. In response to WHO a proposal of requirements for raw water quality which is suitable as the source of drinking water has been elaborated [40–44].

The current guidelines in the authors' country, Czechoslovakia, for assessing the suitability of a surface water or groundwater for use as a public water supply are laid down as regulations. The primary regulations, as listed in Table 3.52, include maximum permissible levels for inorganic and organic chemicals, turbidity, coliform bacteria, and radiological constituents. The World Health Organization standards for drinking water are similar.

As reported in Table 3.52 maximum requlations have been set for only six anthropogenic organic compounds and total trihalomethanes. It is anticipated that this list will be expanded as the health risks of other synthetic chemicals are evaluated.

Recently, a number of volatile organic compounds have been detected in groundwater supplies. The presence of these compounds is serious because many of them have been found to pose a carcinogenic or mutagenic risk to humans. The gravity of the problem is compounded by the long residence time in groundwater aquifers.

For reasons of aesthetics and health, it is generally considered desirable to maintain natural water systems at as high a quality level as possible. Many factors affect stream water quality. Wastewater discharges and other human activities often have a significant impact on this quality and such activities may lend themselves to control by legislation.

In this particular proposal of WHO, physical, chemical and bacteriological indicators of water quality are considered. In Czechoslovakia, for example, the colour of water is to be kept below the colour corresponding

Table 3.52. Contaminant limits set in interim primary regulations for drinking water

Contaminant	Maximum permissible level
Inorganic chemicals	
Arsenic	0.05 mg l^{-1}
Barium	1.0
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10
Selenium	0.01
Silver	0.05
Fluoride[a]	1.4–2.4
Organic chemicals	
Endrin	0.0002 mg l^{-1}
Lindane	0.004
Methoxychlor	0.1
Toxaphene	0.005
2,4-D	0.1
2,4,5-TP silvex	0.01
Total trihalomethanes	0.1
Turbidity	1–5 NTU
Coliform bacteria	1/100 ml (mean)
Radiological	
Gross alpha	15 pCi/l
Radium 226 and 228	5
Gross beta	50
Tritium	20,000
Strontium 90	8

[a] Level varies with temperature.

to 300 mg l^{-1} Pt; turbidity and the content of suspended matter are not subject to statutory controls because of their easy separability.

From the viewpoint of *chemical properties*, the constituents present in raw water are assessed as follows:

(1) The content of substances which influence the *suitability* of water for public supply are limited. These include: total evaporation residue, total iron, manganese, copper, zinc, magnesium sulphate and sodium sulphate, sodium alkyl benzene sulphonate.

(2) Permissible concentrations of those substances which can *influence human health* were determined; for nitrates in raw water, for example, the value is 50 mg l^{-1}.

Fluorine compounds at a concentration of up to 1 mg l^{-1} were found to be efficient for the development of bones and tooth protection, particularly in children. Concentrations higher than 1–1.5 mg l^{-1} are detrimental to health. The permissible concentration of fluorides in raw water is 1.5 mg l^{-1}.

(3) *For toxic substances* maximum concentrations are set and these should not be exceeded. To illustrate this, permissible concentrations of some toxic substances are presented (in mg l^{-1}): derivatives of phenol (0.002), cadmium and selenium (0.01), arsenic, chromium and lead (0.05), cyanides (0.20). Maximum permissible total beta-activity for radioactive compounds is 1 Bq l^{-1}.

(4) *Compounds indicating contamination* but having no direct effects on human health; however, they characterize contamination of the water source by wastewaters. For some indicators the permissible value is given in brackets (mg l^{-1}): COD(Mn) (10), BOD_5 (6), NH_3 (0.5), extractable substances (0.5), fats (1.0).

Bacteriological criteria of raw water relate to the presence of coliform bacteria. According to their number in 100 cm^3 of water, four classes exist: I (0–50), II (50–5000), III (5000–50,000), IV (more than 50,000).

Each type of raw water requires a specific treatment. The best quality water is merely disinfected; polluted surface water usually needs treatment by coagulation, filtration and disinfection. Seriously contaminated water is used only in unavoidable cases because of the difficulties involved in its treatment.

The above specified criteria for raw water quality are of an informative character. The final assessment of the suitability of a water source is obtained from laboratory or pilot-plant tests based on corresponding analyses. In the case of a public supply it is necessary to perform long-term tests, particularly under extreme meteorological, hydrological and seasonal conditions.

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3.7 Service and industrial waters

Service water is safe from the viewpoint of hygiene, as long as it is not used as drinking water or for cooking. It can originate from any source providing it meets the sanitary and technological requirements. Such water is used for washing, bathing, and production processes where the staff is in direct contact with it.

As for its physical properties (temperature, colour, turbidity, odour) the criteria for service water are not so stringent as those for drinking water, however, it must not be repulsive, it must not contain toxic substances, and from the health aspects it must satisfy the standard for drinking water.

Industrial (technological) water is used for various processes in industry and agriculture. It is classified according to the application into process waters (in which water becomes part of the product), waters for cooling, irrigation, washing, rinsing, concreting, etc.

In the manifold types of production processes in industry, waters of very different properties are required, depending on the type of plants and on the technological processes. For example, the foodstuff industry requires hygienically safe water, production of pharmaceuticals and fine chemicals requires distilled water, for other industries (metallurgical, engineering, etc.) simply treated or even untreated surface water is sufficient. Unsuitable quality of industrial water can cause a deterioration in the quality of products, reduced production capacity and equipment corrosion. Except for some specific requirements for the quality of water for the different industrial sectors, some requirements are common to the majority of operations [1–8]:

Water

- must be colourless, without turbidity and sedimenting substances, and it must be fat- and oil-free,
- it should contain only a low concentration of iron, manganese, dissolved substances and organic impurities,
- it must not be corrosive against metals and building materials,
- it must be hygienically safe.

3.7.1 Cooling water

Cooling water which removes heat from surface coolers and condensers is the type of water most frequently required by industry. To avoid the deterioration of heat transfer by cooling water and to ensure the adequate service life of equipment, it should not cause

- scaling or incrustations,
- sedimentation of mechanical impurities,
- sedimentation of biological impurities,
- equipment corrosion.

The composition of sediments leading to a decrease in the heat transfer depends on the temperature and composition of the water. Up to 40°C only calcium carbonate is separated, and at higher temperatures calcium sulphate also. The requirements for cooling water depend on the type of the circulation system, of which there are only two types:

- *open circuit* (cooling water is cooled by direct contact with air); it can be either through-flow or circulation type,
- *closed circuit*, which is always the circulation type; its cooling water is only a medium which transmits heat to be removed to another cooling medium (water, air).

In cooling water the content of calcium, sulphates and hydrogen carbonates is limited. Sulphates should be avoided because of the problems with concrete structures. Calcium sulphate can react with a component of cement — calcium aluminate — and form with it etteringite ($Ca_6Al_2[(OH)_4(SO_4)]_3.2H_2O$) whose crystals are more voluminous than those of the original aluminate. Changes in the volume can cause destruction of concrete.

The content of hydrogen carbonates is quite low because of the intensive ventilation of cooling water in an open circulation system and thus, the majority of free CO_2 is removed, so that the following calcium carbonate equilibrium shifts to the left:

$$CaCO_3(s) + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

and calcium carbonate separates in the form of continuous solid coatings. These coatings impede heat transfer, and reduce the inner diameter of pipes; however, they protect them against corrosion. On the other hand, water must contain a certain minimum concentration of hydrogen carbonate so as to avoid corrosive effects of residual CO_2 [9].

3.7.2 Feed water

Difficulties which occur in the operation of steam boilers due to the composition of feed water vary according to the boiler construction, its capacity, operating pressure, purpose of the steam use and heat loading of the heating surface. With increasing pressure in the boiler the temperature of water rises, and porous sediments are formed on the walls of the boiler system, which consist of colloidal suspended corrosion residues originating from other parts of the equipment. In these sponge-like sediments, substances from feed water are concentrated and chemical reactions take place which cause corrosion of the walls. With increasing pressure it is unavoidable to reduce the content of salts in feed water, to limit alkalization by means of sodium hydroxide, and to reduce sodium phosphate dosing. The limitations on feed water quality are increasing with the requirements for long-term continuous operation of heavy-duty boilers and turbines. In these cases feed water should have a composition approaching the composition of chemically pure water [3, 10–12].

3.7.3 Water for foodstuff and pharmaceutical industries

Water for foodstuff and the pharmaceutical industries should always satisfy the standard for drinking water, except in the case of waters which are not in contact with products (cooling waters, water for beet fluming, rough washing of products, etc.).

Sugar factories form a very large sector of the foodstuff industry and require large amounts of water (17–18 m^3 per 1 t of sugar beet). The demands for industrial water can be significantly reduced by introducing the recycling of treated wastewaters. There are no special requirements for the quality of diffusion fluming and wash waters. More stringent are the requirements for the quality of pulp (diffusion and pulp press) waters. These must be soft and bacteriologically safe. Hard water increases ash content in beet juice, hindering crystallization and reducing the sugar yields.

Dairy plants use drinking water for washing and cleaning. The contents of magnesium must be low since it could cause a bitter taste in the butter. The content of iron should be less than 0.1 mg l^{-1}; copper and manganese should not be determinable by common analytical methods. The water consumption when processing 1 l of milk averages 5–8 l. Of that, about 40% is used for cooling.

Canning factories for fruit and vegetables require the quality of drinking water appropriate for washing the fruits and vegetables, and the water is also used as an additive to preserves, fruit juices, etc. The content of calcium and magnesium should be low since these elements react with pectin compounds in fruit and influence the taste of the product. For processing of 1 kg of fruit 5–15 l of water is required (depending on the kind of fruit).

Slaughterhouses and the meat industry require water of the quality of drinking water for cleaning the meat and cooking of meat products; moreover, this water should be soft because the ions of the elements of alkaline earth elements cause whitening of meat.

Starch factories need industrial water for flotation and washing of potatoes and for starch extraction. Water for extraction should be of drinking water quality.

In breweries, large quantities of industrial water are used for steeping barley in the production of malt, for beer brewing for washing the barrels, floors, etc. and for feeding the boilers for steam heating of process vats. All industrial waters must be safe from the viewpoint of health, but water used for beer brewing must be of particularly high quality. This water must be colourless, odourless, it must not contain iron, magnesium, ammonia, or sodium chloride. Water for barley steeping should be soft. All requires higher concentrations of Ca^{2+} and SO_4^{2-} ions, whereas the water for the stout should contain the lowest possible concentrations of these ions. Higher concentrations of iron and manganese negatively influence fermentation and cause turbidity of beer. Famous breweries pay exceptional attention to water treatment since water influences quite significantly taste, bitterness, foamability as well as the colour of the beer.

Pharmaceutical industry requires not only health safe, but frequently demineralized industrial water (produced by distillation or ion exchangers) [1, 2, 4].

3.7.4 Water for textile and paper industries

In the *textile industry*, water is used for processing of different raw materials (cotton, wool, flax, hemp, natural silk and artificial fibres). The water used must be clear, colourless and must not contain suspended constituents. Further requirements concern a low content of calcium and magnesium, and absence of iron and magnesium because calcium and magnesium form greasy soaps which worsen the product appearance; iron and manganese are easily separated in alkaline media in insoluble forms and thus, they cause staining of the final product. In the wool industry water must be suitable also from the bacteriological aspect, otherwise the products may be attacked, for instance, by moulds.

In the *paper industry* the quality of industrial water is considered very important since it directly influences the properties of paper. Water should be colourless, clear and must not contain iron, manganese, humin and other substances which could cause colouration or staining of paper. The requirements for the production of special papers (e.g. cigarette paper, filtration paper, paper for packing the food, medical instruments, etc.) are even more demanding, since this water must also be hygienically safe [1, 13].

3.7.5 Water for chemical industry

In chemical industry, which is one of the greatest consumers of water, as much as 70% is used for cooling. This sector of industry also requires water for dissolving of raw material, heating of apparatus and equipment, for raw material transportation, washing of products, washing of technological equipment, removal of waste, etc. The requirements for water quality are very varied and depend on the particular production processes. Sometimes untreated water is sufficient, sometimes mechanically treated and even demineralized water is required.

The requirements for the quality of water used in the production of viscose, viscose staple and organic dyestuffs are quite high.

The requirements for the quality of water used in *polymerization processes* (e.g. in the production of polyvinyl chloride, polystyrene) are particularly stringent. In this case, process water should have the quality of distilled water [13].

3.7.6 Water for the building industry

The requirements for water used in the building industry for preparation of a concrete mix and mortar are not stringent. The majority of natural waters can be used except for swampy, muddy, mineral and wastewaters. Water used for the preparation of concrete mixes (so-called *concrete* or *mixing water*) is added to concrete in relatively small quantities and thus even higher amounts of certain constituents may not have negative effects.

Concrete water should be approximately neutral (the permissible pH value ranges from 4.5 to 8.0), and it must not contain high amounts of organic matters; high amounts of sulphates, chlorides and magnesium are undesirable. Requirements for water used for the treatment of concrete during its setting (so-called *treatment water*) and for waters which are in contact with completed structure (so-called *attack waters*) are more stringent because some waters can damage concrete. Aggressivity of attack water is influenced by the type of aggressivity, concentration of aggressive components, the mode of the contact between water and the material, its resistance to attack, and the temperature of the water [13, 14].

Aggressive waters are divided into several groups:

Waters with a low content of salts. The most important process is leaching of soluble constituents of material. As far as concrete is concerned, particularly the release of $Ca(OH)_2$ during the hydration of cement should be borne in mind.

Acid waters. Waters of this group contain mineral or organic acids which dissolve calcium components of concrete, which are thus removed from it. Acids whose calcium salts are quite soluble (HCl, HNO_3) corrode concrete more quickly than those whose calcium salts are insoluble. The pH of water should not decrease below 6.7.

Waters containing aggressive CO_2. These are the most frequently occurring waters. Aggressive CO_2 reacts with $Ca(OH)_2$ generated during the hydration of cement. Calcium constituents of concrete are transformed into more readily soluble calcium hydrogen carbonate due to the effect of CO_2; the soluble compound is gradually removed by permeating water — particularly if hydrostatic pressure is applied (e.g. dam reservoirs), or if waters flow around concrete. The running water removes corrosion products, and because of the continual disturbance of the equilibrium the corrosion process is re-established. These processes are expressed by the following reactions:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$H_2O + CaCO_3 + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

(see also Section 3.4).

Sulphate waters. The influence of these waters, mostly groundwaters, on concrete is the most intensive. The main reason for the destruction of concrete by sulphate waters is the reaction of sulphate anions with tricalcium aluminate to form the already mentioned strongly hydrated compound. This compound crystallizes in needles with a considerable increase in volume. Due to the considerable crystallization pressure the concrete cracks, becomes porous and the destructive effects of aggressive water penetrate deeper through the cracks formed.

Waters with an increased content of magnesium. If concrete is in contact with waters of this type a reaction with $Ca(OH)_2$ takes place to form low soluble $Mg(OH)_2$ and replacement of calcium by magnesium ions occurs in silicates. As the Mg^{2+} ions are smaller than the Ca^{2+} ions the strength of concrete decreases.

The specific quality characteristics of surface waters that have been used as sources for industrial water supplies are summarized in Table 3.53 [15, 16]. Unless otherwise indicated, units are mg l^{-1} and values are maxima. For no type of water all maximum values are shown.

3.7.7 Water for agricultural production

One of the essential preconditions for the development of agricultural production is an availability of sufficient quantity of water of the appropriate quality for plant and animal husbandry. An adequate supply of good quality water is of essential importance for improvement of milk yielding capacity of cows, beef production and also for raising the yields per hectare of crops, vegetables and other types of products.

The quality of *water for irrigation* is very important as it influences not only soil and irrigated plants, but also the service life and maintenance of the water system (irrigation network, channels, etc.).

As regards *physical properties*, temperature, content of suspended constituents, colour and odour are important.

As for chemical aspects, the total quantity of non-volatile dissolved substances and their composition are important. Content of chlorides, sulphates and boron, as well as the ratio of sodium to calcium and magnesium are important. If water with a high concentration of soluble substances and sodium with respect to calcium and magnesium is used for irrigation, *salting of soils* can occur. Salted soils are less fertile, or they can be completely infertile. A raised quantity of boron in irrigation water (limiting concentration B $\sim$ 1.0 mg l^{-1}) can result in complete defoliation of plants. In the case of gases, oxygen must be present in water; carbon dioxide, free chlorine and hydrogen sulphide have negative effects. Toxic substances, crude oil and its products, and radioactive substances are not permissible, oils and fats are undesirable [17, 18].

The suitability of the use of surface or wastewaters for irrigation is assessed by hygiene, epidemiological and veterinary authorities.

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Table 3.53. Summary of specific quality characteristics of surface waters

Characteristics	Boiler makeup water		Cooling water			
	Industrial 0 to 1500 psig	Utility 700 to 5000 psig	Fresh		Brackish[a]	
			Once through	Makeup recycle	Once through	Makeup recycle
Silica (SiO_2)	150	150	50	150	25	25
Aluminium (Al)	3	3	3	3		
Iron (Fe)	80	80	14	80	1.0	1.0
Manganese (Mn)	10	10	2.5	10	0.02	0.02
Copper (Cu)						
Calcium (Ca)			500	500	1,200	1,200
Magnesium (Mg)						
Sodium and potassium (Na, K)						
Ammonia (NH_3)						
Hydrogen carbonate (HCO_3)	600	600	600	600	180	180
Sulphate (SO_4)	1,400	1,000	680	680	2,700	2,700
Chloride (Cl)	19,000	19,000	600	500	22,000	22,000
Fluoride (F)						
Nitrate (NO_3)			30	30		
Phosphate (PO_4)		50	4	4	5	5
Dissolved solids	35,000	35,000	1,000	1,000	35,000	35,000
Suspended solids	15,000	15,000	5,000	15,000	250	250
Hardness ($CaCO_3$)	5,000	5,000	850	850	7,000	7,000
Alkalinity ($CaCO_3$)	500	500	500	500	150	150
Acidity ($CaCO_3$)	1,000	1,000	0	200	0	0
pH, units			5.0–8.9	3.5–9.1	5.0–8.4	5.0–8.4
Colour, units	1,200	1,200		1,200		
Organics						
Methylene Blue active substances	2[d]	10	1.3	1.3		1.3
Carbon tetrachloride extract	100	100	(e)	100	(e)	100
Hydrogen sulphide (H_2S)					4	4

[a] Water containing in excess of 1,000 mg/l dissolved solids.

[b] May be $\leq 1,000$ for mechanical pulping operations.

[c] No large particles ≤ 3 mm diameter.

[d] 1 mg/l for pressures up to 700 psig.

[e] No floating oil.

t have been used as sources for industrial water supplies [15, 16]

Process water							
Textile industry	Lumber industry	Pulp and paper industry	Chemical industry	Petroleum industry	Prim. metals industry	Food and kindred products	Leather industry
		50		50		For the above 2 categories the quality of raw surface supply should be that prescribed by the NTA Subcommittee on Water Quality Requirements for Public Water Supplies	
0.3		2.6	5	15			
1.0			2				
0.5							
			200	220			
			100	85			
					230		
				600	480		
				850	570		
		200^b	500	1,600	500		
				1.2			
				8			
150		1,080	2,500	3,500	1,500		
1,000	(c)		10,000	5,000	3,000		
120		475	1,000	900	1,000		
			500		200		
					75		
6.0–8.0	5–7	4.6–9.4	5.5–9.0	6.0–9.0	3–9		
		360	500	25			
					30		

3.8 The recipient and its pollution

The area into which sewage waters are discharged, i.e. waters which have changed their quality after being used, is called the *recipient.* Mainly surface waters — rivers, brooks, lakes, ponds or seas, and sometimes also groundwaters serve as recipients.

The quality of water in a recipient is negatively influenced by wastewater discharge, which becomes obvious from aesthetic defects, chemical and bacterial pollution, deterioration of biocenosis, retardation of self-purification processes, sludge deposits and other negative phenomena.

Discharged wastewaters may contain only residual pollution which is impossible to remove by the used technological treatment employed; the costs for total wastewater treatment would be prohibitive. The degree of purification required is determined with regard to the recipient and the requirements for subsequent utilization of the water [1–7].

The pollution of water in the recipient due to worsening of its quality, limits or renders impossible subsequent utilization. Deterioration of water quality is generally of a physical, chemical and biological nature, these processes being combined in different ways.

Physical deterioration of water quality is evident first of all from sludge occurrence — insoluble admixtures of inorganic or organic origin, which are either dispersed in the water or form putrescent sediments on the bottom. The water acquires an undesirable turbidity and colour. Discharge of warmed waters unfavourably influences the water temperature in the recipient, thus reducing the oxygen solubility [8–11].

Chemical deterioration of water quality is caused by admixtures of solid, liquid or gaseous phases which are water-soluble. These particularly include free acids, nitrates, chlorides, sulphates, salts of heavy metals, cyanides and phenols, and gaseous substances. Such substances can entirely destroy biological revival and the self-purification capability of the stream as a consequence of exhaustion of dissolved oxygen from water [12–16].

Biological deterioration of water quality is primarily caused by toxic substances, products of putrefactive degradation, pathogens and radioactive substances. A schematic illustration of the effect of pollutants on water quality in the recipient is shown in Fig. 3.39.

The best classification from the aspects of the effect of wastewaters on surface waters and biological life in them is that based on the prevailing type of pollution. From this viewpoint also possibilities and methods of their

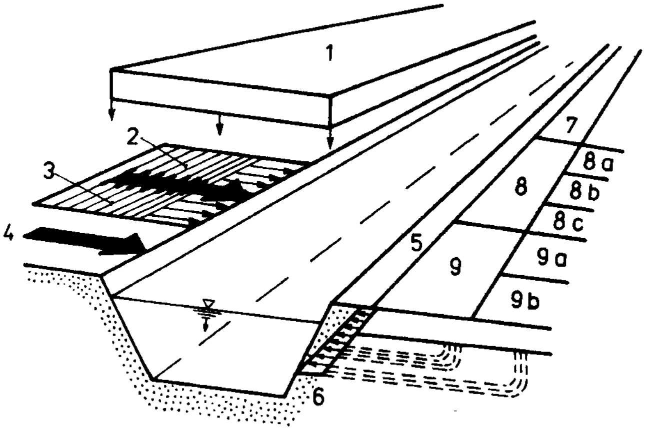

Fig. 3.39. Schematic illustration of the effect of pollutants on water quality in a recipient. 1 — pollutants from the atmosphere, 2 — municipal wastewaters, 3 — sewers, 4 — industrial wastewaters, 5 — surface run-off, 6 — sub-surface run-off, 7 — contribution from non-inhibited areas, 8 — waste depots: 8a — municipal, 8b — communal, 8c — sludge from wastewater treatment plants, 9 — agriculture and forestry: 9a — animal production and natural fertilizers, 9b — industrial fertilizers and pesticides

purification become evident, as well as participation of biological processes in the mineralization of this pollution, etc.

Such a classification includes the following groups of wastewaters:

— putrefactive,
— toxic,
— waters containing inorganic sludge,
— waters containing fats and oils,
— warmed waters,
— waters containing radioactive substances,
— waters containing pathogenic microorganisms [17–18].

3.8.1 Discharge of wastewaters into a recipient

Discharge of waters into a recipient is permitted only to such a degree that the interests of other authorized users remain unaffected.

Discharge of wastewaters should not result in the change of natural physical, chemical and biological properties of waters, and formation of detrimental conditions for health must be avoided. Water must be suitable for all purposes, i.e. it should have a quality which satisfies the needs of public supply and the requirements for industrial and agricultural production [19–21].

The quality of water in the recipients must not be influenced by the discharge of wastewaters. It is necessary to avoid

- considerable increase in the content of suspended constituents,
- production of foam on the surface to an extent which would represent 20% of the total surface, or formation of a continuous oil film, or other detrimental floating substances,
- increase or decrease of the concentration of hydrogen ions by more than one unit of pH,
- non-permissible reduction of dissolved oxygen content,
- change of water temperature by more than ±5°C in comparison with the normal ambient temperature,
- non-permissible change in the colour of water.

Wastewaters from infectious hospital wards, research and examination institutions from the field of human and veterinary medicine, institutes for the production of inoculation agents, waters from slaughterhouses and leather plants, from wool washing, and from gelatine production plants, etc. must not be discharged into the recipient. Where necessary, additional disinfection or sterilization processes should be carried out.

If wastewaters contain substances with immediate high oxygen consumption, they must be treated before being discharged into the recipient, e.g. by oxygenation.

The size (water capacity) of the recipient, degree of water pollution in it and its self-purification capability are important factors. Others factors include the number of discharged wastewaters, their quality and degree of pollution.

A low water capacity of streams fairly frequently causes emergency situations because large volumes of discharged wastewaters are not diluted down to the permissible degree of pollution in the required time.

When evaluating the effect of discharged wastewaters on the quality of water in the recipient it is necessary to take into consideration the self-purification capability of the stream, maintenance of normal life of fish, required quality of water in the locality of the nearest user, toxic effects of discharged substances and prospective development of the locality in question.

Discharge of wastewaters into surface waters is connected with a very serious type of deterioration of the quality of surface waters — *eutrophization.* This is a series of natural, or artificially induced biological processes caused by an increase in inorganic nutrients in surface waters.

Due to their content of biogenic elements, particularly of phosphorus and nitrogen, treated wastewaters can also cause intensive reproduction of algae, cyanobacteria and diatoma leading to the so-called lake bloom, particularly in stagnant surface waters (lakes, water reservoirs).

Sensory properties can deteriorate, sometimes also toxins are generated which have unfavourable effects on aquatic organisms. Water from such a source has an unpleasant odour, taste and colour, and its treatment for conversion into drinking water is very difficult.

One of the possibilities to protect surface water against eutrophization is the "tertiary" wastewater treatment following the conventional mechanical and biological treatment. The permissible concentrations are 0.02 mg l^{-1} of phosphorus and 0.2 mg l^{-1} of nitrogen [22–24].

Serious dangers for the quality of water and the life of aquatic organisms are caused by *emergency situations* in the water quality. These are sudden, unexpected and usually short-term deteriorations of the water quality in a stream which results in lowered utility properties of the water, causing at the same time biological, hygienic, aesthetic, technological and other defects. The cause of such emergency situations is discharge of seriously polluted wastewaters or other substances which are commonly not present in wastewaters, washing of harmful substances into waters, etc.

Such emergency situations are triggered particularly by crude oil and oil products, toxic substances, organic putrefactive substances with high oxygen demand, acids and alkalies, health detrimental substances, radioactive substances, substances changing organoleptic properties and appearance of water, insoluble and soluble non-toxic substances and other factors.

The final quality of water in the recipient into which wastewaters were discharged, is considerably influenced by *self-purification.* This involves a series of naturally occurring physical, chemical, biological and biochemical processes through which pollutants are removed from surface waters without any activity of man. The technological and economic importance of such self-purification processes lies in the fact that they can be considered as a kind of reserve treatment for removal of residual pollution after wastewater treatment.

The *physical processes* involved in self-purication include stirring and dilution of wastewaters by river water, diffusion of gases, sedimentation, processes induced by solar radiation, thermal stratification, etc.

As regards the relevant *chemical processes*, hydrolysis and oxidation of substances are of the greatest importance; neutralization, precipitation and oxidation-reduction reactions and photochemical degradation can also take place.

For the removal of pollution by self-purification, the activity of microorganisms, particularly of bacteria, is decisive, as well as that of plants and animals living in water. Self-purification will therefore be discussed in a separate chapter, the Biology of water [25–32].

The biological state engendered by the pollution of water with biologically degradable organic compounds is called *saprobity*, and it is an important factor for the water quality in the recipient.

The presence of impurities in water is demonstrated not only by a change in their physical and chemical properties, but also by a change in their biological properties. This is apparent from extinction of many representative species of zooplankton and phytoplankton, and by the development of other types of organisms, including microbes. In other words, to ech stage of pollution corresponds a certain biocenosis.

The determination of the species living in wastewaters of the site studied enables one to evaluate the current state of the quality of water; the presence or absence of species is assessed. Thus, saprobity is a biological reflection of water pollution.

Wastewaters frequently contain *toxic substances*. Their presence is unfavourably manifested in stopping the life processes of aquatic organisms which can thus become extinct in extreme cases.

Toxic substances in wastewaters come either from products of man's activity (heavy metals, cyanides, phenols, pesticides, detergents) or from natural anaerobic processes (formation of ammonia, hydrogen sulphide, etc.) [33–39].

The effects of toxic substances are shown in the reduction of numbers of species and quantity of microorganisms. Toxic substances in wastewaters are determined within the framework of biological analysis of water using laboratory *tests of toxicity*.

Wastewaters discharged into surface and groundwaters cause serious damage and losses for the national economy. Costs for water treatment increase, service life of equipment is shorter, valuable raw materials and products are lost, fish die, etc. For example, losses to the national economy caused just by industrial wastewaters discharged into the streams, amount to about 700 mil. Czechoslovak Crowns (35 mil. U.S.A. dollars) per year.

Polluting substances in wastewaters often represent products whose manufacture is fairly costly (for example, synthetic and cellulose fibres, phenols, acids, fats, etc.). Their retention and utilization can thus increase the production in the works itself, or can serve as a raw material for other products. At the same time, this reduces the negative influence of wastewater discharge on the quality of water in the recipient.

3.8.2 Dissolved oxygen balance in a stream

The course of mineralization of organic pollution by aerobic processes during self-purification is decisively influenced by molecular oxygen dissolved in water. The most important sources of oxygen in water are atmospheric oxygen and assimilation activity of phytoplankton and green plants.

Oxygen is introduced into water through the water surface. At a constant temperature the solubility of oxygen is directly proportional to the partial pressure above the liquid (Henry's law). Oxygen dissolved in polluted water is used for mineralization of organic pollution, therefore, its concentration usually becomes lower than the equilibrium concentration [40–43].

Time dependence of the dissolved oxygen consumption on biochemical degradation of organic substances (expressed in terms of BOD) is shown in Fig. 3.40.

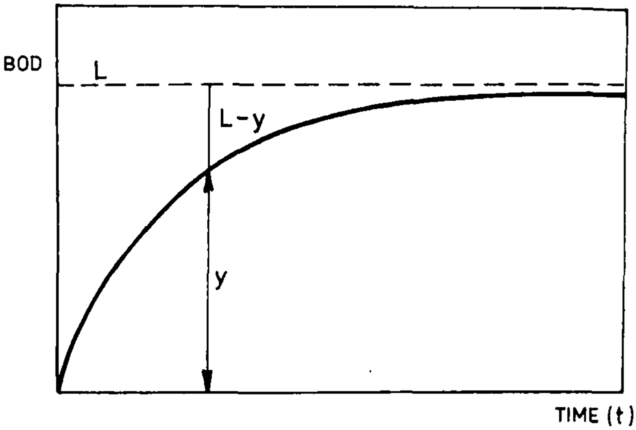

Fig. 3.40. Dependence of biochemical oxygen demand on time. L — total BOD, y — BOD value in time t

Oxygen conditions in the stream decisively influence two simultaneously proceeding processes:

- — re-aeration (transfer of oxygen through the water surface), and
- — deoxygenation (consumption of dissolved oxygen for biological degradation of organic substances).

The time dependence of these two processes is evident from curves 1 and 2 in Fig. 3.41. Their resultant is the *oxygen sag curve* (curve 3) expressing the time dependence of the concentration of dissolved oxygen in water.

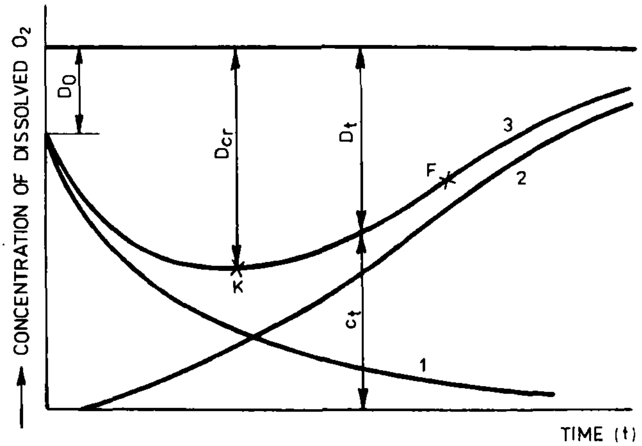

Fig. 3.41. Oxygen curves. 1 — deoxygenation, 2 — re-aeration, 3 — oxygen sag curve, D_0 — initial deficiency, D_{cr} — critical deficiency, D_t — deficiency in the time t, c_t — concentration of dissolved oxygen in the time t, K — critical point, F — inflexion point

From the moment when substances capable of undergoing biochemical aerobic degradation enter the surface water, the concentration of oxygen in water begins to decrease from the initial value (oxygen deficiency increases). However, with increasing deficiency, the quantity of oxygen introduced into water through the water surface increases.

At the so-called critical point K the rate of oxygen consumption and the rate of oxygen transfer through the surface achieve equilibrium. The coordinates of this point give the *critical time* t_{cr} at which the concentration of dissolved oxygen c_{cr} is maximum (critical) in the surface water (oxygen deficiency is maximum).

The critical concentration of oxygen should not be lower than 4 g m^{-3} so that the conditions for the life of aquatic organisms, especially fish, are not impaired.

Beyond the critical point, re-aeration predominates over deoxygenation. The concentration of oxygen dissolved in water increases, and after a certain period of time it approaches the value of equilibrium concentration.

The coordinates of the critical point (critical time and critical concentration of oxygen) determining the position of the minimum on the oxygen sag curve are important parameters for a given stream. They can be determined by calculation from the oxygen sag curve. At a known mean flow rate of the stream the oxygen sag curve also represents the course of the oxygen concentration in water along the stream.

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3.9 Wastewaters

Wastewater is the general term used to describe any water whose quality has been changed after its use in human habitations, industry, health care institutions, agricultural installations, and other complexes or facilities, as well as other waters flowing off from such places and threatening the quality of surface or groundwaters. They also include contaminated atmospheric waters in rainfall periods, which carry away accumulated pollution from streets and other public areas [1–3].

Wastewaters are most frequently discharged into surface waters, rarely into groundwaters, or they are stored in special reservoirs (e.g. radioactive wastewaters). According to particular qualities, wastewaters are classified as follows:

- fresh,
- putrefactive,
- infectious,
- radioactive, and
- toxic.

The total quantity of wastewaters (including cooling waters) is ever increasing, as the sources of the production of wastewaters are increasing which is evident from their ever more varying qualitative composition.

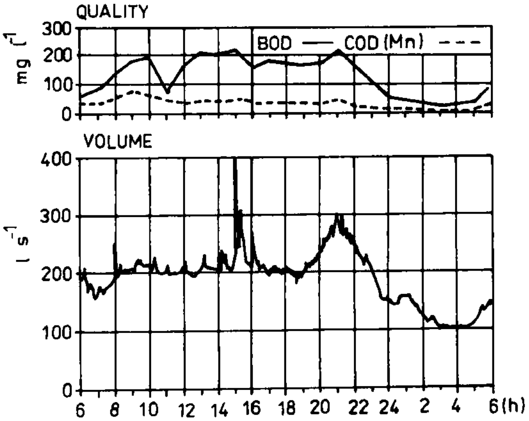

Fig. 3.42. A record of measurement of the quantity and quality of wastewaters

The quantity and quality of wastewaters are determined by direct measurements, calculation, or modelling. Figure 3.42 lists the changes in the quality and quantity of wastewaters expressed by two indicators.

Wastewaters are divided into the following two classes:
- sewage, and
- industrial wastewaters.

Agricultural wastewaters, due to their character and the methods of disposal, are a special group of wastewaters (see Section 3.9.4).

Sewage waters are wastewaters from households and sanitary facilities of industrial and agricultural plants. The total amount in Czechoslovakia, for example, has been estimated at 7×10^8 m^3 per year, which corresponds to a flow rate of about 22 m^3 s^{-1}.

A significant feature of sewage waters is the high proportion of organic substances able to degrade microbiologically to form bad-smelling gases and matters which lend these substances a non-attractive appearance.

An important constituent of sewage waters from the health viewpoint are the germs of infectious and parasitic diseases which, particularly in the case of mass occurrence pose a serious threat to further utilization of both surface and groundwaters.

Although the composition of sewage waters can vary slightly, it is generally fairly constant, thus allowing mainly the same methods for their treatment [4–5].

The loading of municipal wastewater treatment plants is higly dependent on the content of organic, easily degradable substances, usually expressed in the terms of BOD_5 per capita per day. This loading generally ranges from 54 to 70 g BOD_5 per capita per day.

Industrial wastewaters are liquid waste formed during extraction of inorganic and organic raw materials and in the course of their industrial processing. Composition and quantity of polluting substances in industrial wastewaters obviously depend on the production in question, and are typical for each sector of industry. Wastewaters running off from the particular product lines are called *process waters.*

The higher the industrialization of a national economy and the greater the introduction of new technological processes, the higher is the quantity of wastewaters produced; as regards qualitative aspects, the amounts of biologically difficult-to-degrade compounds as well as of toxic substances are increasing [6–8].

Depending on the particular technological processes in which the water was used, industrial wastewaters differ in their character of pollution, chemical composition and physical properties. In some cases the contents of substances is so high (e.g in sulphite waste liquors, mother liquors from crystallization) that it is difficult to talk about water as such.

Currently, agricultural large-scale production represents a very serious source of pollution and threat to the quality of surface and groundwaters because of the application of large amounts of industrial fertilizers and plant protection chemical agents, concentration of animal husbandry in large-capacity breeding units and increasingly intensive employment of mechanization [9–12].

Municipal wastewaters are a mixture of sewage and industrial wastewaters flowing through the municipal sewerage system. They also contain contaminated atmospheric waters and waters used for cleaning roads and public areas.

The proportion of sewage and industrial waters in municipal waters depends on the balance between the size of settlement and the size and character of industrial production in the locality in question. Application of a particular treatment depends on the type of industrial wastewaters, or on the use of unified or separated sewerage system [13–14].

3.9.1 Sewage wastewaters

Sewage wastewaters contain contaminating substances from sanitary facilities, kitchens, bathrooms and laundries.

The quantity of sewage waters in a household connected to the public sewerage system is governed by the demand of water per capita. This quantity varies during the day, the week and the year. The overall flow rate variations depend on the size of the town or settlement, the lowest per capita rates being in large towns, with a maximum at midday or evening hours.

The daily water demand per capita depends on the equipment installed in flats and settlements. Under Czechoslovak conditions, a demand, for example of about 280 l per capita per day, is taken into consideration in flats with bathrooms, central heating and hot water distribution. The average demand of water is 150–200 l per capita per day.

The main proportion of contaminatig substances occurring in sewage wastewaters is ascribed to faeces and urine. They provide between 45 and 80% of organic substances in sewage. Supposing that the average water demand is 200 l per capita per day the sewage wastewater will contain about 225 mg l^{-1} of organic substances from faeces and 175 mg l^{-1} of organic substances, and 125 mg l^{-1} of inorganic compounds originating from urine.

In the case of faeces, particularly lipids, proteins, polysaccharides and products of their decomposition (e.g. aliphatic acids, amino acids, amines, etc.) are concerned in the case of urine the highest amount of organic compounds is due to nitrogen substances, particularly urea; to a lesser extent amino acids, ammonia nitrogen, uric acid, etc. are present. Urine contains a considerably lower amount of nitrogen-free organic matters (e.g. oxalic acid, glycides, phenols, etc.).

As urea undergoes fast biological degradation in sewage waters, the fraction of ammonia nitrogen promptly increases to the detriment of other nitrogen compounds. An amount of about 16 g of nitrogen per capita per day is approximately standard, nitrogen being present in the form of nitrogen organic compounds.

Inorganic compounds originating from urine provide particularly sodium, chlorides, potassium, sulphates and phosphates in sewage wastewaters.

Faeces and urine excreted by man per day represent about 110 g of dry matter of which organic substances contribute about 72% and the remaining quantity is ascribed to inorganic substances. Of the organic substances urea is the most prominent compound, as regards quantitative aspects; chlorides predominate among the inorganic substances. Considering the water demand to be 200 l per capita per day, the concentration of urea in sewage water should be 150 mg l^{-1}, that of chlorides 45 mg l^{-1}, total nitrogen 86 mg l^{-1} and total phosphorus 6 mg l^{-1}.

Other sources of contamination in sewage waters which increase the content of soluble and insoluble substances of both inorganic and organic origin are the constituents of washing agents and detergents from laundries and bathrooms, soaps, tensides, phosphates, carbonates, silicates, and the like, as well as the constituents of sweat. Furthermore, there are residues of animal and plant food, fats, and constituents of washing and cleaning agents from kitchens [15, 16].

3.9.1.1 Properties and composition of sewage waters

The substances of inorganic and particularly of organic origin introduced into water undergo immediate changes mainly in the degree of dispersion of insoluble substances. In the early stages of sewerage processes non-dissoluble substances are crumbled and dispersed and subsequent sedimentation takes place. Soft components such as faeces are disintegrated to a colloidal form by pumps. At the same time also other components are dissolved. Because of increase of the surface area of insoluble constituents, sorption, chemical and biological processes can be applied more efficiently. As regards physico-chemical processes, for example, changes in conductivity and pH of water should be mentioned.

Due to a higher concentration of tensides, dispersion and emulsifying processes can occur, but in some cases coagulation of colloid substances can take place.

However, the most remarkable changes are those due to biological effects. As long as there is sufficient oxygen in water, aerobic processes take place by which oxygen is quickly consumed. In the case of oxygen deficiency the initial oxidation processes are changed into reduction ones and anaerobic processes predominate. During aerobic processes oxygen compounds are produced and the final products are carbon dioxide, water, sulphates, nitrates, etc.

Anaerobic processes are undesirable in a sewerage system since bad smelling products are produced, some products can disturb the processes in the biological section of the wastewater treatment plant due to their toxicity, and finally, some substances can increase the corrosive effects of sewage. Of the organic substances present in sewage, saccharides and polysaccharides (sugars, starches, cellulose) which are suitable food for bacteria are degraded first. Urea is degraded by bacteria to ammonium carbonate.

During the decomposition of proteins into simpler substances sulphur compounds are released which are reduced to hydrogen sulphide, and nitrogen compounds are reduced to ammonia. Colloid proteins are transformed into solutions via degradation into peptones, amino acids and finally into ammonia and carbon dioxide.

Inorganic salts are also reduced, for example, sulphates are transformed into hydrogen sulphide or sulphides, nitrates into nitrites, ammonia and nitrogen.

In addition to bacteria which degrade organic substances by hydrolysis and oxidation-reduction processes, wastewater also contains different ferments and enzymes (formed by cells), which also take part in the decomposition of organic substances.

The colour of sewage waters is usually grey, sometimes even yellow-brown. They are intensely turbid. Under anaerobic conditions generated hydrogen sulphide reacts with the compounds of iron to produce FeS, and causes darkening of water.

The odour of fresh sewage waters is not too intensive. Only after the exhaustion of dissolved oxygen (after several hours) when anaerobic reduction processes start to take place, does the water begin to smell intensively.

The temperature of sewage waters ranges in winter from 8 to 12°C and does not drop below 4–6°C, its temperature in summer is as high as 20°C. Higher temperatures can be caused for example, by discharge of warmed waters into the sewerage system. Variations in the temperature during the course of a day are small, particularly in winter. The temperature of water significantly affects the rate of decomposition processes.

Sewage waters are weakly alkaline, the pH value is usually not higher than 7.5.

From the physical viewpoint the substances present in sewage waters are divided into *suspended* and *dissolved* solids. Insoluble substances are subdivided into *sedimentable* and *non-sedimentable* ones. Floating substances form a special group.

Suspended solids include colloidal and coarse disperse systems, as well as living organisms.

The relative proportion of particles of a certain size in the case of suspended solids is influenced by dispersing effects of tensides and condensed phosphates. Because of their increasing quantity in sewage waters, a higher quantity of non-sedimentable substances has been recently reported.

Of the total quantity of all substances present in sewage waters about half are inorganic substances and the other half are organic ones (expressed in per cent by weight). One third are suspended and two thirds are dissolved solids. Suspended solids are mostly organic, the dissolved solids are mostly of inorganic origin. This classification does not express exactly the relative representation of inorganic and organic compounds, it represents only a rough estimation. The residue of dry matter after heating comprises inorganic substances, and organic compounds are those lost during heating.

Table 3.54. Average composition of sewage waters

Matters	Inorganic	Organic (mg l^{-1})	Total	BOD_5
Insoluble, of this	75	200	275	150
sedimentable	50	150	200	100
non-sedimentable	25	50	75	50
Soluble	375	250	625	150
Total matter	450	450	900	300

The data on average composition of sewage waters for a water demand of 200 l per capita per day are presented in Table 3.54.

Of the total amount of dissolved solids about 60% are inorganic and 40% organic matters. This ratio is reversed in the case of suspended solids, being approximately 3:7.

These data indicate that it is generally true to say that suspended solids are mostly of an organic character and dissolved solids of an inorganic character.

The ratio of organic and inorganic substances in sewage waters produced by man is constant, in general, under a given set of living conditions. Changes in the composition and quantity of these two main groups of substances, organic and inorganic, can also be due to the development and use of new preparations in households and sanitary facilities (for example, cleaning and washing agents).

The quantity of waste substances per capita per day expressed in terms of BOD_5 ranges from 54 to 70 g (see Table 3.55).

Table 3.55. Specific production of pollution

Matters	Inorganic	Organic (g per capita per day)	Total	BOD_5
Insoluble, of this	30	60	90	31
sedimentable	20	40	60	19
non-sedimentable	10	20	30	12
Soluble	50	50	100	23
Total matter	80	110	190	54

3.9.1.2 Inorganic and organic substances in sewage waters

Inorganic substances present in sewage waters are essential constituents of drinking and service water, and they are also substances originating from faeces, urine, waste from households, washing, cleaning and laundry agents, and from soiled streets. The most important species are chlorides, sodium, potassium, phosphates and inorganic forms of nitrogen. Evaluation of the content of inorganic substances in sewage waters is important particularly in the case of their application for irrigation in agriculture, where a high content of dissolved mineral substances in water is harmful. The standard limits particularly the content of dissolved solids — chlorides and sulphates.

Chlorides usually originate from urine. Seven to nine grams of chlorides are produced per capita per day. Higher content of chlorides can be caused by wastes from neutralization stations, recovery plants for water treatment by ion exchangers, or washings from streets after the use of sodium chloride in winter. Concentration of chlorides in sewage waters is usually expressed in tens of mg l^{-1}.

Phosphorus compounds in sewage waters, assuming that they are not already present in drinking and service waters, come from urine, faeces and synthetic detergents.

Man produces daily, mostly in urine, about 1.6 g of phosphorus which is in agreement with the content of phosphorus in sewage waters before the development of the production of detergents, which adds about 6 mg l^{-1}. From the production and application of synthetic detergents containing phosphates as activating additives, the content of phosphorus in sewage waters in developed countries has increased significantly. From this increase in phosphates (mostly in the form of condensed phosphates) a value of as much as 5 g of phosphorus per capita per day is reached, and the total concentration of phosphorus in sewage waters can amount to 10 mg l^{-1}.

The most important *nitrogen compounds* in sewage waters are ammonium nitrogen, urea and amino acids which can be either free or bonded in proteins and their degradation products. Urine with its prevailing amount of urea is the main source of nitrogen compounds in sewage waters. The urea is degraded by biological hydrolysis into ammonia nitrogen, therefore, the highest quantity of urea is present in fresh sewage waters.

Other forms of organically bounded nitrogen also readily undergo mineralization, therefore, the quantitative representation of individual forms depends to a considerable degree upon the time factor.

Saccharides and organic acids in sewage waters are among the most numerous compounds. Because of their solubility they are present mostly in the liquid phase of sewage waters. However, high molecular weight polysaccharides (cellulose, starch and products of their partial hydrolysis) are present mostly in the solid phase. In the liquid phase of sewage waters as much as half of organic carbon can be present in the form of saccharides. Of the simple saccharides, glucose, saccharose and lactose are predominant. Saccharides easily undergo biological decomposition to form aliphatic organic acids, therefore, the relative proportion of saccharides and organic acids varies and depends on several factors.

As regards organic nitrogen-free acids which volatilize with water vapour, acetic acid in particular occurs in sewage waters, followed by propionic, butyric, valeric, formic and caproic acids. Non-volatile acids are lactic, citric, glutaric, oxylic and other acids. These acids occur in concentrations of tenths or even units of mg l^{-1} (expressed in the terms of carbon).

Lipids include fats, waxes, steroids, phospholipids, and also hydrocarbons and free higher fatty acids and their salts — soaps belong in this category. By standard analysis lipids are determined as *extractable substances*; the quantity produced by man is about 15 g per day which corresponds to an average concentration in sewage waters ranging from 50 to 100 mg l^{-1}. Other sources of extractable substances in sewage waters are by-products of the foodstuff industry, laundries, etc. which is evident from the considerable increase in the quantity of these substances.

In sewage waters, the substances of the lipid group are present either free, emulsified or adsorbed on suspended solids. Because they are present in sewage water mostly in the insoluble form, their biological degradation is slower than the degradation of dissolved organic substances, such as saccharides or amino acids. Free lipids are floating substances which impede the rate of oxygen penetration through the water surface.

A considerable part of lipids in sewage waters is formed by fats (30–80%), higher fatty acids (particularly unsaturated ones) and hydrocarbons. The fact that the major fraction is present in unsedimentable emulsified form should be taken into consideration when proposing their separation.

At present, *tensides* have become permanent components of sewage waters. A sharp increase in the consumption of detergents dates from 1950 and this growth is ever increasing.

The early biologically difficult-to-degrade anion tensides with branched structures were gradually replaced by linear alkylbenzene sulphonates which degrade more easily, and since 1970 the consumption of non-ionic tensides has also increased.

The content of the anion tensides in sewage waters under conditions in eastern Europe is measured in units of mg l^{-1}; in some countries with a high consumption of tensides their concentration may reach more than 10 mg l^{-1}. Due to their sorption capacity tensides occur in both the liquid and solid phase of sewage waters. Of the original concentration as much as 50% of tensides can be adsorbed on suspended solids, and these can be employed for their removal in the treatment process.

On the other hand, tensides can increase the share of non-sedimentable substances in sewage waters due to their dispersing and emulsifying effects. In the biological section of a wastewater treatment plant, particularly nonionic tensides can cause other difficulties (excessive foaming in the activation reservoirs, foam stabilization, etc.).

Recently, increasing amounts of crude oil and oil products, as well as other products with an unfavourable influence on the processes of biological treatment in municipal wastewater treatment plants, are being introduced into sewage or municipal wastewaters. Therefore, for the discharge of wastewaters into the public sewerage system special rules must be observed exactly specifying what can be or must not be discharged into the public sewerage system, and at what concentrations [17–20].

3.9.1.3 Evaluation of organic pollution

Since sewage waters contain mostly *easily-degradable* organic substances it is possible to use the BOD value, determination of COD or total organic carbon for evaluation of their total organic pollution.

At the demand of 200 l of water per capita per day, an average BOD_5 value of about 300 mg l^{-1} can be expected. About half of the BOD_5 value is ascribed to dissolved solids and a half to the total quantity of suspended solids. About 65% of total BOD_5 is attributed to BOD_5 of the dissolved and non-sedimentable solids which means that by sedimentation alone the BOD_5 of sewage water can be reduced by one third.

The specific quantity of BOD_5, i.e. 60 g per capita per day can be derived from the given BOD_5 values and water demand.

In countries with a higher daily demand of water per capita (e.g. in USA, Switzerland, Sweden) sewage waters are more diluted and thus they show lower BOD_5 values (lower than 100 mg l^{-1}). Also, the value of the specific quantity of BOD_5 is higher (70 BOD_5 per capita per day).

For the determination of COD of sewage waters, potassium dichromate in 50% sulphuric acid can be used, by which the majority of organic substances is chemically well oxidized. The determination of COD with potassium permanganate is not suitable. The COD value of raw sewage water is approximately twice the BOD_5 value. For raw sedimented or filtered sewage water the ratio BOD_5:COD ranges from about 0.44 to 0.55.

Total contents of organic substances present in sewage waters can also be determined by measuring the organically bonded carbon.

The indirect method is based on oxidation of the organic substances present by a wet or dry technique and subsequent determination of CO_2.

Of the direct methods, the method based on the sorption of organic substances from water on activated carbon, subsequent desorption by organic solvent and gravimetric determination has been widely used.

The ratio of COD and organically bonded carbon depends on the content of oxygen in the organic substances present and ranges from about 2.5 to 3.0. The ratio of BOD_5 to organically bonded carbon is about 1.5 in the case of raw sewage waters [21–26].

3.9.2 Industrial wastewaters

The quantity and composition of industrial wastewaters depend on the type of technological process in which the water was used. Thus, the production technology, raw materials used, auxiliary substances and additives, and many other factors determine these parameters. It is clear that each industrial sector has its typical wastewaters.

The quantity of industrial wastewaters is expressed in different ways, usually as a specific amount referred to a specific unit of raw material or products.

In comparison with sewage waters industrial waters are noted for a higher concentration of substances, greater heterogeneity of contaminating substances and more substantial variations in the composition depending on the type of production [27–29].

In the individual production sections so-called *technological wastewaters* are produced which have certain typical properties and composition. In addition to these, normal sewage waters occur in the works, and in the rainfall periods the contribution of the rainfall waters must be omitted. Therefore, wastewaters from industrial operations are a mixture of different types of wastewaters. Industrial wastewater treatment is therefore much more complicated and difficult than the treatment of sewage waters. Also, the effect of such water when discharged into a recipient is different and in most of cases also more harmful because the quantity and quality of wastewaters in industry is noted for high variability, and maxima and minima are not necessarily in agreement with the extremes in the changes of municipal wastewaters.

Industrial wastewaters from sites incorporated into settlements are usually discharged together with sewage waters into one sewerage system and fed into a common municipal wastewater treatment plant.

For orientation, a comparison of the scope of pollution of industrial wastewaters with sewage waters (e.g. for the calculation of loading the treatment units in the common wastewater treatment plant) involving the so-called *population equivalent*, or *equivalent number of inhabitants* has been used. Its calculation is based on the value of pollution in BOD_5 per capita per day (54 or 60 g). In the case of industrial wastewaters the average value of the total pollution BOD_5 ($g\ m^{-3}$) and water demand Q ($m^3\ d^{-1}$) per production unit or initial material (t, m^3, pc, etc.) are taken as the basis.

The population equivalent is then calculated as follows:

$$E = \frac{BOD_5 \cdot Q}{54,\ \text{or}\ 60}, \quad \text{or in general}$$

$$E = \frac{\text{daily production of pollution}}{\text{specific quantity of pollution}}$$

Thus, *the population equivalent is the quantity of pollution* expressed in the corresponding units of the given type of pollution which is the same as the pollution of this type produced daily by one person.

In addition to BOD_5 other criteria can also be used for the calculation of population equivalents, for example, COD or the content of suspended solids, which can be more important for some industrial wastewaters. The population equivalent usually refers to the specific unit of raw material or product.

For wastewaters polluted mainly by undissolved inorganic substances (e.g. from metallurgical and mining operations) the population equivalents can be calculated in such a way that the value of specific production of undissolved substances per capita per day (90 g) is substituted into the above formula.

The population equivalent is a conventional unit which does not express all the properties of industrial wastewaters. Moreover, their values vary at each change in the production technology which has an impact on the composition of wastewaters (e.g. changes such as saving of water, introduction of recirculation, etc.). The quoted values of population equivalents differ, therefore, quite considerably in the literature.

Since higher values of the specific quantity of pollution than 54 g per capita per day are used at present, it is recommended to quote the value which was chosen for the calculation of the equivalent number of inhabitants.

Table 3.56. Equivalent number of inhabitants of some areas of production calculated by means of BOD_5 (54 g per capita per day)

Production area	Specific unit of raw material or product (1000 kg)	Equivalent number of inhabitants per specific unit
Diaries and cheese plants	1000 l of milk	50–256
Slaughter-houses	of live weight	144–460
Sugar production	of sugar beet	50–78
Malt houses	of cereals	11–111
Breweries	1000 l of beer	167–390
Distilleries	1000 l of cereals	1500–3900
Yeast plants	of yeast	5600–7800
Starch factories	of maize	560–1000
Tanneries	of skin	1100–3900
Wool scouring mills	of wool	2300–5000
Dye works	of material	2300–3400
Sulphite pulp mills	of pulp	3900–6100
Paper mills	of paper	230–1000

For illustration and to compare pollution of some industrial wastewaters, Table 3.56 presents the values of equivalent number of inhabitants for certain areas of production.

In addition to the population equivalent, the term *coefficient of pollution* has also been introduced, which is a measure of pollution and harmfulness of industrial wastewaters and expresses how many times are the wastewaters in question more polluted and harmful than sewage waters.

For the common treatment of municipal and industrial wastewaters, the so-called *pollution coefficient*, Pc, is used in some countries (e.g. FRG), given by equation

$$Pc = Ek$$

where E is the equivalent number of inhabitants referred to the specific unit of product, raw material or worker (assuming an 8-hour working day), k — difficulty coefficient of treatment after mixing municipal and industrial wastewaters. The values of the pollution coefficient for some industrial branches are listed in Table 3.57.

The pollution coefficient is in fact the equivalent number of inhabitants modified to fit the treatment process.

Table 3.57. Pollution coefficient *Pc* for some production branches

Production branch	Specific unit of raw material or product	Pollution coefficient (*Pc*) per specific unit
Meat plants with slaughter	A big piece	200
Diary and cheese plants	100 kg of cheese	100
Fish utilization plants	100 kg of fish	50
Vegetable and fruit utilization plants	100 kg of products	50
Edible fat plants	100 kg of product	50
Sugar factories	100 kg of sugar beet	70
Breweries without malt plants	100 l of beer	100
Malt plants	100 kg of cereals	10
Distilleries	100 kg of cereals	200
Distilleries	100 kg of potatoes	150
Yeast plants, distilleries	100 l of molasses	600
Starch factories	100 kg of cereals	50
Tanneries	100 kg of skin	500
Wool scouring mills	100 kg of wool	300
Sulphite cellulose production	100 kg of pulp	500
Paper making	100 kg of goods	20
Coal washers	ton of coal	100
Production of rayon	100 kg of goods	70
Production of soap	100 kg of soap	100

3.9.2.1 Classification of industrial wastewaters

Industrial wastewaters can be classified from different viewpoints, e.g. according to the origin, composition, suitability of biological or other type of treatment, potential for causing damage, etc.

According to their quality, the wastewaters from industrial works can be divided as follows:

— sewage and rainfall,
— cooling, and
— technological waters.

Technological waters can be further subdivided according to their quality into

— exceptionally harmful, which must be preliminary treated or specially disposed of,

- polluted mostly by biologically easily degradable organic substances with the possibility of biological treatment,
- polluted mostly with inorganic or organic substances which are resistant to biological decomposition, with possibility of chemical treatment,
- relatively safe.

From the viewpoint of the prevailing group of pollutants industrial wastewaters are usually subdivided as follows:

- prevailing inorganic pollution (mine waters, waters from coal and ore processing),
- prevailing organic pollution (wastewaters from foodstuff industry),
- combined types (wastewaters from the production of sulphite pulp, synthetic resins, wastewaters from refineries of mineral oils, leather works) [30–31].

The most frequently occurring wastewaters in practice are combined types and pollution by both organic and inorganic matters is equally important. Apart from these two predominating groups of substances it is also necessary to evaluate the presence of different harmful agents (e.g. toxic substances, tensides, oils) which can influence the overall character of wastewater by their effect, or can have negative effects on the treatment processes.

In wastewaters with predominating inorganic pollution the contaminating substances can be either in dissolved or suspended forms. The dissolved solids can be *non-toxic* with the most frequent occurrence of sodium, potassium, calcium, chloride, sulphate ions, etc.; or *toxic*, for example, ions of heavy metals, cyanides, radioactive substances, etc. [32–35].

Due to the development of new industrial branches producing great amounts of different organic substances, and due to the genral "chemization" of industrial and agricultural production and the modern way of life, many new kinds of substances are introduced into wastewaters, and quite often their properties are unknown, particularly with regard to their biological degradability and behaviour in the biochemical processes of their mineralization.

Such compounds which do not undergo biological degradation in either aerobic or anaerobic conditions, and toxic substances particularly disturb the natural recycling. From the viewpoint of a water system they deteriorate the quality of polluted water resources and affect their use as drinking and service waters. Even after treatment of such polluted waters, these compounds may be introduced in their original or partially chemically or biochemically changed form into drinking water and can have serious impacts on health. Based on the determination of biological degradability and toxicity of new chemical compounds it is possible to predict their behaviour in both the natural environment and biological wastewater treatment plants, in self-purification processes either in water or in soil.

The partial degradation of organic compounds is not sufficient. To guarantee that the natural environment will not be exposed to the residues of these substances and that the biological balance will be maintained in nature requires thorough biological degradation of these new organic compounds [36–37].

In wastewaters with prevailing organic pollutants, these compounds can be subdivided from *the viewpoint of biological degradability and toxicity* as follows:

(1) *Non-toxic and biologically degradable substances*, for example, saccharides, amino acids, aliphatic acids, proteins, etc., which are all non-detrimental compounds. These substances are present most frequently in wastewaters from the foodstuff industry (sugar production, starch factories, dairies, etc.).

(2) *Toxic substances but biologically degradable*, for example, phenols, organophosphorous pesticides, linear sulphophenylalkanes, etc. This group includes phenolic wastewaters, and wastewaters from the production of synthetic resins, etc. Following the decrease in the concentration of these otherwise toxic substances below the limit value their biological degradation takes place and thus they are eliminated from the environment (and from recipients).

(3) *Non-toxic substances, but biologically difficult-to-degrade*, for example, lignin sulphonanes, polyethylene glycols, etc. Wastewaters with substances of this character are formed, for example, in the production of sodium cyclamate. The compounds of this group are not toxic, but due to their slow biological degradation they are accumulated in the environment. Their long-term effects at higher concentrations can represent a serious danger for living organisms.

(4) *Toxic substances and biologically difficult-to-degrade substances*, for example, chlorinated hydrocarbons, nitroanilines, some tensides, and others. These substances are present in wastewaters from the production plants of chlorinated pesticides and other chlorinated hydrocarbons. Because they are the most dangerous substances they should in no event be introduced into the environment. Their production and use should be limited as far as is possible, better still they should be completely avoided.

The quality of wastewaters is given by the character of substances present in them, the degree of their pollution is given by the concentration of particular substances occurring in them. The substances in industrial wastewaters can be subdivided into the following groups from the viewpoint of their physical form:

— suspended solids which include solid particles of different size (e.g. sand, clay, parts of animal bodies, fibres, etc.),
— colloids,
— dissolved solids providing true solutions with water,
— substances which form a continuous layer on the water surface (e.g. fats, oils, crude oil and related substances).

Industrial wastewaters are often mineralized to a high degree due to the high concentration of chlorides, sulphates and other salts — sodium, potassium or calcium ones, the concentration of which can be as much as tens of g l^{-1}. Concentrations of ions (e.g. Na^+, Cl^-, SO_4^{2-}) higher than 10 g l^{-1} can negatively influence biological treatment processes of these waters. Such salts are introduced into wastewaters particularly from neutralization and salting out of different products, or from neutralization of acid or alkaline wastewaters.

The content of the most important ions in these wastewaters considerably differs from those of natural waters. The most frequently occurring cation is Na^+ rather than Ca^{2+} which occurs in high amounts in natural waters, and of anions it is Cl^- followed by SO_4^{2-}, instead of HCO_3^-. Alkalinity of these waters is caused by OH^- or CO_3^{2-} ions; the HCO_3^- ion is absent in more concentrated acid or alkaline waters.

An important property of industrial wastewaters is their acidity or alkalinity expressed in terms of pH value. In addition to the determination of pH or neutralization capacities (acid and alkaline, respectively), it is necessary to determine whether the resulting pH is caused by organic or inorganic compounds. Only then is it possible to decide if preliminary neutralization should be included prior to biological treatment.

Biologically-easily-degradable organic acids or alkalies are eliminated during biological treatment and their acidity or alkalinity therefore have no effect when such waters are discharged into the recipient.

From the viewpoint of their effects of organic pollution in wastewaters and total impact on the recipient the amounts of nitrogen and phosphorus are important, as their presence is essential for biological treatment, and moreover they must be present in such forms which are utilizable by microorganisms for the production of new biomass. If they are lacking, it is necessary to add them prior to the biological treatment.

Recently, the determination of nitrogen and especially of phosphorus has become particularly important because of their ever increasing amounts in natural waters. An excessive content of these important biogenous elements particularly in stagnant surface waters (lakes, reservoirs) results in a serious problem — *eutrophization of waters* [38, 39].

3.9.2.2 Assessment of organic pollution

Similarly to sewage waters, also in industrial wastewaters the determination of COD by means of potassium dichromate in sulphuric acid is used for the evaluation of total organic pollution. With regard to the high content of chlorides in industrial wastewaters, it is necessary to pay attention to the correctness of its determination and appropriate methods for its elimination.

The determination of biochemical oxygen demand (BOD_5) together with other determinations, e.g. COD, is used for the assessment of the contribution of biologically degradable organic compounds to the overall organic pollution. It is necessary to take into consideration the high content of organic pollutants in wastewaters which must therefore be diluted, as well as the fact that the quality of harmful or toxic substances may influence the adaptation and quantity of microorganisms and thus also correctness of the determination.

The BOD_5 value and other parameters characterizing wastewaters are important also for assessment of the possibilities of biological wastewater treatment. Wastewaters from inorganic based industry (e.g. from the production plants of industrial fertilizers, production of soda, from glass and ceramic industries) whose BOD_5 values are lower than 50 mg l^{-1} cannot be biologically treated [40–42].

Biological treatment is not recommended for wastewaters with BOD_5 ranging from 50 to 100 mg l^{-1} because insufficient quantity of biomass is formed from the organic substances present. However, these wastewaters can be treated when mixed with wastewaters from urban units.

Concentrated wastewaters with high BOD_5 values (of the order of units of g l^{-1}, e.g. from the production of synthetic resins, extraction of caprolactam, sulphite waste liquors) must be sufficiently diluted before biological treatment.

If BOD_5 is properly determined, data on the relative proportions of biologically degradable substances can be obtained from the ratio of BOD_5: COD. If this ratio is higher than 0.5 then the wastewater in question contains mostly biologically degradable organic substances. These are, for example, wastewaters from starch factories (0.57), yeast plants (0.64) and sugar factories (0.70).

If an industrial wastewater has a constant composition it is possible to assess the BOD_5 value from COD and vice versa.

Wastewaters containing organic substances which undergo fast biological degradation are called digested waters. They are entirely mineralized within quite a short time interval when properly diluted and under aerobic conditions.

In the case of excessive pollution oxygen is often completely consumed due to its rapid uptake and aerobic processes are changed into anaerobic ones with all the resulting negative phenomena. In anaerobic processes hydrogen sulphide with its typical odour is formed from proteins. In the presence of iron, iron monosulphide is produced causing a dark to black colour of wastewater and sludge, especially a digested one.

On the curve of biochemical oxygen demand often the so-called *lag-phase* occurs which is related to the time interval required for adaptation and reproduction of microorganisms able to decompose certain specific pollution species present in these waters. If these wastewaters are discharged into the recipient the self-purification process can be slowed-down, just on account of this property [43, 44].

As organic pollution predominates in the total pollution of many industrial waters, the BOD_5 value is also essential parameter in the technology of industrial wastewater treatment; on this value the calculation of treatment technology is based.

3.9.3 Rain wastewaters

Until recently atmospheric precipitation which runs off via the sewage system was considered quite clean and only its positive function of dilution of other wastewaters in the sewer system was evaluated.

However, in localities with intensive industrial and agricultural production rain waters are contaminated when falling through the polluted atmosphere, and by washing away surface matters and by whirling of sediments in sewers they are enriched by other impurities.

These processes can result in the removal of a quantity of pollution through the common sewer system from housing estates via discharge chambers into the recipient (expressed in the terms of BOD_5) which equals the residual pollution in the run-off from a mechanical-biological wastewater treatment plant. Because the character of precipitation is discontinuous and varies with time, the immediate effect on the recipient is less favourable. In the case of more intensive rainfalls, within a short-time interval the loading of the recipient can be 50 to 100 times higher than that in dry periods.

Therefore, rain waters introduced into the sewer system should be considered as wastewaters.

The quantity of rain wastewaters leaving via the common sewer system which is used most frequently in most western countries, is the result of hydrological, meteorological, geographic, landscape and other circumstances of the locality in question, as well as other factors (e.g. character of surface, methods of cleaning of public areas, character and gradient of sewers, etc.), and also the ratio of dilution in discharge chambers.

Since it is a mixture of precipitation and municipal wastewaters, *the quality of rain wastewaters considerably varies* and depends on many factors. For example, the duration of a rain-free period during which pollution is accumulated on the surface of a gathering ground, as well as sedimentation of suspended solids in sewers with insufficient gradient are important factors. If has been suggested that for removal of pollution from a gathering ground and washing of sewers, a rainfall with minimum capacity of 3–10 l s^{-1} ha^{-1} is required.

Rain wastewaters are contaminated primarily by microorganisms, suspended solids, components of municipal wastewaters and whirled sediments of sewers. Recently, pollution by crude oil substances, heavy metals and other toxic substances has increased as a consequence of increasing pollution of the natural environment [45, 46].

The quality of rain wastewaters is usually expressed by means of *the curve of pollution* (Fig. 3.43) which illustrates the time course of a given pollutant in given studied sewer system profile.

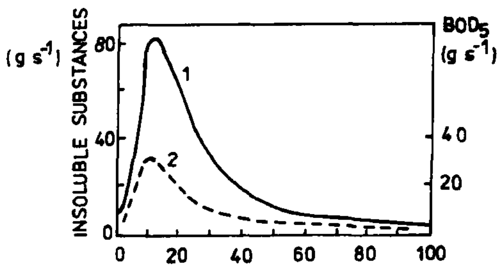

Fig. 3.43. Curves of rain wastewater pollution. 1 — insoluble matters, 2 — BOD$_5$

When evaluating the effect of rain wastewaters on the recipient *the curve of loading by pollutants* (Fig. 3.44) is recommended, which expresses the time dependence of the mass flow rate of the pollutant, where the mass flow rate is a product of the pollutant concentration and wastewater flow rate.

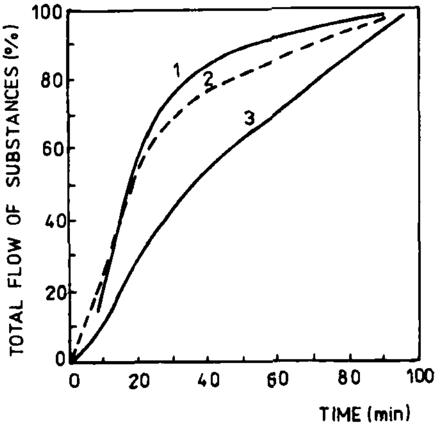

Fig. 3.44. A curve of loading with rain wastewater pollutants. 1 — insoluble matters, 2 — BOD_5, 3 — run-off

3.9.4 Agricultural wastewaters

It has been assessed that agriculture contributes 40–60% to the total water pollution and this contribution is ever increasing. Wastewaters in agriculture are in fact less important from the viewpoint of the pollution produced. More important are organic wastes from industry which are introduced into surface and groundwaters by washing or uncontrollable leaks [47, 48]. The main sources of agricultural pollution threatening water quality can be classified according to their origin into the following groups:

(1) *Sources from plant production*

— washings from fields due to water erosion,
— industrial fertilizers in their application to soil and handling,
— biocidal substances in their application to soil and washing of the equipment for their application,
— drainage waters and extracts during excessive doses of irrigation water,
— wastes from plant products.

(2) *Sources from animal husbandry*

— leakage of liquid manure from large-scale breeding of cattle and pigs,
— leakage from natural fertilizers and composts in their application and handling,
— silage liquids,
— washings from runs and pastures,
— aquatic fowl breeds,
— wastes from large-scale fowl breeding.

(3) *Other sources*

— leakages of fuel, lubricating and heating oil substances,

— wastewaters from agricultural production complexes,
— water polluted during washing of agricultural machines.

Animal husbandry is the main source of organic wastes in agriculture. It covers particularly excrements of farm animals which are, partly uncontrollably introduced into waters directly at the site of origin, and partly after their application to the fields in the form of fertilizers used for plant production. It is supposed that about 10% of this organic waste is introduced into streams. In Czechoslovakia, for example, the total quantity of wastes from livestock is higher than the amount produced by humans.

Another source of pollution of animal origin is silage liquids produced during preservation of green fodder by silaging. About 5% of the produced quantity of silage liquids is introduced into the streams.

The expected increase in the total pollution of waters produced by animal husbandry is presented in Table 3.58.

Table 3.58. Expected increase of water pollution by wastes from animal production

Year	Number of LCU[a] (thousands)	*Waste components in thousands tons per year*			
		Dry matter	BOD_5	N	P
1970	2885	4259	1766	183.7	40.8
1985 min.	3120	6753	2797	291.0	63.9
max.	3500	7579	3155	331.5	73.2
2000 min.	3340	9563	3955	407.4	90.6
max.	4010	11,567	4816	499.1	111.7

[a] Large cattle unit (LCU) = 500 kg of live weight.

An important source of pollution in the field of plant production is pollution resulting from chemization of agriculture. In the case of unfavourable meteorological conditions (e.g. excessive precipitation) after application of chemical agents to agricultural land, this pollution can even cause emergency situations for water resources in the given locality [49–51].

The quantities of nutrients eluted annually from soil to which 325 kg of pure NPK nutrients per hectare were applied are listed in Table 3.59.

Table 3.59. Average quantity of naturally washed-out nutrients (kg ha^{-1})

Elements	Quantity	Elements	Quantity
Calcium	26.4	Nitrogen NO_3^-/NH_4^+	8.0/0.3
Potassium	4.0	Sulphur	1.5
Magnesium	3.2	Phosphorus	0.02
Sodium	2.2	Chlorine	20.2

3.9.4.1 Composition and properties of animal excrements

Excrements in the form of urine and faeces are unavoidable components of animal husbandry. In the past the sources of this type of pollution were dispersed and did not seriously threaten the quality of surface or groundwaters.

Intensification of animal husbandry has resulted in construction and development of large-scale breeding units particularly of black cattle, pigs and poultry, producing amounts of wastes that often represent very serious problems without a foreseeable solution. The danger caused by these waters also results from changed technology in large-scale breeding.

The daily production of excrements (faeces and urine) in the breeding of black cattle and pigs, per 1000 kg of live weight, is presented in Table 3.60.

Table 3.60. Daily production of wastes in black cattle and pig breeding farms (calculated per 1000 kg of live weight)

Index	Unit	Black cattle	Pigs
Waste	kg	75	65
Dry matter	kg	7.5	8.5
BOD_5	kg	1.8	2.5
Nitrogen	gN	380	530
Phosphorus	gP	67	170
Potassium	gK	400	200

It has been reported in the literature that pollution from 1 pig equals pollution from 3.8 humans, and that from 1 black cattle corresponds to 32.5 humans, from a calf it corresponds to 4.2 humans [52, 53].

By chemical analysis of excrements, specific constituents are determined. Primarily nitrogen and mineral substances are determined, which are important from the viewpoint of metabolism and nutrition of livestock, as well as from the viewpoint of the content of nutrients important for the use of excrements as fertilizer.

A survey of three groups of substances present in excrements are shown in Table 3.61.

Urine is an aqueous solution of inorganic and organic compounds including mineral substances, nitrogen compounds from protein metabolism, as well as of non-protein nitrogen compounds, vitamins, hormones and enzymes.

Table 3.61. Participation of water, organic and inorganic substances in the excrements of domestic animals (%)

Species	Water content	Organic substances	Inorganic substances
Black cattle	80–88	10–16	4
Pigs	65–85	10–20	10
Sheep, goat	65–75	20–30	10
Hen	75–80	10–15	10

The quantity and composition of urine depends on stabling, nutrition, intake of water (in the form of drinking water and water for fodder) and other factors.

The BOD_5 value for undiluted urine from black cattle is 15–18 g l^{-1} and that for faeces is about 18.6 g l^{-1}. These values for urine from pigs range from 6 to 11 g l^{-1}. The BOD_5 value decreases during storage.

In comparison with sewage water, the BOD_5 of urine is 50 times higher. Therefore, even small amounts of this waste cause serious changes in the oxygen balance of a stream, or considerably influences the course of the waste treatment processes.

Urine typically has a particularly high content of ammonia nitrogen which is present in weakly alkaline media in the form of non-dissociated hydrate of ammonia with very toxic effects on fish.

The content of nutrients in faeces and urine of black cattle (dairy cows) and pigs is listed in Table 3.62.

Table 3.62. Content of nutrients in faeces and urine of black cattle and pigs (%)

Elements	Dairy cow		Pig	
	Faeces	Urine	Faeces	Urine
N	0.35	0.61	0.54	1.16
P	0.12	0.00	0.59	0.08
K	0.06	1.08	—	—
Ca	0.50	0.50	0.82	0.01
Mg	0.09	0.09	0.13	0.01

The table shows that the amounts of nutrients in the faeces of corn-fed pigs is sometimes much higher than that in the faeces of black cattle. This concerns particularly calcium, phosphorus and nitrogen.

The change to the litterless housing of livestock has resulted particularly in the fact that instead of the traditional production of two types of wastes

— manure and urine — only one product is produced in large-scale animal husbandry — liquid manure. This change is reflected in the composition of natural manure which called for a change in the mode and organization of fertilization.

Liquid manure of black cattle and pigs is a mixture of solid faeces and urine with a certain unavoidable portion of technological water. The contribution of technological water, which should not be higher than 20% of the total quantity of liquid manure has the greatest effect on the quality, physical and chemical properties of the liquid manure.

The higher the quantity of technological water, the higher the volume of liquid manure, and hence its fluidity; concentrations of nutrients and organic substances decrease and the tendency for the separation of liquid manure into three layers increases. These changes have unfavourable impacts on higher investment costs for storage reservoirs, and operational expenses are increasing due to the decrease of the total efficiency of fertilization.

Quantities and composition of liquid manure in the large-scale breeding farms of black cattle and pigs are presented in Tables 3.63 and 3.64.

Table 3.63. Quantity and composition of liquid manuring in large-scale breeding farms of black cattle (500 pc)

Type of	Dung-water quantity		Nutrients quantity $(kg\ yr^{-1})$			
	$(l\ d^{-1}pc^{-1})$	(m^3yr^{-1})	N	P	K	Total
Young cattle	22	4,015	18,469	6,022	10,439	34,930
Fattening cattle	65	11,863	54,569	17,794	30,843	103,208
Dairy cows	55	10,038	46,174	15,057	26,098	87,331

Table 3.64. Quantity and composition of liquid manuring pig large-scale breeding farms

Capacity of farm	Dung-water quantity		Nutrients quantity $(kg\ yr^{-1})$			
	$(l\ d^{-1}pc^{-1})$	(m^3yr^{-1})	N	P	K	total
5,000 pc	7.5	13,688	54,490	6,844	20,532	84,866
10,000 pc	7.5	27,375	114,975	13,688	41,063	169,725
25,555 pc	7.5	68,438	287,440	34,219	102,657	424,316

Liquid manure of black cattle and pigs contains nutrients that are readily taken up by plants. This concerns all of the most important nutrients —

nitrogen, phosphorus and potassium. Also the contents of magnesium, sodium and trace elements (B, Cu, Zn, Mn, Mo, Co) are significant. The pH value (7.0–7.7) is also favourable and thus, no acidification of soil during fertilization takes place [54].

However, the easy availability of nutrients for plants can cause considerable losses, particularly in the case of improper application, and in the case of limited storage capacities, also when applied under unsuitable climatic conditions.

Based on long-term observations it has been found that from an average annual dose of nitrogen — 1000 kg ha^{-1} — applied in the form of liquid manure to sandy soil, 150 kg of N were utilized by plants, 50 kg of N enriched the soil, 100 kg of N were removed by water and 700 kg of N escaped into the air.

In this way particularly nirogen, phosphorus and microbial pollution are introduced into waters with all the consequent negative impacts on the water quality limiting its further use.

3.9.4.2 Silage liquids

If silage liquids leak into surface and groundwaters they are considered to be an aggressive and toxic agricultural waste produced during preservation of green fodder by fermentation — particularly by anaerobic lactic fermentation (silaging). The substances formed protect the preserved fodder against undesirable putrefaction.

Processing, utilization or disposal have not yet been satisfactorily solved. With regard to the increasing amounts of this waste, silage liquids have become a serious problem not only for agriculturists, but also in the domain of water management and hygiene, as their leakage into streams causes serious damage, including fish mortality.

Silage liquids are dark brown to black in colour, intensively turbid and bad smelling. The organic substances include mainly aliphatic acids (butyric, acetic and lactic), as well as different saccharides (glucose, galactose, fructose, etc.). In the case of inorganic compounds, iron, manganese and ammonia nitrogen are important since they significantly participate in the total harmfulness of this type of agricultural waste [20, 48].

The amount of silage liquids occurring during the process of silaging varies and depends on many factors. The higher the dry matter content in the preserved green mass of plants, the lower the production of silage liquids, and vice versa. Green fodders contain about 75–90% of water. Within a correctly applied technology of silaging, the silage liquids remain in silage pits and are fed together with the silage fodder. From leaking silage pits, however, the silage liquids can penetrate the surface and groundwaters, thus seriously threatening their quality.

In the case of wet silages (e.g. beet crowns) the amount of silage liquids is as much as 40% of the total silaged weight; in most of cases of silaging other types of fodders this quantity amounts to 15–20%, in haylage the silage liquids are practically negligible.

Chemical analysis shows that the dry residue of silage liquids ranges from 3 to 9%. Organic matter in the dry residue ranges from 85 to 90%, the ash content makes 10–15% of dry residue.

Silage liquids, except the liquids from clover silage, contain rather a low amount of nitrogen (0.03–0.28%) and about half of this is in the ammonia form. From the aspects of nutrients the potassium content is also significant (0.10–0.37%) whereas the quantities of other nutrients (P, Ca, Mg) are very low. Silage liquids, however, have unfavourable effects particularly on stagnant surface waters (eutrophization).

Silage liquids are noted for quite high acidity, the pH value ranging from 4.2 to 4.9. The concentration of organic acids which degrade in streams and wastewater treatment plants quite quickly, ranges from 7 to 12 g l^{-1}. Therefore it is necessary to apply lime to soil when these acids are used as fertilizers.

In comparison with sewage waters the silage liquids have a very high concentration of mostly easily-degradable organic substances and therefore high oxygen demand is recorded in their aerobic microbial degradation. One liter of leaking silage liquid corresponds to about 250 l of sewage wastewater as concerns the degree of pollution.

Biochemical oxygen demand (BOD_5) of silage liquids ranges from 50 to 80 g l^{-1} and chemical oxygen demand (COD) is 30–110 g l^{-1}. From these BOD_5 values, the pollution with silage liquids produced during silaging of 1 ton of beet crowns corresponds to 15–24 kg BOD_5 or a value of 280–445 of population equivalents. In the case of uneven run-off of this waste the corresponding values are higher.

The characteristic properties of silage liquid produced during silaging of beet leaves are presented in Table 3.65.

3.9.4.3 Sources of water pollution from plant production

This group of pollution sources includes — in addition to washings from fields due to water erosion and drainage waters — particularly those which

Table 3.65. Characteristic properties of silage liquid from silage of beet leaves

Properties, composition	Unit	Value
Sedimenting substances	mg l^{-1}	0
Total suspended substances	mg l^{-1}	165–416
pH	—	3.6–4.60
Electrolytic conductivity	mS m^{-1}	16,500–17,300
Chlorides Cl^-	mg l^{-1}	3,400–7,000
Sulphates SO_4^{2-}	mg l^{-1}	590
COD(Mn)	mg l^{-1}	61,800–109,800
BOD_5	mg l^{-1}	49,000–73,800
Organic acids	mg l^{-1}	10,000
Total nitrogen (N-total)	mg l^{-1}	1770–2130
Total phosphorus (P-total)	mg l^{-1}	1440–1500
Potassium K	mg l^{-1}	3652–3880

are related to chemism of agricultural production — industrial fertilizers and chemical plant protection agents.

From the viewpoint of water management the application of high doses of industrial fertilizers as one of the important intensifying factors in plant production for the increase of acreage yields is unfavourably manifested in the increasing rate of surface and groundwater pollution. Non-industrial pollution of water resources in developed countries amounts already to about 60% and the contribution of industrial fertilizers is significant.

When using water resources for a public supply of drinking water, the greatest danger lies in an *emergency excess of nitrates.* In many basins the content of nitrates has doubled within the last 20–25 years. If this development of pollution with nitrates continues there is a possibility of deterioration of all sources of drinking waters within several decades.

A similar development of pollution has also been observed in the case of other biogenous elements. *Phosphorus* in surface waters which originate from the run-off from agricultural lands to which phosphorus fertilizers have been applied stimulates considerably the eutrophization of waters, contributing thus to secondary, even more serious deterioration of the drinking water sources.

The problem of losses of *potassium* or *magnesium* is largely an economic problem and together with other elements it does not pose a serious threat to the water quality in water resources from the hygienic viewpoint. The values presented in Table 3.59 yield information on the contribution of biogenous elements to water contamination which can be expected due to the infiltration of nutrients from industrial fertilizers.

The application of *chemical plant protection agents* has enabled an exceptional increase in the productivity of agriculture and yields in plant production by 15–20%, on the other hand, it has distrubed the biological equilibrium; it has unfavourable effects on the soil edaphon and the hydrosphere.

Particularly the substances with low biodegradability, due to which they accumulate in the environment, represent a serious danger and thus an increasing threat for man and animals. Therefore, application of some substances of this character has been forbidden in many countries (e.g. DDT). Figure 3.45 presents the time dependence of residual concentration of such pesticides.

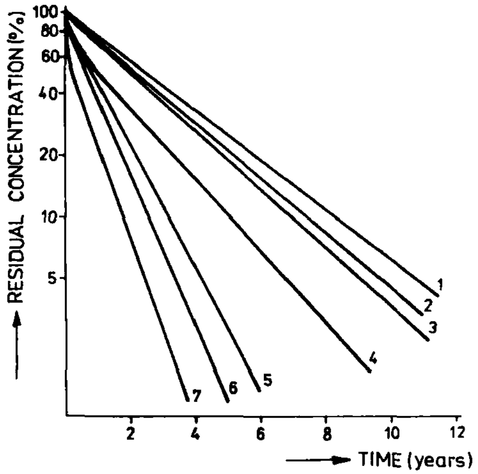

Fig. 3.45. Time dependence of residual concentration of some pesticides. 1 — DDT, 2 — dieldrin, 3 — endrin, 4 — lindane, 5 — chlordane, 6 — heptachlorine, 7 — aldrin

From the viewpoint of water management the use of pesticides is a serious danger particularly when these substances are introduced into precipitation, surface, ground-, drainage or wastewaters. The cases of water contamination are often due to the neglect of essential safety measures during their application, purification and decontamination of machines used for their application and transport, and aerial application, particularly in unsuitable periods.

Currently, there are no equivalent agents available to replace the used types of pesticides, i.e. agents with lower health risks. The solution of this serious problem could consist in the development of more biodegradable types of chemical protection agents, and particularly in the careful observation of all safety measures for the handling, application and removal of this source of pollution [55, 56].

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3.10 Physical, physico-chemical and chemical methods of treatment and purification

Processes and methods used in water technology can be divided into 2 basic groups.

The first group involves processes employed for water treatment as distinct from wastewater treatment. The term "water treatment" includes technological, mechanical, chemical and biological processes and procedures by means of which unsatisfactory physical, chemical and bacteriological properties of water are improved.

In the case of water treatment, this concerns particularly the processes of surface or groundwater treatment into drinking, service or industrial waters.

The selection of particular processes or their combinations depend on many factors, especially on the requirements for the quality of treated water and the original composition of the raw water, particularly from the viewpoint of this pollution [1–5].

For the treatment of raw water into drinking water the following processes are used: mechanical pre-treatment, sedimentation, filtration, clarification, removal of carbon dioxide, iron and manganese, adsorption on activated carbon and processes ensuring its suitability from the aspects of hygiene [6, 7].

In some types of groundwaters, the content of Ca and Mg must be reduced to the set value, and this is mostly performed by decarbonization (water softening). On the other hand, some surface waters require increased amounts of calcium and magnesium salts (water hardening).

When treating sea water or strongly mineralized groundwaters to produce drinking water, electrodialysis, reverse osmosis, evaporation or freezing out can be used.

When treating industrial waters, particularly feed waters for steam boilers, or cooling waters, especially the majority of dissolved inorganic substances, primarily calcium and magnesium salts should be removed by deionization or demineralization of the water.

The second group involves processes of wastewater treatment. Some processes of water treatment can also be employed for wastewater treatment, others are specific only for the technology of wastewater treatment [8–10].

Currently, *wastewater treatment* is the most important way of the surface water quality improvement. The main products resulting from wastewater treatment are purified wastewaters with certain residual pollution given by the efficiency of the treatment technology, together with sludge and gas. The technological treatment process is carried out in *wastewater treatment plants*, and it results in the disposal or utilization of the products formed.

Depending on the type of wastewaters, treatment plants for municipal, industrial, agricultural and other wastewaters are recognized. In a wastewater treatment plant two technological systems usually operate: a system for wastewater disposal and a system for sludge disposal.

Several processes take place in the given technological system, each of them having a certain technological purpose. These processes generally run in separate units; but several processes can occur in a particular unit.

The technological system of wastewater disposal (purification of wastewaters themselves) includes equipment for mechanical, biological, chemical and physico-chemical treatment [11–13]. *The sludge technology* involves equipment and systems appropriate for sludge disposal (see Section 3.11) [14–18].

The structure of technological wastewater treatment plants depends on both the quality and the quantity of wastewaters, as well as on the requirements for the after-treatment water quality.

Municipal wastewater treatment plants and the treatment plants for wastewater from some branches of the foodstuff industry have a fairy standardized structure.

However, on account of the wide range of industrial and agricultural wastewaters it is impossible to design universal technological lines for these types of wastewaters.

Currently, *mechanical and biological wastewater treatment* with anaerobic stabilization of sludge is used most frequently, with various modifications of the last stages of sludge disposal.

After-treatment of biologically treated waters is required when further treatment processes have to be used in cases where the mechanical and biological treatment is insufficiently effective. If these further treatment processes follow mechanical and biological treatment, one refers to the *"third stage" of treatment* [19–22].

Industrial wastewaters are noted for a considerable time variability in both quality and quantity. Therefore, standardization of the quantity and the quality is the essential precondition of optimization of the whole treatment process, and this must include coping with emergency situations and must provide a constant treatment effect. Because of this, equalization basins with a sufficient time interval of dwell are situated at the beginning of the technological line.

A technological line of wastewater treatment plants involves some of the following processes or their combinations: quantity and quality equalization, straining, sedimentation, flotation, physico-chemical and chemical treatment, natural biological treatment, activation, biofiltration, aftertreatment of biologically treated wastewaters and disinfection [23–27].

The aim of selection of appropriate processes is to achieve the required water quality by employing a technically, economically and operationally simple technological line involving the minimum introduction of other substances into the treated water.

During a treatment process pollutants of either organic or inorganic origin are to be removed, or both together.

The process for removal of organic pollutants depends on the biological degradability of the organic matters — i.e. on whether they are easily degradable, or not. To remove biologically difficult-to-degrade *organic matters* or toxic substances, chemical or physico-chemical methods need to be used because the biological processes are not efficient. In the chemical processes, oxidation and incineration are the most important; in the case of physico-chemical processes, adsorption precipitation, adsorption, extraction, flotation and degasification need to be considered [28–31].

For removal of toxic *inorganic substances* precipitation, oxidation, reduction, ion exchange, adsorption and other procedures are used [32, 33].

If excessive amounts of dissolved inorganic substances are to be removed, electrodialysis, reverse osmosis, freezing out and ion exchange are the recommended procedures.

To remove biologically easily degradable substances, *aerobic biological processes* in particular are used (biological filters and activation). In the first stage, *anaerobic methods* are used for removal of organic pollutants present in wastewaters at very high concentrations. These processes are also applied in mineralization (stabilization) of sludge from wastewater treatment plants. The biological methods of wastewater treatment plants will be discussed in more detail in a separate section [34–39].

3.10.1 Physical and physico-chemical processes

3.10.1.1 Equalizing of quantity and quality

In spite of the fact that quantity and quality equalizing is not a treatment process, the *equalizing tanks* frequently constitute an important part of the technological process.

For the *quantity equalization* of wastewaters, tanks with constant discharge are available; the *quality equalization* takes place in so-called levelling tanks which may be either stirred (pneumatically or mechanically), or through-flow (Fig. 3.46).

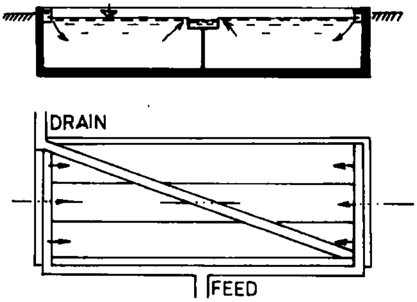

Fig. 3.46. Through-flow levelling tank

Equalization of physical and chemical properties of surface waters (e.g. temperature, content of suspended solids, chemical composition) before the main treatment is carried out on chemical composition is performed in retention resevoirs [40, 41].

3.10.1.2 Straining and microstraining

Straining is the simplest separation procedure for suspended substances, these being trapped by rakes or screens with smaller mesh dimensions than those of the separated material. This process is usually used for removal of the large-size floating impurities.

Straining as the only stage is used in such cases where the requirements for water quality are not too high (industrial water, water for irrigation in agriculture, etc.). However, most frequently it is the first stage preceding subsequent stages of both treatment and purification of wastewater.

Floating impurities trapped by rakes or screens are generally strained mechanically. They are disposed of by composting, dumping, incineration, pressing, etc. Mechanically wipped-off rakes are shown in Fig. 3.47.

Microstraining is a type of mechanical separation in the course of which suspended matter is trappped on the surface and inside a thin netting with smaller meshes than the trapped particles (10–20 μm).

The system operates as a rotary drum screen with continuous washing to prevent clogging of the meshes (Fig. 3.48). Such systems are part of a technological line as a substitute for sedimentation; in the case of wastewater purification they can replace flotation equipment. The efficiency of separation carried out in this way is about 60%.

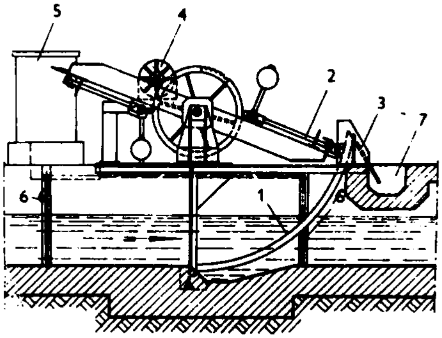

Fig. 3.47. Mechanically wipped-off rakes. 1 — rakes, 2 — wipping equipment, 3 — separator of scraped material, 4 — gears, 5 — control room, 6 — sensors for measuring the level height, 7 — reservoir for scraped material

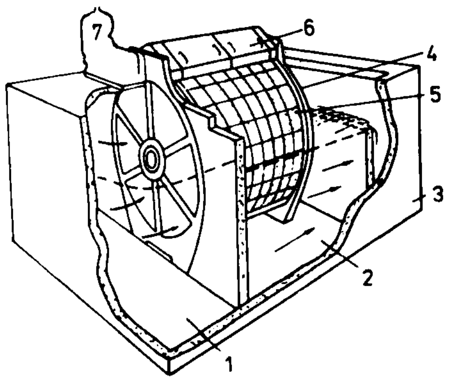

Fig. 3.48. A microfilter scheme. 1 — inlet space, 2 — space of filtered water, 3 — steel vessel, 4 — revolving drum, 5 — a sieve of stainless steel, 6 — space for nozzles with pressure water, 7 — motor

3.10.1.3 Sedimentation

Sedimentation is one of the most wide-spread separation procedure in both water treatment technology and the wastewater treatment. Separation of suspended particles is based on gravity.

Depending on the character of particles, separation of either grained or floccular suspensions is to be considered. In the case of suspension concentration simple sedimentation, discontinuous sedimentation or concentration should be distinguished.

The structures for separation of substances by sedimentation — gravel and sand traps, sedimentation and slot tanks — are simple to construct and undemanding in their operation.

The gravel and sand traps are used especially in wastewater treatment plants for trapping the mineral proportion of suspended particles with a higher specific weight. They protect other parts of the technological line (such as pumps) against mechanical damage and secure its trouble-free operation. They are not used so frequently for water treatment, except when treating water from surface flows — rivers and brooks.

According to the flow direction, horizontal and vertical sand traps are used, as well as sand traps with transversal circulation. The simplest type is a chamber sand trap (Fig. 3.49).

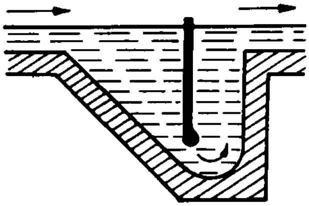

Fig. 3.49. Chamber sand trap

Depending on the quality of suspended material and on their location in the technological line, *settlers* can be classified into primary and secondary types.

The *primary settlers* are installed at the beginning of the technological line, usually after the rough pre-treatment, or after coagulation.

The *secondary settlers* are situated after the biological treatment and serve for sludge separation, particularly after activation. In the case of after-treatment of biologically treated waters further settlers can be used. The primary and secondary settlers have the same structure.

The most frequently used settlers are classified according to the flow direction into horizontal, radial and vertical types. In the treatment and purification wastewater plants with a higher capacity, only continuous operation settlers are used. Figure 3.50 illustrates a vertical sedimentation tank with a sludge scraper.

When treating drinking water with chemical substances, highly efficient microfilters are used in the functioning of the primary settlers.

However, settlers are also used for separation of floccules formed during coagulation in the process of clarification. The most convenient method is to arrange a fast mixer, flocculation and settling tanks into one unit with a horizontal through-flow of water (Fig. 3.51) [42, 43, 46].

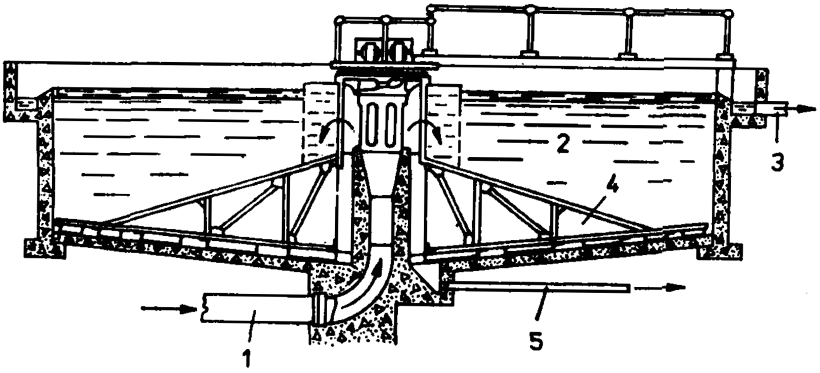

Fig. 3.50. Vertical sedimentation tank with a sludge scraper. 1 — supply of raw water, 2 — space for settling, 3 — water discharge, 4 — sludge scraper, 5 — sludge removal

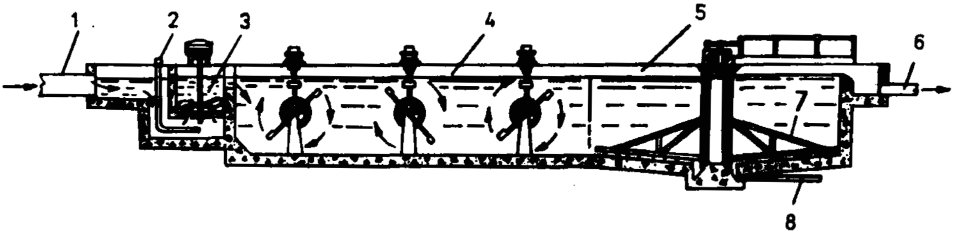

Fig. 3.51. Horizontal sedimentation tank for separation of sludge after water clarification. 1 — supply of raw water, 2 — dosing of chemicals, 3 — quick mixing, 4 — flocculation tank, 5 — sedimentation tank, 6 — clarified water system, 7 — sludge scraper, 8 — sludge removal

3.10.1.4 Filtration

Filtration is a process of separation of suspended particulate matters from water on the grain surface and in the pores between grains by the flow of water through a filtration layer. The filtration layer is porous, formed by granular material, or a filtration netting. Filtration is classified into *volume* (*depth*) and *flat* (*cake*) *filtration.*

Filtration is one of the most important stages for water treatment since, being frequently the last link in the technological process, it decides the quality of the treated water.

Filtration in wastewater treatment is used for removal of suspended organic matter (e.g. floccules of activated sludge) in biologically treated wastewaters, thus improving considerably the quality of the treated water.

From the hydraulic and technological viewpoints, *filters* are divided into *slow-* (*English*) and *high-rate filters*; the latter are subdivided into pressure or open filters.

For filtration, mostly quartz sand is used. In the case of high-rate filters, impurities are trapped in the gaps among the grains and the filtration layer gradually becomes clogged from the surface to the depth of the layer. When the filter capacity is exhausted it is necessary to stop the filtration and remove the sludge from the filtration layer by back-washing. Alternation of filtration and washing is a characteristic feature of the separation process. The separation processes in the case of slow filters are not equally efficient within the whole sand filtration layer; the most important part takes place in the surface layer, the so-called biological membrane. The mechanical effect of porosity is minimal. Therefore, regeneration of these filters is carried out merely by raking the top 3–5 cm sand layer, which is usually washed.

The finest suspended particles (e.g. sludge forming particles) and microorganisms are removed with high efficiency by precoat filters (e.g. candle-type).

In *slow-rate filtration* biological, physical and chemical purification processes take place in the sandy filtration layer and thus, top quality water with preserved biological values is obtained. Therefore, this process is used for the treatment of drinking water.

The main purifying factor is a 1.5–2 cm thick biological membrane formed on the surface of the filtration layer after a certain time of operation. Thus, the resulting purification effect in slow-rate filtration is a sum of the mechanical effect of the porosity of the filter beds and the activity of microorganisms. A cross-section of a slow-rate filter is shown in Fig. 3.52.

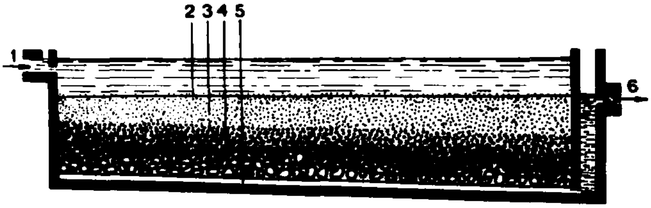

Fig. 3.52. A cross-section of a slow filter. 1 — supply of raw water, 2 — biological membrane, 3 — quartz sand, 4 — gravel, 5 — drain, 6 — run-off of filtered water

Currently, *high-rate filtration* is the most frequently used method for the surface water treatment. As opposed to the slow-rate filtration the layer of a filter bed consists of larger sand grains (diameter 0.5–2 mm) which allows a considerable increase in the rate of filtration.

When water flows through a high-rate filter, suspended particles are trapped in its entire volume. The high-rate filter is regenerated via expansion of the filter layer using a stream of wash water or a mixture of wash water and air.

Open high-rate filters are used particularly in drinking water treatment plants because of their high reliability. In water treatment practice, two types of filters are used most frequently — American and European. They differ particularly in grain size and height of the filter packing, as well as in the mode of regeneration.

In the industrial water treatment plants mostly *pressurized high-rate filters* are used since they are more economical. They are more efficient as they permit operation at a higher inlet pressure, and thus at high filtration rates. The use of pressurized high-rate filters in water plants depends on the general approach to water treatment technology, water source level, as well as the height of the treatment plant and consumer's site, energy availability and the treatment plant capacity. A cross-section of a typical closed high-rate filter is shown in Fig. 3.53 [44–46, 48].

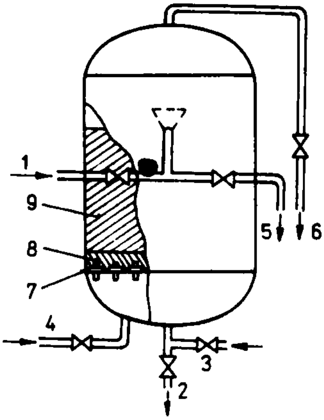

Fig. 3.53. A cross-section of a closed high-rate filter. 1 — inlet of filtered water, 2 — run-off of clean water, 3 — supply of washing water, 4 — supply of air, 5 — discharge of washing water, 6 — deaerator, 7 — filtration nozzles, 8 — support layer, 9 — filtration material

3.10.1.5 Flotation

Flotation is the physico-chemical process of separation of substances from water in which the substances accumulate on the water surface and thus they can be removed. In water technology, flotation is frequently connected with other processes, for example, oxidation, coagulation, and therefore, the substances appearing on the surface differ in their composition from those observed at the beginning of flotation.

In water technology, various modifications of classical flotation are used depending on the water quality, quantity and type of substances present in these waters, and the size and shape of particles, etc. Apart from the separation of suspended particles, flotation is more and more used for the condensation of activated sludge, particularly in wastewater treatment practice.

From the viewpoint of the process principles, flotation is classified into natural, bubbling (either with mechanical dispersion of air or with release of gases from the solution), biological, chemical, electro and ion flotation systems.

Natural flotation is applied in the primary settlers, oil and grease traps, various separators and other vessels through which wastewater with suspended material less dense than water flows at a slow rate.

Bubbling flotation is used particularly for the separation of oils and fats from wastewaters (Fig. 3.54).

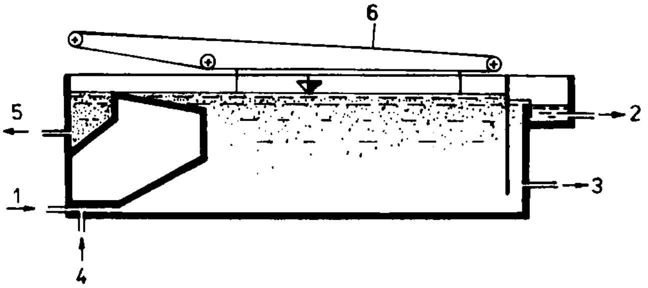

Fig. 3.54. Scheme of a longitudinal floating system for the separation of oils and fats. 1 — supply of wastewater, 2, 3 — run-off of clean water, 4 — supply of water with air, 5 — floated substances, 6 — scraper of floated foam

Pressure flotation is used especially for the treatment of industrial wastewaters from petrochemistry, pulp and paper mills, production plants of fibreboards, canning factories and other plants producing wastewaters with a high amount of substances whose density approaches the density of water. It is also used for sludge concentration [46].

3.10.1.6 Clarification

Clarification is a physico-chemical process used for removal of fine suspended particles and colloid substances causing especially turbidity and colouring the water.

Clarification is one of the most important physico-chemical processes in water technology. It is used for both water treatment and industrial wastewater treatment in the case where they contain toxic, biologically difficult-to-degrade substances, or substances which cannot be separated because of their size. In recent times it is also used for after-treatment of biologically treated wastewaters.

Chemical agents cause coagulation — agglomeration of dispersed particles into bigger units, when pollutants are incorporated into the formed floccules of ferric or aluminium hydroxide. The floccules are separated from water by mechanical methods, for example, sedimentation or filtration.

Coagulation takes place in two stages. In the first stage, so-called *perikinetic coagulation*, a coagulant is mixed with the water and is evenly dispersed in the whole volume of water. There are different types of high-rate mixers used for this purpose. The resulting chemical reactions are very fast and lead to the formation of microfloccules.

The next stage is the so-called *orthokinetic coagulation* taking place during slow mixing. This stage is essential for the formation of readily separable floccules having a size of 0.5–0.6 mm. The process of formation of large floccules from microfloccules is called *flocculation*. This process appears in a slight water turbulence which can be achieved in slow-rate mixers.

The most important chemicals for clarification are the *primary coagulants* able to induce coagulation. These are particularly iron trichloride ($FeCl_3.6H_2O$), aluminium sulphate ($Al_2(SO_4)_3.18H_2O$) and iron sulphate ($FeSO_4.7H_2O$). In water, these chemicals form corresponding flocculant hydroxides by gradual hydrolysis.

The effect of the primary coagulant can be increased by addition of so-called *auxiliary coagulation agents*. These substances are based on organic polymers (polyelectrolytes), activators of flocculation, mineral acids and alkalies adjusting pH to a value required for the hydrolysis leading to coagulation. The optimum dose of coagulation agents is determined experimentally by a coagulation test.

Depending on the pH at which clarification is carried out, acid, neutral and alkaline clarification processes are known.

For water clarification, systems with sludge sedimentation are used, as well as coagulation filtration and separation of suspended particles in a cloud of floccules.

Clarification with sludge sedimentation is used particularly in drinking water treatment plants. The water flow is horizontal; after rapid and slow mixing the solid phase is separated in the sedimentation tanks.

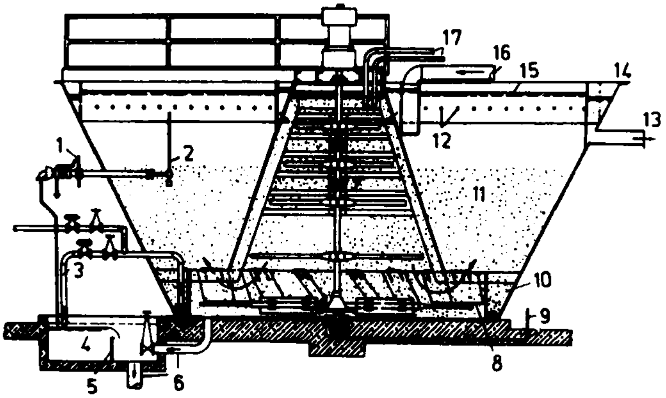

Fig. 3.55. A typical clarifier — precipitator type. 1 — indicator, 2 — sampler, 3 — automated sludge discharge, 4 — sludge tank, 5 — overflow, 6 — discharge valve, 7 — flocculation area, 8 — rectifying partitions, 9 — pressure water for bearing lubrication, 10 — sludge thickener, 11 — flake cloud, 12 — inlet openings, 13 — discharge of clean water, 14 — circumferential trough, 15 — water level, 16 — supply of raw water, 17 — dosing of chemicals

Coagulation filtration is recommended for the treatment of raw water with a relatively low content of suspended particulate matter. The coagulant supply is connected to the piping in front of the filter water inlet. The perikinetic stage of coagulation takes place in the piping and in the upper part of the filter; the orthokinetic stages take place in the filtration bed where floccules of hydroxide are trapped.

In clarifiers based on *separation of suspended particulates by the cloud of floccules*, the combined effect of sedimentation and filtration through a fluid layer formed by hydroxide floccules is utilized. Suspended solids are removed from such water in the form of sludge, either from the space occupied by the cloud of floccules, or from the clarifier bottom. The water flow in such a clarifier is vertical. Several processes take place in the clarifier at the same time: formation of suspensions by coagulation, trapping of suspension in the cloud of floccules, separation of floccules from clarified water, condensation and removal of the excess of floccules. Figure 3.55 illustrates a scheme of a clarifier with imperfect flotation. Flotation of the cloud of floccules is mechanical.

In the case of clarifiers with intensive sludge circulation an accelerator is most widely used (Fig. 3.56) [47, 48, 59].

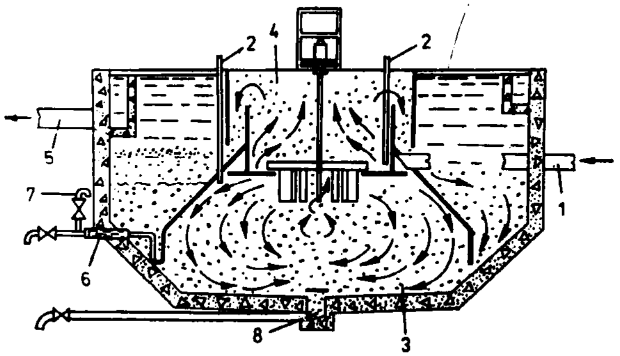

Fig. 3.56. A scheme of a clarifier with intensive sludge circulation. 1 — inlet of raw water, 2 — dosing of chemicals, 3 — first reaction space, 4 — second reaction space, 5 — discharge of cleared water, 6 — discharge of sludge, 7 — sampling, 8 — outlet hole

3.10.1.7 Ion exchange

Ion exchange in water technology is based on the capability of certain substances — ion exchangers — to exchange ions from their own molecules for the ions from solution. Different required effects for removal of undesirable components from water are achieved by particular cation or anion exchangers, or by their combination.

At present, ion exchangers are used mostly for special cases of water treatment, particularly of feed water for high pressure boilers in power plants. In treating wastewaters, ion exchangers are mostly used to separate toxic and radioactive substances.

In the majority of cases, the ion exchange is carried out in such a way that the solution (treated or wastewater) flows through a column packed with a granular ion exchanger (Fig. 3.57). A working cycle consists of four phases: (a) *In the sorption phase*, the proper exchange of ions takes places. (b) *Ion exchanger washing*, before regeneration, serves to loosen the ion exchanger layer and to wash out the trapped particles. (c) In the course of *regeneration*, elution of the trapped ions takes place and the ion exchanger is transformed into its original working form by recovering its exchangeability. (d) *Washing out of the column* with water removes the regeneration agent [49, 50].

For water deionization, a combination of an ion exchanger filter with a packing of a weak alkaline anion exchanger following the filter, with a cation exchanger in its H form in the system and equipped with a ventilation tower for CO_2 removal is recommended.

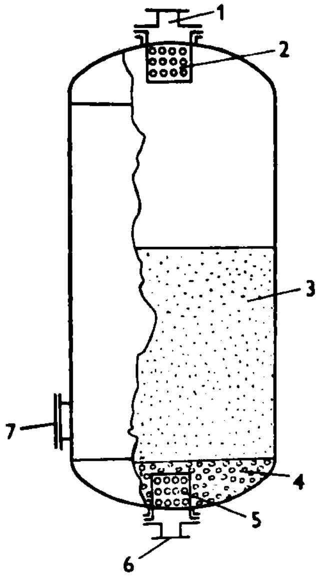

Fig. 3.57. A scheme of an ion exchanger filter. 1 — water supply, 2 — water distribution system, 3 — ionex packing, 4 — support layer, 5 — filtration bottom, 6 — discharge of treated water, 7 — handling hole

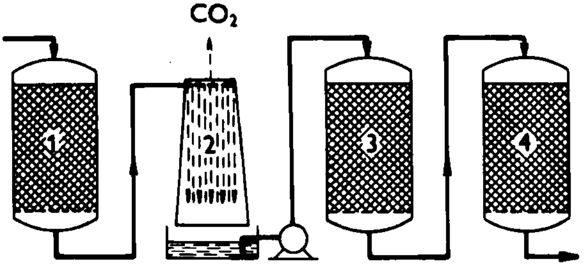

Fig. 3.58. Arrangement of ionex filters for water demineralization. 1 — ionex filter with cation exchanger, 2 — venting tower, 3 — ionex filter with a packing of a weakly alkaline anion exchanger, 4 — ion exchanger filter with a packing of a strongly alkaline anion exchanger

For the preparation of demineralized water with a quality approaching chemically pure water, an ion exchange system is used, as shown in Fig. 3.58.

For water treatment with the maximum requirements for water quality, 5–6 member demineralization plants are employed, the cation exchanger members being doubled and the last member being a combined ion exchanger. Ion exchange filters can be in either linear or circular arrangements.

To remove fine suspensions from water, and substances of colloidal character and oily substances which can suppress necessary diffusion processes by clogging the packing water should be usually pretreated by acid or alkaline clarification, by addition of lime or by a combination of clarification and chlorination.

Ion exchangers can be used for removal of Fe^{2+} and Mn^{2+} ions from water, as well as for removal of fluorides, ammonia and oxygen. For water disinfection, silver-impregnated anion exchangers with sterilizing effects can be used. For water dechlorination, resistant cation exchangers in the NH_3 form are recommended. Trials of ion exchangers for removal of phenols from water have also been carried out.

3.10.1.8 Adsorption

If an aqueous solution is in contact with a solid substance with a large surface area, concentrations of substances on the surface of the solids automatically increase and the concentration in the solution is thereby reduced.

Adsorption is used in many ways as a separation process in water technology. Granulated activated carbon is the preferred adsorbent, but new types of adsorbents with selective adsorption effects are based on polymers [56].

In water technology activated coal is used for removal of odour and a bad taste of drinking water. In wastewater treatment, sorption is a convenient technological process used instead of the biological stage in connection with chemical treatment, or so-called biosorption not only for after-treatment at the third stage of the treatment, but also for wastewater treatment itself.

Adsorption helps to achieve a more efficient removal of organic substances particularly from wastewaters containing biologically difficult-to-degrade and resistant substances produced by the petrochemical industry, refineries, and factories for the production of basic organic substances and plastics.

For *water treatment by clarification*, powder activated coal is used, which is fed together with the coagulation agent and separated by sedimentation along with the floccule-like sludge. Otherwise, adsorbers with granular activated coal are used, these being after the filtration stage in the technological line.

Sorption on activated coal during *treatment and after-treatment* of wastewaters is performed mostly by means of granular activated coal (grain size 1.5–4 mm) which is used for the filling of pressure filter columns. A layer of activated coal can be as much as 2.5 m thick (Fig. 3.59).

Downflow columns with a constant height of the layer are convenient for waters with a low content of pollutants. Conversely, for waters with a high

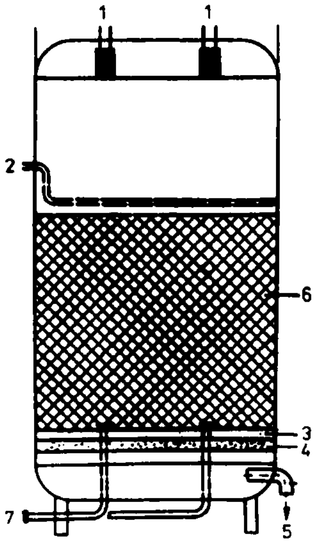

Fig. 3.59. A scheme of a pressure filter with activated coal. 1 — supply of raw washing water and its discharge, 2 — supply of washing water, 3 — sand, 4 — gravel, 5 — discharge of treated water, 6 — activated coal pack, 7 — emptying hole

content of suspended matters, columns containing an expanded layer with upward flow are used.

For regeneration of exhausted activated coal mostly thermal regeneration is used; other processes include, for example, biological regeneration [43, 47, 51–54].

3.10.1.9 Extraction

Extraction is a diffusion process in which the water, from which a certain component is to be separated, is brought into contact with an extraction agent in which the separated component is more soluble than other components of the treated or purified wastewater.

In the case of wastewater purification, extraction is used either for elimination of some toxic and radioactive substances, or in cases where some important raw material can be recovered in this way. Extraction can be exemplified by the purification of phenolic wastewaters by extraction with benzene. The most convenient units are continuous extraction systems with counter-flow operation. Extraction is an expensive and complex process, therefore, it is used only when the costs are balanced by the value of the products obtained [55, 56].

3.10.1.10 Membrane separation processes

Separation of components from a solution by membrane separation processes is based on selective membrane permeability.

Of the various membrane processes, *electrodialysis, reverse osmosis* and *ultrafiltration* are applied in water technology. They are used particularly for reduction of the salt concentration in waters with a high mineralization of natural (sea water, some kinds of groundwaters) or anthropogenic origin (wastewaters with a high inorganic pollution).

All membrane processes require through pre-treatment of the inlet water. Water must be free from colloids and suspended particulate matters which could cause mechanical clogging of the membranes and production of precipitates. Pre-treatment is a common process, such as, for example, adjustment of pH by addition of proper agents, filtration, and ore clarification [55, 57].

3.10.1.11 Degassing

The presence of some water-soluble gases in water, for example, CO_2, O_2, H_2S is undesirable since they cause corrosion of metallic and concrete components of the systems used in water technology and industry. Thus, water degassing is one of the most efficient anticorrosion measures. This process is also necessary for feed waters used in boilers. For water degassing both thermal and chemical procedures are required.

Thermal degassing is brought about by the disturbance of the equilibrium state on water heating, when spontaneous degassing takes place before boiling point is reached. Water in the form of droplets comes into contact with heating steam which results in removal of dissolved gases. Removal of gases from the system (reduction of partial pressure of gases in the gaseous state) stimulates the process of degassing.

Depending on the pressure in the system, pressure or vacuum thermal degassing processes are distinguished.

Chemical degassing is based on addition of appropriate chemicals, and is used for oxygen removal only. The reduction of oxygen content in the feed waters for high pressure boilers is a stringent requirement.

In plants where the pressure in boilers is up to 6 MPa, sulphites are used for degassing of feed waters; hydrazine is more convenient for higher pressures [3, 4, 58].

3.10.1.12 Distillation

Distillation is a process for the separation of homogeneous liquid mixtures, based on different boiling points of the individual components. Thus, distillation can be used for separation of such liquid pollutants from wastewaters which have different vapours pressures (different volatility) at the given temperature. Distillation is recommended for some kinds of wastewaters, particularly for those from chemical production plants.

Simple distillation is used for demineralization (desalting) of water by its evaporation at the boiling point and subsequent condensation, but it is a very energy-intensive process.

For wastewater purification, distillation with water vapours is used, as well as distillation in the flow of gases (entrainment) and azeotropic distillation. *Distillation with water vapours* is used for removal of, for example, phenols.

Distillation by entrainment of gases is used for removal of some undesirable components from wastewaters from chemical and petrochemical industries, e.g. of hydrogen sulphide, ammonia, phenols, etc. [48].

3.10.1.13 Electrochemical processes

Some electrochemical processes can be also used in water technology, particularly for the treatment of seriously polluted, toxic and oily wastewaters from, for example, pulp and paper production, the wood-working industry, some foodstuff industry operations.

If iron or aluminium electrodes are used for the treatment of wastewaters, the ions of iron or aluminium generated at the anode after connecting to a d.c. source act as a coagulant. Fine and colloidal impurities coagulate in the form of well-sedimenting floccules.

The *electroflotation* method employs fine oxygen and hydrogen bubbles formed during electrolysis of purified water suspensions.

The electrochemical processes also include *electrodialysis* [48].

3.10.1.14 Radiation-chemical processes

The practical utilization of radiation-chemical processes in water technology is based on the destructive and bionegative effects of a high-energy radiation on aqueous systems.

As the sources of radiation both gamma radiation (^{60}Co, ^{137}Cs) and electron accelerators can be used. The effect of high-energy radiation on aqueous solutions (wastewaters) is mostly indirect. Polluting components are reduced or oxidized by means of the products of water radiolysis — radicals and molecular products. Radiation technology can also be employed to remove resistant and biologically non-degradable pollutants present in wastewaters (for example, chlorinated hydrocarbons, pesticides, etc.).

Living organisms, such as viruses and bacteria are highly sensitive to the effects of the high energy radiation. These bionegative effects can be used for securing hygienically safe drinking water, and disinfection of wastewaters and sludges.

3.10.2 Chemical processes

3.10.2.1 Neutralization

Neutralization is applied to many processes in water technology. In water treatment it concerns particularly removal of aggressive CO_2 from water which consists in addition of alkaline agents to water (e.g. $Ca(OH)_2$, $NaOH$, Na_2CO_3) or in filtration through various materials removing carbon dioxide (marble, dolomite, fermago, etc.).

In many industrial plants, acid or alkaline wastewaters are produced. They can be neutralized by mutual mixing, by filtration of acid wastewaters through a filter bed consisting of limestone or dolomite, or by discharge of acid wastewaters into a recipient where hydrogen carbonates are used for neutralization of acids. And finally, it is via the addition of chemicals (for example, lime, limestone, HCl, H_2SO_4, CO_2) that the pH of wastewater is adjusted to the required value. Neutralization is a very sensitive process requiring accurate dosing of chemicals [4, 59, 60].

3.10.2.2 Precipitation

Precipitation is a process in which dissolved compounds are separated from the reaction medium in the form of low soluble compounds in their solid states, which can then be separated by sedimentation, filtration, centrifugation, flotation, etc. Precipitation is carried out either by a chemical change of dissolved substance, or by a change of the reaction medium. As precipitants, mostly acid, base or salt solutions are used.

If the substances removed enter the crystalline lattice of the precipitating solid phase, one refers to primary effect precipitation reactions. During the precipitation reactions with a secondary effect, pollutants enter the particles of the precipitate via sorption or mutual coagulation.

The process of coagulation (water clarification) by ferric or aluminium salts belongs mainly to the second group of precipitation reactions (see Section 3.10.1.6).

The transition category between these two groups of reactions is represented by the process of alkaline clarification, during which suspended colloid substances are removed by coagulation, and calcium, magnesium, iron and manganese by precipitation.

Precipitation reactions are used in water treatment for the removal of Ca and Mg by decarbonization (addition of lime), employing the low solubility of $CaCO_3$ and $Mg(OH)_2$.

Calcium and magnesium can be removed from water by precipitation with lime, sodium hydroxide and phosphates, or by a suitable combination of these precipitation agents (Fig. 3.60).

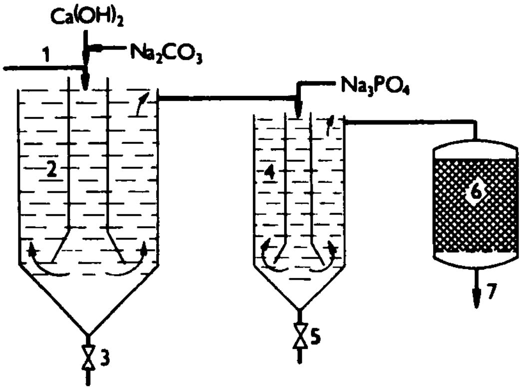

Fig. 3.60. Equipment for water treatment by a double-stage precipitation with lime, soda and phosphates. 1 — raw water supply, 2 — reactor for the precipitation with lime and soda, 3, 5 — sludge discharge, 4 — reactor for the phosphate precipitation, 6 — high-rate filter, 7 — discharge of treated water

For the removal of iron and manganese from water, the low solubility of hydroxides of the higher oxidation states of these metals is employed.

Silicates and SiO_2 are removed by making use of their low solubility in saturated lime water.

The *magnetic water treatment* has similar effects as a removal of Ca and Mg from water.

In wastewater treatment the precipitation reactions are an excellent practical solution for the removal of very serious pollutants of a toxic character — heavy metals and cyanides. Ions of heavy metals are mostly removed in the form of hydroxides, carbonates or sulphides [4, 43, 47, 48, 59, 60].

3.10.2.3 Oxidation and reduction

Oxidation processes are applied in many techniques used for drinking and service water treatment, as well as for the wastewater treatment.

In the case of drinking water it is necessary to remove microorganisms threatening human health. For the disinfection of water, oxidation processes based on the effects of the following oxidizing agents are frequently used: chlorine and its compounds (hypochlorides, chloramines, chlorine dioxide), ozone, hydrogen peroxide, potassium permanganate and others.

The technique for the removal of iron and manganese during water treatment employs the oxidation of bivalent well-soluble forms to multivalent low-soluble hydrated oxides, which can be removed from water either by sedimentation or filtration. Oxidizing agents in this case are atmospheric oxygen, chlorine, potassium permanganate, ozone and chlorine dioxide.

For chemical degassing of water where removal of dissolved oxygen is required, sulphites and hydrazine are used as oxidizing agents (see Section 3.10.1.11).

In the technology of wastewater treatment the oxidizing techniques are used particularly for elimination of organic pollution. Cyanide wastewaters can be treated by oxidation with chlorine; here, cyanides are oxidized up to elementary nitrogen and carbon dioxide.

The oxidizing effects of ozone can be used for oxidation of phenols and oil hydrocarbons present in wastewaters. Ozone seems to be a very promising oxidizing agent also for the after-treatment of biologically treated wastewaters, reducing total amount of organic substances. Due to the high energy demands for the preparation of ozone, its application to wastewater treatment is rather limited.

For disinfection of purified wastewaters (e.g. infectious wastewaters) mainly chlorine, chlorine dioxide, or ozone are preferred.

Reduction processes are important for the treatment of wastewaters from the plants for the surface finishing of metals, containing salts of hexavalent chromium. Reducing agents, such as $FeSO_4$, SO_2, Na_2SO_3, $NaHSO_3$ reduce hexavalent chromium in acid media (pH 3–5) to the trivalent form, and this is precipitated in the form of chromium trihydroxide.

Reduction processes are also used for the elimination of organic nitro compounds by forming amino compounds, which are sometimes less harmful and biologically more readily degradable [47, 59, 61–64].

3.10.2.4 Incineration

This process is used for elimination of particularly harmful liquid wastes and sludges, such as black liquors from pulp production, and acid condensates from oil processing factories. It is carried out in a dry or wet mode.

In the (incineration) reactor, used for the *dry process*, water evaporation is followed by pyrolysis of organic matter to form pyrolysis gas and carbonized residue.

In the case of *wet incineration* at higher temperatures (up to 350°C) and a high pressure (5–15 MPa), organic pollutants are degraded into carbon dioxide and water, or lower fatty acids (Fig. 3.61). The disadvantage of this process lies in the high investment and operating costs.

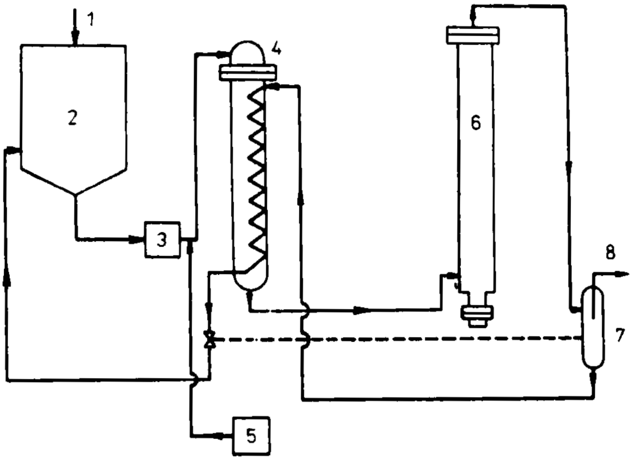

Fig. 3.61. A scheme of wet incineration. 1 — supply of concentrated sludge, 2 — tank, 3 — pump, 4 — heat exchanger, 5 — compressor, 6 — reactor, 7 — separator, 8 — discharge of combustion products

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3.11 Sludges, their disposal and utilization

In the chemistry and technology of water, sludge is defined as a suspension of solid substances (dry matter of sludge) produced during water treatment and purification. Sludges in general do not have given and time-constant properties. They can be either solid or semisolid; after dewatering they are converted into solid waste. Sludges also include sediments on the bottoms of rivers, dams and lakes.

Sludge is thus a two-phase system consisting of a solid and liquid phase (sludge water). The percentage water ratio in sludge is called *wateriness* (p_w). Hence, the *sludge dry residue* p_s (% by weight) can be calculated from the following simple relationship: $p_s = 100 - p_w$.

Processing, utilization or disposal of sludges (sludge technology) is an independent technological field. The sludge obtained often represents a considerable quantity from the total amount of processed wastewaters. There are cases where such a large quantity of sludge is produced that its disposal is more difficult than the wastewater treatment process itself [1–3].

3.11.1 Sludge classification

Two types of sludges are produced in water treatment plants:

— from settlers (*primary sludge*),

— from after-sedimentation settlers (*secondary sludge*).

The secondary sludge is usually pumped from the after-sedimentation into the primary settlers, and processed together with the primary sludge as a *mixed sludge*. Here, the primary sludge is the prevalent material.

Both the primary and mixed sludges are called *raw sludge*.

Fresh primary sludge from municipal wastewater treatment plants is yellow-brown, brown or even grey, and it usually has a granular structure and consists of insoluble substances wich have passed through a catch-pit and rakes. It also contains a remarkable quantity of colloidal substances with the ability to bind water and to retain it — therefore, dewatering in this case is rather difficult.

Secondary (activated) sludge has a flaky structure, it contains at least 98% water. During sedimentation the particles of sludge present are agglomerated, and thus their weight increases. The character of secondary sludge is influenced by the treatment system used.

The secondary sludge is brown to brown-red, with an earth-like smell.

In the *putrefactive sludges*, organic substances easily undergoing biological degradation predominate, whereas in the *non-putrefactive sludges* (mineral ones) inorganic substances prevail.

3.11.2 Sludge stabilization

Organic substances present in putrefactive sludges are biologically degraded during storage, which results in hygienic defects. Therefore, they need to be stabilized.

Sludge stabilization is a process of destruction of the microbial, easily available organic component. In practice it takes place most frequently via the sludge fermentation under aerobic or anaerobic conditions.

In the case of *aerobic sludge stabilization* some organic compounds are degraded to CO_2 and H_2O, however, a certain portion remains unchanged. Organic nitrogen is released during fermentation by hydrolytic processes, first in the form of ammonia which is then oxidized through nitrites to nitrates.

By *anaerobic sludge stabilization* more complicated organic substances (proteins, lipids, glycides) are degraded due to the activity of a complex bacterial microflora into simpler compounds (fatty acids volatilizing in water vapours). They become the substrate for strictly anaerobic methane bacteria mineralizing these compounds at the second stage to the simplest substances of a mineral character (CH_4, H_2O), partly released into the sludge gas (biogas). At the same time a considerable proportion of the organic nitrogen is released in the form of ammonia. Sulphates are reduced to H_2S which is also a product of protein degradation. Sludge stabilized by methane digestion (so-called anaerobically stabilized *digested sludge*) is a black amorphous substance of granular character. It has a slight tar-like smell and is well dehydrated.

The ratio of organic substances to inorganic ones is usually $\sim 1:1$ in the digested sludge, whereas in the raw sludge it is 2:1. It is considered that in the course of anaerobic stabilization the organic sludge dry weight decreases by about 45–65%. The liquid phase which is separated from the sludge (so-called *sludge water*) is very seriously polluted (BOD_5 is even as high as 2000 mg l^{-1}). Under normal conditions it is possible to consider 1 l of sludge water per capita per day.

3.11.3 Chemical composition of sludges

The chemical composition of the primary, anaerobically stabilized and activated sludge is presented in Table 3.66. Dry weight of the primary sludge varies within the range 4–8% (in mixed sludge 3–5%), that of the digested sludge within 7–13% and that of the activated sludge up to 2% [1, 4–8].

Table 3.66. Composition of primary, anaerobically stabilized and activated sludges in per cent of dry mass

Compound	Sludge		
	primary	anaerobically stabilized	activated
Lipids	5.7–44.0 (mean 33)	2.0–17.0 (mean 7.0)	5.0–12.0
Proteins	19.0–28.0	10.0–21.0	32.0–41.0
Cellulose	3.8–10.8	0.56–9.8	7.0
Hemicellulose	3.2–4.6	1.0–1.6	—
Lignin	5.8–8.5	5.1–8.4	—
Humic acids	4.0	8.6	—
Pentozans	1.0	1.6	2.1
Total nitrogen (N)	2.0–4.5	1.0–4.0	6.2
Total phosphorus (P)	0.53–1.1	0.66–1.2	1.1
Total phosphorus (P_2O_5)	1.2–2.6	1.5–2.7	2.5
SiO_2	13.8–25.8	27.6	8.5
Fe_2O_3	3.2	6.0	7.2
Al_2O_3	2.1	4.3	3.2
CaO	2.7–5.6	5.7–12.4	1.7
MgO	—	0.47–2.8	—
K_2O	0.2–0.4	0.3–0.6	—
Na_2O	—	0.1—0.55	—

Some of the undesirable components found in sewage sludge are shown in Table 3.67. This table refers to sludge from a primary settler, although many of the same components are found in secondary settler sludges [9].

Important, frequently dominant compounds in sludges are usually *proteins*. The majority of proteins are present in activated sludge. The quantity of proteins is a reliable indicator of the age of sludges, since they are gradually degraded via proteolytic processes into simpler components (polypeptides, peptides and amino acids) which undergo deamination processes to release ammonia. Similarly, the content of proteins is also an indirect measure for assessment of the degree of technological sludge processing necessary under both aerobic and anaerobic conditions, because

Table 3.67. Undesirable components commonly found in sewage sludge from a primary settler [9]

Component	Level, ppm by dry weight unless otherwise stated
Organics	
PCB	0–105
DDT	0–1 (found much less frequently now)
DDD	0–0.5 (found much less frequently now)
Dieldrin	0–2
Aldrin	0–16
Phenol	Sometimes encountered
Heavy metals	
Cadmium	0–100
Lead	Up to 400
Mercury	3–15
Chromium	Up to 700
Copper	80–1000
Nickel	25–400
Zinc	300—2000
Pathogenic microorganisms	
Human viruses	Generally present
Salmonella (in raw sludge)	500 viable cells/100 ml
Salmonella (in digested sludge)	30 viable cells/100 ml
Faecal coliforms (raw sludge)	1×10^7 viable cells/100 ml
Faecal coliforms (digested sludge)	4×10^5 viable cells/100 ml

proteins are degraded to lower organic and/or mineral compounds in a similar way. At present, efforts to employ all possible sources of waste material containing proteins for feeding purpose are ever more intensive.

A considerable proportion of the sludge dry matter is that ascribed to *lipids* (ether and petroleum-ether extractable substances), consisting of free fatty acids, their esters and substances incapable of undergoing saponification. The content of fatty acids in sludge is a value which is useful for characterizing the biochemical conditions in the anaerobic process of sludge stabilization.

Other important components of sludges are *polysaccharides* (celluloses, hemicelluloses, starch).

Among other organic components *lignin, humus acids, surfactants, tannins, pectins*, etc. are present at lower concentrations.

The knowledge of the content of *total nitrogen* and *phosphorus* in sludge offers only approximate and quick assessment of their fertilizing value from the viewpoint of these important components in plant nutrition.

The prevailing inorganic compound in sludge is SiO_2.

Alkalinity of sludge from municipal wastewaters is usually proportional to the concentration of calcium and magnesium bicarbonates. The presence of strongly alkaline components from industrial sources (hydroxides, carbonates, phosphates, silicates, sulphides, etc.) can increase the pH above 8.3. Sludge from industrial sources may alternatively contain even higher quantities of hydrolysable mineral salts and thus pH can decrease below 4.5.

The odour of sludge is the result of its chemical composition or changes in its composition taking place under the effect of physical, chemical, biochemical or biological processes. Although this parameter is a matter of subjective observation, it is important for the assessment of the origin of sludge and the appropriate means of sludge processing.

3.11.4 Sludge gas (biogas)

During anaerobic microbial processes, gaseous products are released from the degraded organic substances of sludges in the form of *sludge gas (biogas)*. Its main components are methane and carbon dioxide. It regularly contains low amounts of nitrogen. It originates from atmospheric air which enters the fermentation tank together with sludge even during very careful operation. Molecular nitrogen is usually quantitatively consumed in the anaerobic environment, and thus the sludge gas contains only traces of it. If nitrogen is found in the sludge gas, it always is an indicator of air leakage into the fermentation area. The quantitative composition of sludge gas defined by the ratio $CH_4{:}CO_2$ depends on the composition of the substrate and conditions of fermentation. Therefore, it is also a sensitive indicator of the course of methane fermentation in digestion tanks.

If the substrate contains high amounts of glycides a considerable quantity of hydrogen is also generated, particularly at the initial stages of fermentation.

The quantity of sludge gas generated from 1 kg of total or organic solids of sludge is usually the main indicator of the digesting properties of sludge. Sludge of domestic origin produces about 430 l of gas per kg of total solids, or 600 l of sludge gas from 1 kg of organic solids [10].

3.11.5 Types of water in sludges

From the technological viewpoint, content of water in sludge is its most important property. Sludges from municipal and industrial wastewaters can contain as much as 99.5% of water. It is impossible to dispose or utilize them in this form. Therefore, it is necessary to reduce the content of water (increase the solids) in the treated raw sludge, and to reduce its volume so that transportation and further eventual sludge treatment is as economical as possible.

When removing water, the state of the sludge is changed in addition to the change of the volume, which influences its properties, as shown in Table 3.68.

Table 3.68. Physical properties of sludge in dependence on the amount of water [11]

Content of water (%)	Properties of sludge
85–100	Liquid, usually readily pumped
75–85	Viscous, cannot be pumped
70–75	Pasty-plastic, viscous
40–70	Friable, frequently solid
10–40	Loose, very hard
10	Powdered

From the aspects of the occurrence of water in sludge and the possibility of its separation, the types of waters are as follows:

— gravitational (free, filling, interspatial),
— colloidally bonded,
— bonded by capillary forces,
— bonded in cell material.

Gravitational free water, which is in the cavities between sludge particles, is present in the highest amounts. This water can be removed very easily (for example, by several hours of sedimentation in so-called thickeners).

Colloidally bonded water occurs particularly in activated sludge. This water is bonded by surface forces on the interface of the individual sludge particles. The larger the sludge surface area (the finer the sludge particles), the higher is the content of colloidally bonded water. This water can be easily removed because the electric charge of colloid particles can be readily manipulated. To release colloidally bonded water, the electric charge of the particles must be neutralized (by intensive mixing, agitation, filtration employing special coagulation of sludges).

When solid particles of sludge agglomerate, capillaries are formed between the sludge particles, and *water* present in them *is bonded by capillary forces*. To remove this water, it would be necessary to exert a force on the water–sludge mixture equal to the force binding this water.

To release *water bonded in cell material*, it is necessary to biologically degrade the cell membrane (anaerobically or aerobically) by heating up to 180°C, or by freezing.

When considering dewatering capabilities sludges are classified as follows:

- easily dewatered (e.g. sludge from inorganic wastewater treatment plants),
- medium dewatering capability (e.g. municipal sludges without marked industrial contents),
- poor dewatering capability (e.g. sludges from chemical and biological treatment).

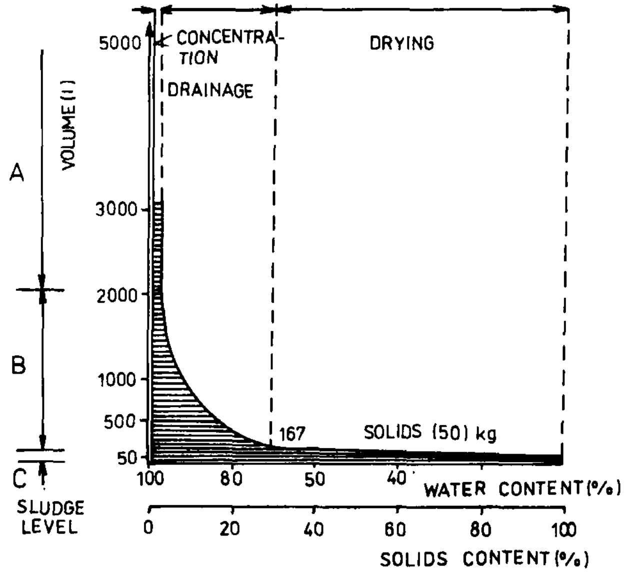

Fig. 3.62. Technically and economically optimum separation of water from readily dehydratable sludge with initial water content of 90%. A — predominantly interspace water separated by concentration, B — predominantly adhesive and capillary water separable by dehydration, C — predominantly internal and adsorbed water, separable only by thermal energy [11]

Figure 3.62 illustrates technologically and economically optimum separation of water in sludge with good dewatering capabilities, and Fig. 3.63 shows sludge with poor dewatering capabilities. Sludge, from which water is easily removed, can be concentrated up to 75% of water content, and then by pressure filtration up to about 25–30% of water. Sludges with poor dewatering capabilities can be concentrated only up to 97–99% of wa-

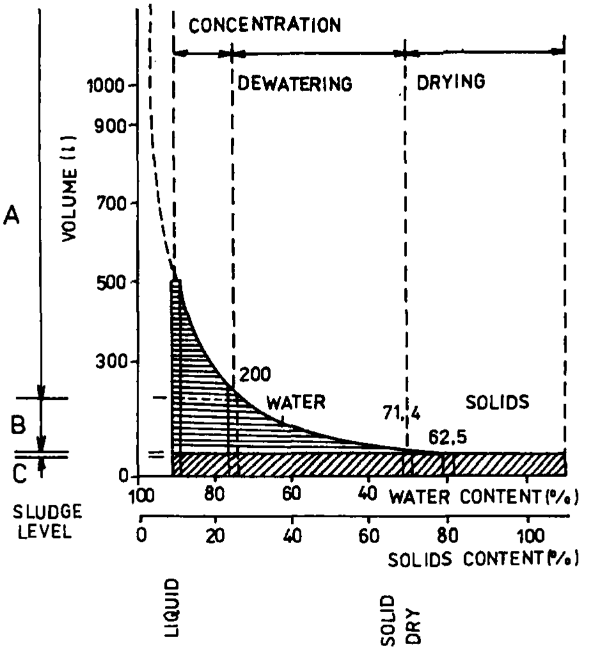

Fig. 3.63. Technically and economically optimum separation of water from difficulty dehydratable sludge with initial water content of 99%. A — predominantly interspace water separated by concentration, B — predominantly adhesive and capillary water separable by dehydration, C — predominantly internal adsorbed water, separable only by thermal energy [11]

ter content; if pressure filtration is applied they can be concentrated only to 70% [11].

3.11.6 Reduction of water content in sludge

Any waste-sludge handling requires separation of the maximum content of sludge water. It is necessary to differentiate the terms "thickening" and "dewatering".

Sludge thickening denotes removal of water by gravitation (in settlers).

Dewatering is usually performed by means of mechanical systems (centrifuges, filter presses, filters, etc.), or by natural dewatering.

By thickening, the water content is reduced to 80–85%, by dewatering to 60%. During drying or incineration the water content is reduced to 40% or less.

The simplest technological procedures is *thickening by settling* employing the sedimentation properties of suspensions. Thickeners are designed for either discontinuous or continuous operation.

The most frequently used technique up to the present for sludge dewatering has involved the use of *sludge fields*, which are also used for drying, in the second stage of dewatering.

The sludge fields are flat earth or concrete basins whose bottom is formed by dewatered filtration gravel sand. The cycle of a sludge field operation has the following stages:

— filling,
— dewatering and drying,
— removal of dried sludge, and
— treatment of the drainage layer. Sludge on these fields can be dewatered and dried to 25–45%.

Sludge lagoons are either natural (abandoned mines, disused river branches), or artificial. Artificial lagoons are constructed behind earth dams with a sludge height of 1–1.2 m. From the operational viewpoint it is recommended that the lagoons should be modified to provide, for example, drainage or overflow for sludge water.

Currently, dewatering in sludge beds and lagoons is considered to be too long and difficult to control. Therefore, instead of these beds, *mechanical dewatering technology* is employed. In this case the following systems are used:

— filter presses, representing the classical equipment for sludge dewatering. Their advantage consists in providing relatively the highest degree of dewatering (about 50% and more), but their disadvantage is their discontinuous (cyclic) operation,
— vacuum filter,
— horizontal (decanting) centrifuges,
— band filter presses, and similar equipment [3, 12–14].

For satisfactory sludge dewatering with any equipment it is necessary to pre-treat the sludge, i.e. to disturb its colloidal structure, in order to release water from the soild phase.

This can be achieved by

— chemical treatment, using inorganic coagulants or organic flocculants (polyelectrolytes),
— thermal treatment — at a temperature of about 180°C and with approximately 45 min dwell.

3.11.7 Utilization of sludge and sludge gas

The possibilities for sludge utilization depend on the technology of production plants which produce particular types of wastewaters. Some types of sludges can be used as fertilizers or feed additives.

The sludge from municipal wastewater treatment plants can be used in agriculture for fertilization. It is performed by transportation and application either of liquid, digested sludge or dewatered sludge. Dewatered sludge is not an ideal fertilizer since it contains nitrogen in excess, whereas the contents of phosphorus and potassium are low. Therefore, digested sludge is mixed with peat or soil; missing nutrients can be added.

The dried sludge residue contains proteins, fats, saccharides, vitamins (thiamine, riboflavin, niacin, pyridoxine, nicotinamide, biotin, etc.) and mineral salts. It therefore represents a potentionally suitable feed additive. Particularly in the case of plant fodders, it can increase their biological value, digestibility and degree of utilization.

Sludge gas (biogas) can be used particularly on the site of its origin. Its high heating value enables its direct utilization in a treatment plant. Sludge gas is used for heating digesting tanks or for degradation of the floating sludge layer. A mixture of sludge gas and air (at ratio of 1:5 to 1:15) is explosive. Compressed sludge gas could be used as a fuel for cars. H_2S is removed on iron ore filters, CO_2 in elution towers [10].

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3.12 Chemical analysis of water

The chemical analysis of waters is essential for checking their purity and their degree of pollution. Water must be analysed and also frequently checked to determine its quality, or deviations from a set standard quality.

The procedure of chemical water analysis can be divided into the following stages:
— sampling, preservation and preparation for the analysis;
— treatment of the species studied into the state in which their presence, quality or quantity can be determined;
— performance of the analysis itself, or determination and measurement,
— processing of the results obtained and their evaluation.

The scope of the date derived from chemical analyses depends particularly on the purpose of the water quality investigation, the type of analysed water and the capabilities of the analytical laboratory performing the analysis.

Hydrochemical practice makes use of complete, short and specific chemical analyses of water. In the latter case only some species or properties of water are determined (hygienic assessment, routine check, evaluation of aggressive properties, etc.).

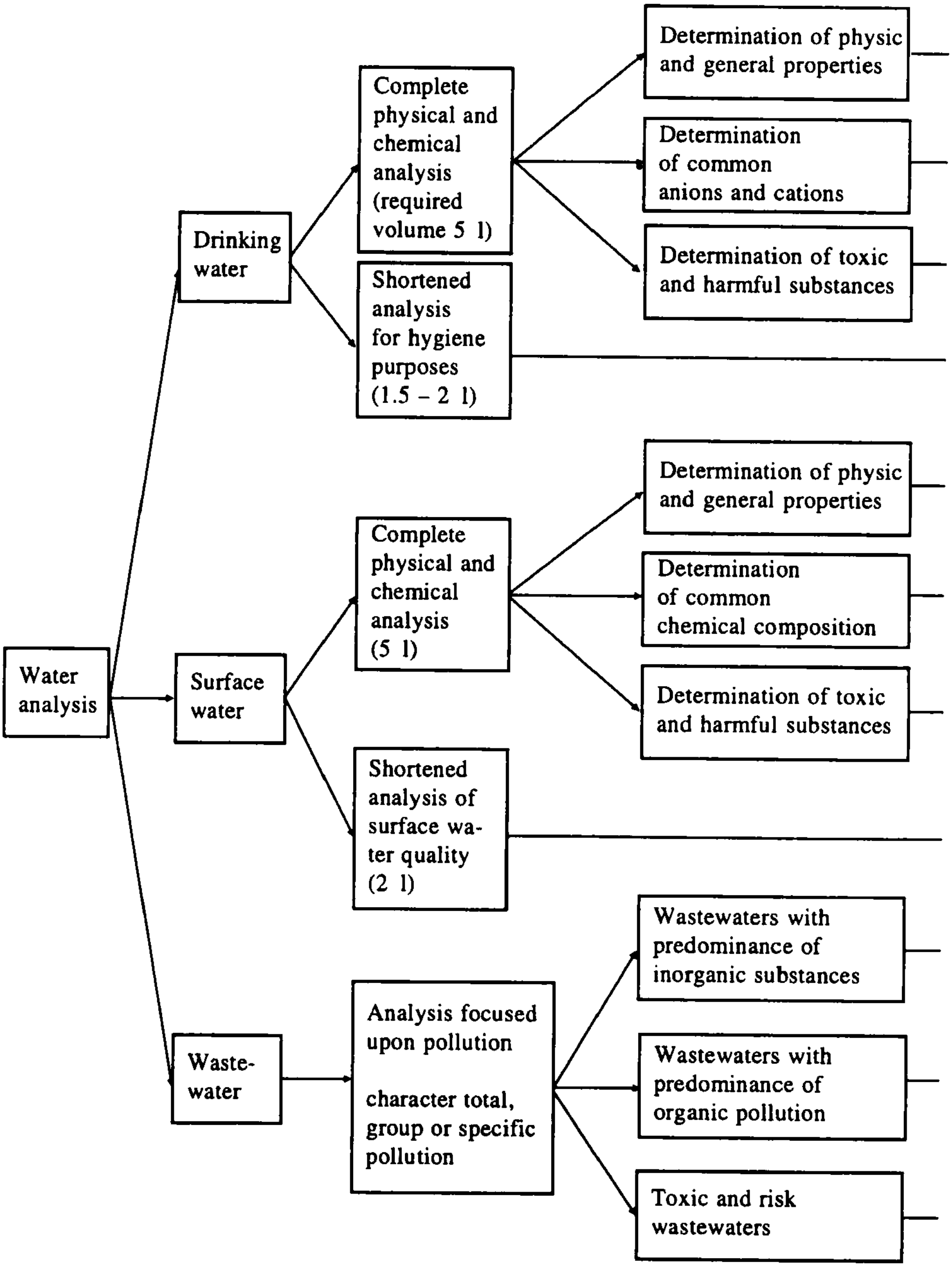
Scheme 3.1 shows characteristics of the analyses of drinking, surface and wastewaters.

3.12.1 Sampling

One of the essential prerequisites for obtaining exact and reliable results of an analysis is that the sample of water to be analysed should represent the average composition of the whole quantity of the water being studied all components being present at the same weight or volume ratio as in the source in question.

3.12.1.1 Modes of sampling and types of samples

Sampling is either *single* or *repeated* (*series*), and samples are either *point* (*single, simple*) or *mixed* (*pooled*) [1].


Water analysis
Drinking water
Complete physical and chemical analysis (required volume 5 l)
Determination of physic and general properties
Determination of common anions and cations
Determination of toxic and harmful substances
Shortened analysis for hygiene purposes (1.5 - 2 l)
Surface water
Complete physical and chemical analysis (5 l)
Determination of physic and general properties
Determination of common chemical composition
Determination of toxic and harmful substances
Shortened analysis of surface water quality (2 l)
Waste-water
Analysis focused upon pollution
character total, group or specific pollution
Wastewaters with predominance of inorganic substances
Wastewaters with predominance of organic pollution
Toxic and risk wastewaters

Temperature, pH, alkalinity, acidity, total hardness, colour, turbidity, odour, taste, total dissolved and suspended solids, oxidizability, aggressive CO_2, Cl_2, ClO_2, O_3, CO_2

Anions: OH^-, Cl^-, F^-, I^-, NO_2^-, NO_3^-, SO_4^{2-}, S^{2-}, CO_3^{2-}, HCO_3^-, PO_4^{3-}, SiO_3^{2-}
Cations: Na^+, K^+, NH_4^+, H^+, Ca^{2+}, Mg^{2+}, Fe, Al, Mn

e.g., Hg, Pb, Cd, CN^-, phenols, tensides, etc.

Determinations of e.g. temperature, colour, turibidity, odour, suspended solids, pH, alkalinity, total hardness, Cl_2, NO_2^-, NO_3^-, Cl^-, SO_4^{2-}, H_2S, PO_4^{3-}, F^-, oxidizability, NH_4^+, Ca^{2+}, Mg^{2+}, Fe, Mn, toxic and risk substances according to expected pollution

Temperature, odour, colour, turbidity, conductivity, total dissolved and non-dissolved solids, oxygen, oxidizability, BOD, pH, acidity, alkalinity, hardness

HCO_3^-, CO_3^{2-}, OH^-, Cl^-, S^{2-}, SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}, NO_3^-, NO_2^-, H^+, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Fe, Al, Mn, organic nitrogen, humin substances

e.g., Hg, Pb, Cu, CN^-, phenols, tensides, sulphite waste liquors, waste products from chemical industry

The analysis can consist of determinations such as e.g.: temperature, colour, total and dissolved solids, oxygen, oxidizability. For other purposes of surface water evaluation a range of analyses according to the watershed pollution and possible effects of this pollution is chosen

e.g., pH, acidity, alkalinity, total, dissolved and non-dissolved solids, then determinations of mineral composition of these waters according to the characters of pollution

e.g., temperature, odour, colour, total, dissolved and non-dissolved substances, oxidizability, BOD, relative stability, pH, alkalinity, Cl^-, SO_4^{2-}, total sulphides and H_2S, total sulphur, NH_4^+, NO_3^-, NO_2^-, organic nitrogen, Na^+, K^+, Ca^{2+}, Mg^{2+}, fatty acids, fats, oils, tensides, phenols, etc.

Determination of toxic and risk pollution

Scheme 3.1

Single (*non-repeated*) sampling provides a picture of the immediate state. The sample is taken only once (using only one sampling device, etc.) and is evaluated individually.

Repeated (*series*) *sampling* is used for the determination of variability of samples in time or space, or both. A number of other samples is always taken and thus a set with a certain number of members is obtained. The results of analyses can be processed and assessed by statistical methods; in the case of a large number in the series, a computer can be used for the processing. Zonal sampling (samples are taken from various depths on the vertical axis of the water column from a determined point on the surface) and time sampling (samples are taken at certain time intervals several times) are cases of repeated sampling.

The samples may be either point or mixed. A point sample is usually obtained by single sampling; a mixed sample is obtained by mixing of several point samples taken over a period of time from one place of the investigated source. An average sample is a type of mixed sample which characterizes the average composition of water in space, time or both.

3.12.1.2 Sample container and sampler

Samples are stored in a transportable container (bottle, carboy, canister). Sample containers are made of glass or plastics (particularly polyethylene).

Samplers are instruments and devices enabling single or repeated samples to be taken either from a position which is not readily accessible (deep samplers) or without the attending personnel (automated samplers). Samplers and their components are made from corrosion-proof steels, usually chrome-nickel with addition of non-magnetic tungsten and molybdenum.

Depending on the principle of their operation the deep samplers are divided into three groups [1]:

(1) *Flushing samplers* — tubes with flap or flat closures at both ends; they are applied down the vertical to the point of sampling without disturbing the homogeneity of water layers. The Friedinger sampler (Fig. 3.64) is an example. In this device, the vertically tilting lids are closed by a weight on the wire. The bottom lid is provided with a valve for emptying the sample container. A sampler with a more complicated closing mechanism (hermetic and pressure types) must be washed in situ by, for instance, multiple rapid dropping down and slow pulling out over an amplitude of the length of the device (1–3 m) [2, 3].

(2) *Non-flushing samplers* employ a suction effect for sampling. This is caused by a pressure difference between the device chamber and water

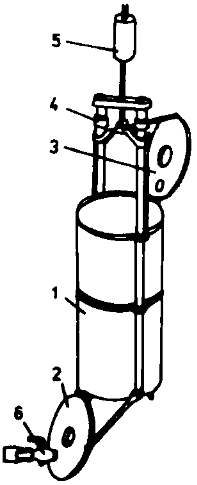


Fig. 3.64. Friedinger's rinse sampler. 1 — sample chamber, 2, 3, — upper and bottom closure, 4 — manipulation mechanism, 5 — manipulation weight, 6 — outflow valve

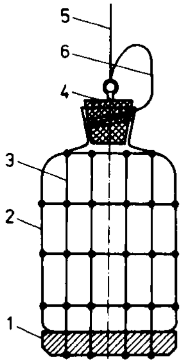


Fig. 3.65. Mayer's immersion bottle. 1 — metal weight, 2 — sampler, 3 — nylon net, 4 — rubber plug, 5 — hanging string, 6 — securing string

at the point of sampling. They differ from the former type particularly in the fact that the volume of sample in them equals the volume taken at the sampling point. The suction effect is achieved in different ways — by the sampler evacuation, by the discharge of air or another inert liquid, by mechanical expansion of the chamber or bellows (or of a polyethylene bag), by a mechanically or otherwise controlled piston, etc. [4–6]. The most common are the bottle samplers, such as the so-called Mayer's immersion bottle (Fig. 3.65), which is the oldest type of deep sampler [1–3]. It is a glass sampler with a weight; from the neck a short cord leads to the plug to which the end of the dropping cord is fixed. A slightly plugged bottle is immersed to the required depth, the plug is released by a sharp pull and the bottle is filled.

(3) *Combined samplers*; these include, for example, all bottle-type samplers whose sample containers are placed in another sealed container (in a device chamber) so that it is filled with a defined volume of water.

Automated samplers function without the need for an operator, giving the possibility of selection of a sampling regime arranged in dependence on time or flow-through quantity. One of these is the sampler shown in Fig. 3.66 [7]. The system has a simple battery-driven peristaltic pump, which can take samples heavily polluted with suspensions of solid material using a suction basket immersed in water. The pump feeds the sample into a 5 l bottle at the required times determined by the timing unit.

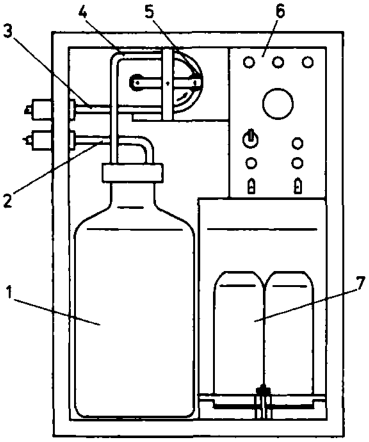


Fig. 3.66. Automatic sampler. 1 — sampler, 2 — overflow tube, 3 — water inlet, 4 — filling tube, 5 — peristaltic pump, 6 — manipulation and signalization chamber, 7 — battery

Recently, automated systems with the possibility of continuous measurement or direct recording of selected components of the analysis and properties liable to change have come into use. This transforms the automated sampling device into a simple automated analyser (monitor). The NAIADA system (CSFR) continuously records the electric conductivity, pH, redox potential, dissolved oxygen content, temperature, quantity of dissolved organic matters (as absorbance in the UV region of the spectrum), water turbidity, and water level. The water sample is fed via a submersible pump into a levelling bottle with a regulating overflow, from where a constant quantity flows under hydrostatic pressure into the particular measuring vessels. The Hungarian system AQUADAT functions on a similar principle, as well as AQUAMER of Poland, PHILLIPS from the Netherlands, etc. [1].

3.12.1.3 Sampling of precipitation water

Horizontal precipitations (dew, frozen mist, ice accretion, condensed fog) are usually not analysed. The quantity of vertical precipitation is measured in practice by a dense network of hydrometrological stations using the standard method of the World Meteorological Organization.

Rainfall water and falling snow samples are collected into a sample container through a funnel, or into a deep and wide dish. An average sample is taken from ice, it is placed in a wide-neck sample container and allowed to melt at room temperature.

Automatic systems for precipitation sampling are usually designed so that it is possible to take dust-free samples. The automatic mechanism of commercially produced systems is focused on opening of the sample containers during rain and closing in the periods without rain. The lid of the system is controlled by a switch sensitive to the very first rain drops or snow flakes. Usually, the conductivity of rain water is utilized which connects two insulated points with opposite electric charges on an inclined and slightly heated plate.

3.12.1.4 Sampling of running water

The sampling place should represent the whole through-flow profile, or the whole through-flow water quantity.

The sample is taken from running water, if possible, from the streamline. If the stream has several branches, the sample is taken from the branch with the highest flow rate. In shallow streams, the sample is taken approximately in the upper third or at a depth of about 20–30 cm from the surface; in the case of deeper streams the depth for sampling depends on the purpose of the analysis. In some cases, zonal sampling is performed across the whole transversal profile with several vertical samplings.

For technological and economic reasons, sampling from big rivers is usually limited to the sampling points in longitudinal direction regardless of the cross-profile. The control profile is generally on the right or left bank depending on the current (position of the streamline); only exceptionally is the middle part of the flow used for sampling, e.g. from bridges or boats.

The depth of small streams (brooks, artificial channels, water mill drives) ranges over tens of cm, the width over several meters. Sampling is simple since the channel usually forms a streamline. However, water quality sensitively and markedly reacts to each pollution and flow-rate change. Therefore, more attention should be paid to the number of samplings when following the changes in the water quality.

In emergency situations samples are immediately taken above and below the source of pollution so that a sudden change in water composition can be detected.

3.12.1.5 Sampling from larger bodies of water

Samples from reservoirs, ponds and lakes are taken from various localities and various depths, usually by means of deep sampling devices. It is not recommended to take an average (pooled) sample since substantial differences in the water quality in different positions of the point samples may cause chemical reactions and mispresent the final results.

Sampling in valley dams over 10 m high is carried out at several predetermined points (profiles) from a boat. Marking of the sampling points by anchored buoys simplifies position fixing. Zonal sampling should be performed to follow the stratification and motion of in-flow water in reservoirs.

Ponds and small reservoirs with a dam lower than 10 m are sampled from boats, employing series and zonal sampling for various analyses. In some cases, the point samples for a given purpose can be obtained from fixed systems of the dam.

Sampling of the sea and ocean waters requires well-equipped oceanographic ships. It also includes the collection of plankton and sampling of the sea sediments and upper layers of the sea bottom.

The emergency situations caused by shipping accidents on the seas as well as by forbidden activities (emptying and washing of tanks in the open sea, deposition of wastes in the sea, etc.) are usually so extensive and damaging that the limitation of consequences and protection against further spreading, e.g. of oil stains on the surface takes a higher priority than immediate special procedures of sampling. Sampling is usually carried out only later in the course of the operations to determine the areal and spatial reach of the pollution, its impacts on aquatic fauna and flora, or the whole ecosystem, including the coastline.

3.12.1.6 Sampling of groundwaters

Reliable groundwater sampling usually requires a permanent in-flow or through-flow of water. Only exceptionally, samples from places which do not satisfy this requirement are necessary in order to identify processes of conditioned stagnation.

Samples from springs are taken beneath the surface, directly into a sample container, or from the outlet pipe. Sometimes, it is necessary to clean the spring, one day before sampling. Its bottom is deepened so that the sample container or other container can be easily immersed in it.

It is recommended to take samples from a spring when pumping experiments take place, and after rain so that constant water quality can be determined, or pollution by surface water.

When taking samples from wells, water is first pumped. If the well was not frequently used, pumping should last 20 minutes, or even more, until the pumped water has a constant temperature. It is necessary to take care that the pumped water is discharged away from the well so that it cannot flow back in or be soaked in. Only then is the sample container filled. To prevent the escape of dissolved gases a funnel should be used into which the neck of the outlet pipe of the pump is immersed. The funnel is filled by pumping, water is allowed to flow through for a while and then the funnel stem is introduced to the bottom of the sample container. After filling it, water is again allowed to flow for a while. If the well has not been used for a long time, water is pumped out, the well is allowed to be fill again and only then is a sample taken.

Useful information can be obtained by taking a sample from a well during summer droughts when the consumption and exchange of water are maximum.

Samples from drills (probes) are taken by a narrow deep sampling device or a pump. The samples from drills in which water has been present for a long time or whose outlet was not well closed are not reliable.

Drainage water is sampled into a sample container directly from the drainage outlet.

3.12.1.7 Sampling in water treatment plants and from water taps

In water treatment plants, sampling water taps with a closing valve are installed. Sampling is performed via rubber hoses fitted to the sampling or water taps; the other end of the hose is introduced into the bottom of the sample container and water is allowed to run until a constant temperature is reached. If toxic substances from the pipe are to be determined (Cu, Pb, etc.), the sample is taken immediately from the first water fraction. Water must be allowed to stand for at least 10 hours before sampling.

3.12.1.8 Wastewater sampling

Wastewater samples require special procedures of sampling because of the wide variation in their quality. Either average, mixed samples (per 24 hours, per shift, per hour) or series samplings are performed, or time correlated samples (samples from different places of the wastewater flows taken with regard to the delay period between the individual sampling places). The representative sample is taken, if possible, in the places of the most intensive flow. Sampling of wastewater reservoirs is identical with that of stagnant waters; sampling cocks are sometimes installed in the pipelines.

Special care is needed in taking samples for the determination of dissolved oxygen content in water. These samples are taken into so-called "oxygen containers" (special calibrated sample containers with a ground-in bevelled stopper). During sampling, the sample must not be in contact with the atmosphere since this would affect the analysis, O_2 must be immediately fixed and precipitated. The sample container should be plugged so that no air bubble remains under the plug.

3.12.1.9 Sampling record

A record of details of each sampling should be kept, noting the following points:
— type and purpose of required analyses,
— type of sample (surface, ground-, wastewater, etc.),
— marking of the sampling site,
— sampling date (day and time),
— marking of the sample containers with sample references,
— air temperature, barometric pressure, weather before and after sampling,
— method of sampling and sampling conditions,
— results of determinations during sampling, preservation method,
— quantity of the sample,
— name and signature of the operator taking the sample.

3.12.2 Analysis of samples in situ and their preservation

Some indicators or components of water should be determined directly at the sampling point so that the errors due to sampling and transport of the samples to analytical laboratory are eliminated. Commercial instruments exist which enable one to determine an increasing number of indicators in situ. The first indicator values analysed are odour (sometimes also taste), as well as water temperature, pH, neutralization capacity, electric conductivity, or the content of free CO_2.

If some of unstable components of water are to be determined, and if it is impossible to perform this analysis immediately on the spot or at the latest 12 hours after sampling, it is necessary to preserve the sample, in order to keep the components and their properties as they were at the time of sampling. However, preserved samples should be analysed at the latest on the third day after their sampling. The changes which appear due to the biochemical processes, can be partly eliminated or reduced by cooling the samples to 3–4°C.

Preservatives and preservation methods used with water samples to minimize sample deterioration are summarized in Table 3.69 [8].

Table 3.69. Preservatives and preservation methods used with water samples

Preservative or technique used	Effect on sample	Type of samples for which the method is employed
Nitric acid	Keeps metals in solution	Metal-containing samples
Sulphuric acid	Bactericide	Biodegradable samples containing organic carbon, COD, oil, or grease
	Formation of sulphates with volatile bases	Samples containing amines or ammonia
Sodium hydroxide	Formation of sodium salts with volatile acids	Samples containing volatile organic acids or cyanides
Mercuric chloride	Bactericide	Samples containing various forms of nitrogen or phosphorus, or some biodegradable organics
Cooling (4°C)	Inhibition of bacteria, retention of volatile material	Samples containing microorganisms, acidity, alkalinity, BOD, organic, C, P, and N, colour, odour
Chemical reaction	Fixes a particular constituent	Samples to be analysed for dissolved oxygen using the Winkler method

Preservation of wastewaters is difficult, especially when insoluble solids are present in the sample, as the preservative may have undesirable effects. Preservation of wastewaters by chemical agents is used in those cases when such agents do not influence another determination, and when it is not possible to perform the determination immediately after sampling.

Ideally the samples should be immediately transported into a laboratory, ensuring that they are not heated and exposed to vibrations while en route.

3.12.3 Determination of micropollutants in waters

It has been shown in the last few decades that the conventional methods for the determination of the water quality characteristics are insufficient for the description of all properties of water which are relevant to its usability. Intensive development of industry and chemization of agriculture have introduced new polluting agents which — although not changing the essential parameters of water (such as BOD_5, OD, pH, total dissolved and non-dissolved solids, neutralization capacity, concentration of carbon dioxide, oxygen concentration) usually characterizing its quality — make impossible to use it in the form of drinking or service water. These "new" polluting agents are called micropollutants (trace pollutants) to imply that their concentration is considerably lower than the concentration of classical components. Generally these substances are undesirable, or are needed only in very low concentrations (in contrast to the classic components). It is generally known that distilled water has a very limited application possibilities.

The concentration range of the micropollutants is very broad (mg l^{-1} down to ng l^{-1}). Table 3.70 presents the potentially important micropollutants of waters.

Table 3.70. Potentially important micropollutants of waters

Micropollutants	
Organic (sensory, toxic, surface active substances)	Inorganic
Phenols Solvents (*n*-alkanes, chlorinated *n*-alkanes, etc.) Oils Polycyclic aromatic hydrocarbons Pesticides (fungicides, insecticides, herbicides, rodenticides, acaricides, nematicides): chlorinated hydrocarbons, organic compounds of phosphorus, triazines, carbamates, etc. Tensides Heteroaromatic compounds Polyhalogenated biphenyls Metabolic products	Metals: As, Cd, Cr, Cu Fe, Hg, Mn, Pb, Zn, etc. Anions: CN^-, S^{2-}, etc.

The identification and determination of micropollutants is one of the most important fields of modern analytical chemistry. The analytical me-

thods used should be (in the order of importance)
- selective and specific,
- sensitive, and
- rapid.

The precision of the method is of a secondary importance, an accuracy of ± 20% is often satisfactory.

When classifying the methods for the determination of micropollutants it is necessary to distinguish between routine analysis, series analysis and an analysis aimed at the solution of research problems.

The preparation of analysed samples for the determination of micropollutants has three targets:

1 — separation of interfering components,
2 — concentration, i.e. enrichment of the sample by the component to be determined,
3 — creation of an optimum chemical environment.

The *separation methods* are important in cases where there is no selective method for the determination of the given component, and when the analytic method itself does not ensure proper selectivity.

Concentration is also a very important process. There are very few analytical methods which can be used for the determination of micropollutants in their original concentration. In the course of the sample preparation it is relatively easy to increase the concentration of the component to be determined by 2–3 orders (exceptionally by 5–6 orders).

The prerequisite of a successful *instrumental analysis* is a suitable chemical environment. For example, it is often necessary to replace water by an organic solvent. Here, also those chemical operations are included in which the derivatives of the component to be determined are formed. The aim may consist in increasing the stability, selectivity, sensitivity, etc.

For the sample preparation the following methods are usually employed:
- liquid extraction (particularly for separation and concentration of organic components),
- adsorption on activated charcoal or other adsorbents (separation of organic components),
- ion exchange (concentration of inorganic ions and ionogenic organic substances),
- freezing out (particularly concentration of organic substances),
- distillation (separation and concentration of organic matters),
- evaporation (separation and concentration of metals),
- electrolysis (separation of cations),
- osmotic separation (separation and concentration of ions).

A more recent development is the use of formed plastics, especially open-cell type resilient polyurethanes, for the separation and/or preconcentration of trace species from water samples. The main advantages of these materials are: a quasimembrane structure which allows rapid solid/liquid or solid/gas contact in column operation and the ability to immobilize a variety of reagents as collectors and so act as a highly versatile solid phase support. The resilience of these foams permit their use in special modes such as automated batch pressure or pulsating column operation [10].

The above presented methods are frequently combined. In the case of the determination of organic pollutants in waters, an important preparatory stage is their trapping on activated charcoal in combination with liquid extraction and removal of interfering pollutants by column chromatography [9].

3.12.4 Determination of physical and chemical water characteristics

Most of our impressions of water quality are based on physical rather than chemical or biological characteristics. We encounter water that is cloudy; it is often coloured by tannins and other organic materials picked up from decaying plants; and backwaters, sloughs and swamps are noted for their characteristic odours. Common analyses used to assess the physical impurities in water and wastewater are shown in Table 3.71 [11].

The main chemical parameters commonly determined in water are summarized in Table 3.72 [12]. In addition to these, a number of other solutes, in particular specific organic pollutants, may be determined in connection with specific health hazards or pollution incidents [35].

3.12.4.1 Temperature

Water temperature is measured during water sampling by a precision mercury thermometer with scale divisions 0.1–0.5°C, or an electric thermometer with a resistance or thermistor sensor. For the temperature measurement at different water depths, special submersible thermometers are used [13, 14].

3.12.4.2 Taste

Taste is determined in drinking waters only by sensory methods and is expressed by description only (salty, fresh, bitter, acid, or also the taste is

Table 3.71. Common analyses used to assess the physical impurities in water and wastewater [11]

Test	Use
Temperature	To design and carry out biological and treatment processes; to determine the saturation concentrations of various gases
Odour	To determine if odours will be a problem
Colour	To assess the presence of natural and synthetic colouring agents in water
Turbidity	To assess the clarity of water
Solids	
Total solids TS (total residue dried at 105°C)	To assess the reuse potential of a wastewater and to determine the most suitable type of process for its treatment; TDS tests assess suitability of water sources for public, industrial, and agricultural uses
Suspended solids SS (total non-filtrable residue dried at 105°C)	
Total dissolved solids TDS (= TS − SS) (total filtrable residue dried at 105°C)	
Total volatile solids TVS (residue after igniting the TS at 600°C)	
Volatile suspended solids (residue after igniting the SS at 600°C)	
Settleable solids	To determine those solids that will settle by gravity in a specific time period; test data used for design of sedimentation facilities

given, e.g. metallic, soapy, hard, earthy). Only a sample which is bacteriologically safe and which does not contain any toxic substances and is at room temperature is tasted (i.e. at 20–23°C) [13, 14].

3.12.4.3 Odour

The *odour* of drinking water is determined by sensation at temperature of 20 and 60°C. It is classified descriptively (e.g. putrefactive, musty, phenolic, chlorine, cucumber, etc.), in terms of a six-point scale and a qualitative description of the odour (Table 3.73).

The *level of odour* can be determined by the threshold odour number, P (dilution of the sample to a concentration at which odour is "just detectable"), or by calculation. The level of odour is usually calculated when

Table 3.72. Chemical parameters commonly determined in natural waters and water supplies

Chemical species	Significance in water	Methods of analyses commonly used
Acidic neutralizing capacity	Water treatment, buffering, algal productivity	Titration
Alkali neutralizing capacity	Indicative of industrial pollution or acid mine drainage	Titration
Aluminium	Water treatment, buffering	Photometry, gravimetry, AAS
Ammonia	Algal productivity, pollutant	Photometry
Arsenic	Toxic pollutant	Photometry, AAS
Barium	Toxic pollutant	Flame photometry, AAS
Beryllium	Toxic pollutant	AAS, fluorimetry
Boron	Toxic to plants	Photometry, plasma emission
Bromide	Sea water intrusion, industrial waste	Photometry, potentiometry
Cadmium	Toxic pollutant	Photometry, AAS, polarography
Calcium	Hardness, productivity, treatment	Titration, gravimetry, AAS
Carbon dioxide	Bacterial action, corrosion	Titration, calculation
Chloride	Saline water contamination	Titration, potentiometry
Chlorine	Water treatment	Photometry, filtration
Chromium	Toxic pollutant hexavalent Cr	AAS, photometry, titration, polarography
Copper	Plant growth	AAS, photometry, polarography
Cyanide	Toxic pollutant	Photometry, potentiometry
Fluoride	Water treatment, toxic at high levels	Photometry, potentiometry
Iodide	Water treatment, toxic at high levels	Photometry, potentiometry
Iron	Water quality, water treatment	Photometry, AAS, gravimetry, polarography
Lead	Toxic pollutant	Photometry, AAS, polarography
Lithium	May indicate some pollution	AAS, flame photometry
Magnesium	Hardness	AAS, titration
Manganese	Water quality (staining)	Photometry, AAS
Mercury	Toxic pollutant	Flameless AAS, photometry
Methane	Anaerobic bacterial action	Combustible-gas indicator
Nitrate	Algal productivity, toxicity	Photometry, potentiometry, polarography

Table 3.72 (continued)

Chemical species	Significance in water	Methods of analyses commonly used
Nitrite	Toxic pollutant	Photometry
Nitrogen (albuminoid)	Proteinaceous material	Photometry
Nitrogen (organic)	Organic pollution indicator	Photometry
Oil and grease	Industrial pollution	Gravimetry
Organic carbon	Organic pollution indicator	Oxidation-CO_2 measurement
Organic contaminants	Organic pollution indicator	Activated carbon adsorption
Oxygen	Water quality	Titration, electrochemical
Oxygen demand (biochemical)	Water quality and pollution	Microbiological titration
Oxygen demand (chemical)	Water quality and pollution	Chemical oxidation, titration
Ozone	Water treatment	Titration
Pesticides	Water pollution	Gas chromatography
pH	Water quality and pollution	Potentiometry
Phenols	Water pollution	Distillation, photometry
Phosphate	Productivity, pollution	Photometry, gravimetry
Phosphorus (hydrolysable)	Water quality and pollution	Photometry
Potassium	Productivity, pollution	AAS, flame photometry
Selenium	Toxic pollutant	Photometry, neutron activation analysis
Silica	Water quality	Photometry, plasma emission
Silver	Water pollution	AAS, photometry
Sodium	Water quality, salt water intrusion	AAS, flame photometry
Sulphate	Water quality, water pollution	Gravimetry, turbidimetry
Sulphide	Water quality, water pollution	Photometry, potentiometry, titration
Sulphite	Water pollution, oxygen scavenger	Titration
Surfactants	Water pollution	Photometry
Tannin and lignin	Water quality, water pollution	Photometry
Vanadium	Water quality, water pollution	Photometry, catalytic effect
Zinc	Water quality, water pollution	AAS, photometry

Table 3.73. Assessment of the intensity of drinking water odours

Intensity	Verbal characteristics	Smell sensation
0	None	Non-detectable
1	Very slight	Odour is not detected by the consumer, however, it can be detected by a specialist
2	Weak	Observed by the consumer if his attention is drawn to it
3	Noticeable	Odour is evident and may cause aversion to water
4	Distinct	Odour evokes attention and thus aversion to water
5	Very intense	Odour is so intense that it is impossible to use water for drinking

water contains one odiferous substance and if the concentration of this substance in water is known (c_1) and its threshold concentration (c_2) in mg l^{-1}:

$$P = \frac{c_1}{c_2} \tag{3.120}$$

For example, the threshold concentration of toluene is 0.5 mg l^{-1}, that of pyridine 2.5 mg l^{-1}, benzene 8 mg l^{-1}, phenol 18 mg l^{-1} [14, 15].

3.12.4.4 Colour

The colour of water is determined by a visual comparative method. It is compared with the colour of a solution of dipotassium hexachloroplatinate(IV) and cobalt dichloride, or with a solution of potassium dichromate and cobaltous sulphate. Results are given in terms of mg of platinum per 1 l of water. Colour (or its intensity) usually depends on the pH value of water, and therefore, it should be referred to this value.

The colour of industrial wastewaters is characterized by measuring the absorption spectrum over the whole range of visible radiation [13, 14, 16, 17].

3.12.4.5 Turbidity

Turbidity is determined by comparison with a standard of formazine using turbidimetry [14], or by nephelometry if mainly colloids are measured [13, 14]. The results are expressed by the formazine unit of turbidity (FT).

The *formazine turbidity unit* is defined as the concentration of a standard suspension of formazine. Formazine is a polymeric reaction product of hydrazine sulphate and hexamethylenetetramine. The suspension formed by a reaction of 1.25 mg l^{-1} of hydrazine sulphate and 12.5 mg l^{-1} of hexamethylenetetramine has a turbidity of one formazine unit. Calibration by nephelometric or turbidimetric measurement is carried out so that the relation 1 FT = 1 mg l^{-1} SiO_2 is valid.

3.12.4.6 Total, dissolved and suspended solids

The *total quantity* of all substances (the sum of all dissolved and suspended solids) present in water is determined by evaporation of a water sample, drying of the evaporation residue at 105°C to a constant weight and weighing of the dry residue. Dissolved and suspended solids are separated (mostly by filtration) and the *quantity of dissolved solids* is then determined according to the amount of dry residue of the filtrate.

Suspended solids can be indirectly determined from the difference between the total quantity of solids and dissolved solids, or directly after their separation from a sample of water and after drying.

The residue after annealing of all dissolved or suspended solids is determined by heating at 600°C to constant weight. *The loss on annealing* is the difference in the weight of all dissolved or suspended solids and the weight of corresponding residues after heating.

In drinking waters, the total quantity of substances is determined, in exceptional cases also that of dissolved and suspended solids. In surface waters all dissolved and suspended solids are determined. In wastewaters all suspended and dissolved solids are determined, depending on the character of the sample [13, 14].

Recently, the term "total mineralization" (or just mineralization) is increasingly used in the analyses of water to express the concentrations of all dissolved inorganic substances [14]. It is given by the sum of weight concentrations of all basic anions and cations including the weight concentrations of inorganic non-ionic dissolved solids (particularly silicon, and in the case of mineral waters, of boron too). It is calculated from the results of chemical water analysis. This value of total mineralization does not experimentally correspond to the determined value of the content of dissolved solids. The quantitative relationship between the calculated value of total mineralization and the value of dry weight of inorganic substances depends on the qualitative composition of water and on the relative amounts of the individual components in water.

3.12.4.7 Neutralization capacity

Neutralization capacity was explained in detail in Section 3.4.1.29. In the analytical chemistry of natural, drinking and service waters the following values of neutralization capacity are usually determined:

— basic capacity up to pH 4.5 — $BNC_{4.5}$ (formerly "apparent acidity"),
— basic capacity up to pH 8.3 — $BNC_{8.3}$ (formerly "total acidity"),
— acid capacity up to pH 8.3 — $ANC_{8.3}$ (formerly "apparent alkalinity"),
— acid capacity up to pH 4.5 — $ANC_{4.5}$ (formerly "total alkalinity").

The $BNC_{4.5}$ value is determined by titration of a water sample using a titrant of NaOH of concentration 0.1 mol l^{-1} with Methyl Orange as an indicator, or with a mixed indicator, or by potentiometric titration. The $BNC_{8.3}$ value is determined by titration of a water sample against NaOH of concentration 0.1 mol l^{-1} or 0.01 mol l^{-1} using phenolphthalein as an indicator, or by potentiometric titration.

The $ANC_{8.3}$ value is determined by titration of a water sample against HCl having a concentration of 0.1 mol l^{-1} using phenolphthalein as an indicator, or by potentiometric titration.

The $ANC_{4.5}$ value is determined by titration of a sample of water against HCl having a concentration of 0.1 mol l^{-1} with Methyl Orange as an indicator or a mixed indicator, or by potentiometric titration.

In the operational control of the processes of water treatment the term, *p-value* is used for $ANC_{8.3}$ in mmol l^{-1} (according to the used phenolphthalein), and $ANC_{4.5}$ value is designated *m-value* (Methyl Orange). From these values the concentrations of the various forms of CO_2, occurrence in water can be calculated (free CO_2, HCO_3^- and CO_3^{2-}).

The minimum value of $ANC_{4.5}$ for drinking water is $c_{H^+} = m = 0.8$ mmol l^{-1}. This m-value corresponds to about 50 mg l^{-1} of HCO_3^-.

Determination of $ANC_{7.0}$ or $BNC_{7.0}$ is important for the analysis of industrial wastewaters [14, 16, 18].

3.12.4.8 Chemical oxygen demand

In waters, and especially in wastewaters, a wide spectrum of various organic substances is present, usually at very low concentrations. Since it is practically impossible to determine each of them separately, it was necessary to find a method determining them as groups and expressing thus the total content of these substances and the level of total water pollution.

Indirect methods were sought which would be based on the oxidizability of organic substances. The quantity of oxygen required for oxidation, or oxidizability of water is a measure of the total amount of substances capable of being oxidized, and is one of the important criteria of pollution. For the chemical oxidation of organic substances we refer to "chemical oxygen demand". *Chemical oxygen demand (COD), is that quantity of oxygen which is required for oxidation of organic substances, with the use of oxidizing agents.* There are several such agents which are used in practice, for example, potassium permanganate and potassium dichromate.

For drinking waters and clean surface waters, *Kubel's method* is used. In this case, the substances capable of oxidation are oxidized with boiling potassium permanganate in the presence of dilute H_2SO_4, Mn^{7+} being reduced to Mn^{2+}

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

The consumption of $KMnO_4$ is determined by back titration of the excess $KMnO_4$ with oxalic acid:

$$2MnO_4^- + 5(C_2O_4)^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The results are given in terms of mg l^{-1} of oxygen, and are presented as *COD by Kubel's method, COD with permanganate, COD(Mn).* The method can be used for the determination of COD(Mn) up to 10 mg l^{-1} without dilution and COD(Mn) up to 100 mg l^{-1} with dilution.

For all types of waters (drinking, surface, waste) *oxidation with dichromate* in a strongly acid environment of H_2SO_4 is used (2 hours boiling) the *dichromate method.* The following reaction takes place:

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

The excess of $K_2Cr_2O_7$ is determined by back titration with a ferrous salt with a redox indicator, ferroin:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The reaction is catalysed by Ag^+ ions.

The use of two concentrations (0.04166 mol l^{-1} and 0.004166 mol l^{-1}) of the $K_2Cr_2O_7$ titrant enables determination of COD(Cr) with an accuracy of 2 or 10 mg within the range of COD(Cr) $>$ 50 mg l^{-1} and COD(Cr) 5–50 mg l^{-1}, respectively. If the sample is undiluted the method can be used for waters with a maximum COD(Cr) of 500 mg l^{-1}.

The results are again expressed in mg l^{-1} of oxygen and are presented as COD with dichromate, COD(Cr).

A disadvantage of the dichromate method for the determination of COD(Cr) in very clean waters, i.e. in drinking and unpolluted natural waters is the low reproducibility of the determinations. Therefore, the less efficient permanganate Kubel's method is still used for these waters [15, 16, 19]. However, in the USA only dichromate method has been recommended for these waters since 1955 [13]. For the determination of COD of wastewaters only the dichromate method COD(Cr) is used throughout the world [13, 14].

3.12.4.9 Total organic carbon

The measurement of total organic carbon (TOC) is the best means of assessing the organic content of a water sample [20]. Organic carbon is oxidized to carbon dioxide (CO_2) by heat and oxygen, ultraviolet irradiation, chemical oxidants, or by various combinations of these. The CO_2 may be measured directly by a non-dispersive infrared analyser or it may be reduced to methane and measured by a flame ionization detector in a gas chromatograph or in a TOC analyser thus equipped. The CO_2 may also be titrated chemically.

Some of commercially available TOC instruments are listed in Table 3.74 [14]. Older TOC instruments used a pyrolysis technique to oxidize organics. A newer approach uses a dissolved oxidizing agent promoted by ultraviolet light. Potassium peroxydisulphate ($K_2S_2O_8$) is usually chosen as an oxidizing agent. Phosphoric acid is also added to the sample, which is flushed with air or nitrogen to drive off CO_2 formed from HCO_3^- and CO_3^{2-} in solution. After flushing, the sample is pumped to a chamber containing a UV lamp (UV radiation of 184.9 nm). This radiation produces reactive free radical species which bring about the rapid oxidation of dissolved organic compounds

$$\text{organics} + HO^{\bullet} \xrightarrow{K_2S_2O_6} CO_2(g) + H_2O$$

After oxidation is complete, the CO_2 is flushed from the system and measured with a gas chromatographic detector or by absorption in ultrapure water followed by a conductivity measurement [12].

Table 3.74. A survey of some commercial TOC analysers [14]

Manufacturer	Type	Oxidation principle	Catalyst	Principle of CO_2 determination	Range (mg l^{-1})
Wet oxidation					
Wösthoff	Hydromat TOC	$K_2Cr_2O_7$–H_2SO_4; 160°C	$AgNO_3$	Conductomery with NaOH	0–50 0-500
Bühler	TOC 1	$K_2S_2O_8$–H_2SO_4	$AgNO_3$	Conductometry with NaOH	0–1000
BASF		$K_2S_2O_8$–H_2SO_4	$AgNO_3$	Infrared analyser	0–10 0–1000
Thermal oxidation with a catalyst					
Beckman	915	950°C	Co_3O_4	Absorption in IR region	0–50 0–4000
Maihak	TOC-Unor	600°C	Pd	Absorption in IR region	0–1 0–15,000
Heraeus	Rapid C	1000°C	CuO	Photometric titration	0–0.5 0–10,000
Strühlein	Coulomat 701	900°C	CuO, Pt	Coulometric titration	0–0.1 0–10,000
Delta Scientific	8055	900°C	Catalyst	Nephelometric titration	0–10
Ionics	1218	950°C	Pd	Absorption in IR region	
Carlo Erba	420	950°C	CuO	CH_4-FID	0–25 0–2500
Phase Sep	TOC-sin	900°C	CuO	CH_4-FID	0–0.1 0–10,000
Photochemical oxidation with ultraviolet radiation					
Sybron Barnstead	PHOTOchem TM	Ultraviolet radiation	—	Conductometry	0–20
Maihak	UV-DOC-Unor	Ultraviolet radiation	—	IR analyser	0–10,000

3.12.4.10 Total oxygen demand

In the instrumental total oxygen demand (TOD) test, organic and some inorganic compounds are converted to stable end products, such as CO_2 and H_2O, in a platinum-catalyzed combustion chamber. The TOD is determined by the loss of oxygen in the nitrogen-carrier gas [11].

3.12.4.11 Biochemical oxygen demand

Biochemical oxygen demand BOD is defined as a quantity of dissolved molecular oxygen consumed within a certain time interval during aerobic biochemical degradation of organic substances present in water. This quantity of oxygen is proportional to the quantity of the degradable organic substances present and therefore it is possible to estimate from the BOD value the degree of water pollution. The abbreviations BOD_5 or BOD_{20} express the number of the days during which the oxygen consumption is measured in the given sample.

Biochemical oxygen demand is determined in the original or appropriately diluted solution from difference between the quantity of dissolved oxygen before and after incubation under standard conditions (20°C, absence of air and light, presence of suitable microorganisms, period of incubation 5 days, sometimes 20 days). The determination of oxygen itself is carried out by Winkler's or Alsterberg's method, polarographically, or by using a selective membrane electrode. It is one of common methods and therefore the conditions of determination must be strictly observed. The method is used for the determination of $BOD_5 > 0.3$ mg l^{-1}; without dilution $BOD_5 \leq 6$ mg l^{-1} can be measured [13, 14, 21].

However, the values of BOD_5 determined by this method also include oxygen used for nitrification (i.e. during biochemical oxidation of ammonia nitrogen and nitrites into nitrates) in addition to the oxygen used for carbonization (i.e. biochemical degradation of organic substances). If the determined value of BOD_5 is to correspond to the general definition of BOD, i.e. oxygen demand for degradation of organic substances, and should thus express only (biologically degradable) water pollution, one of the following methods should be used:

- subtract the quantity of oxygen used for the nitrification processes in the sample during a five days long incubation, from the BOD_5 value obtained by the determination with the standard dilution method,
- when treating the samples for the determination of BOD_5 by the standard dilution method it is recommended to add a substance before incubation which prevents nitrification processes. In the past, ammonium chloride was added as a nitrification inhibitor (inhibition by its own substrate); more recently derivatives of allylthiourea and 2-chloro-6-(trichloromethyl)pyridine have been used [21, 22].

For the determination of BOD, respiratory methods based on the principles of gasometric analyses have also been used [14, 23–29]. By means of respirometers the whole course of BOD and respiratory rates of sludges can be followed. Some instruments register BOD continuously [25, 26]. The automatic analyser BOD Sapromat [27] made in Germany operates on the principle of a macrovolumetric respirometer. With some respirometric methods the loss of oxygen is determined directly in the liquid phase via a membrane oxygen electrode (probes).

The BOD_5 value is one of the indicators according to which the purity of surface waters are classified.

It is also determined in sewage waters, and wastewaters from foodstuff and organic industries. It is an important surveillance factor for the correct functioning of biological treatment plants.

3.12.4.12 Dissolved oxygen

The content of oxygen is important for quality evaluation of surface waters, some types of wastewaters, for evaluation and checking of biological treatment plants, as well as for the study of the corrosive properties of water. Oxygen is usually not determined in drinking water, groundwater and the majority of raw wastewaters.

Winkler's method [30] for the determination of dissolved oxygen is based on the reaction of O_2 with $Mn(OH)_2$ ($MnSO_4$ and KOH are added to the sample)

$$Mn^{2+} + O_2 \xrightarrow{OH^-} Mn(OH)_3$$

and subsequent iodometric titration of the higher oxidation state of manganese:

$$2Mn^{3+} + 2I^- \xrightarrow{H^+} 2Mn^{2+} + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Winkler's method cannot be used for the determination of oxygen if nitrites are present in water, since weakly bound oxygen from nitrites oxidizes the iodide ion in the acid medium

$$2HNO_2 + 2HI \rightarrow 2NO + 2H_2O + I_2$$

and thus the quantity of the determined oxygen increases.

By *Alsterberg's modification* of Winkler's method [31] (the method which is used at present) the disturbing effect of NO_2^- is suppressed by reaction with azoimide (produced from sodium azide in the presence of sulphuric acid):

$$3HN_3 + HNO_2 \rightarrow 5N_2 + 2H_2O$$

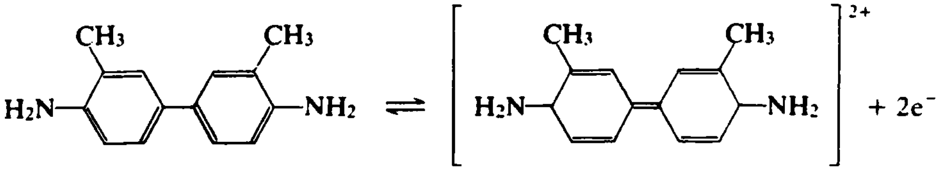
The molecular nitrogen generated does not influence the determination.

In addition to the iodometric method more modern physico-chemical methods are now available, which are also used for the construction of automatic oxygen analysers. These are potentiometric methods with a membrane electrode (probe), based on the measurement of the current generated during the cathode depolarization (hydrogen electrode) with dissolved oxygen. A suitable electrode pair, for example, Ag/Pt covered with a gas permeable membrane, is used [14].

3.12.4.13 Chlorine

Chlorine is determined in drinking waters (which have been disinfected), in wastewaters (where chlorination is required or which contain chlorine-releasing compounds), and in surface waters (in places where there is discharge of wastewaters).

The most frequently used method is *photometric determination with o-toluidine* (4,4′-diamino-3,3′-dimethylbiphenyl) [13, 14, 32]:



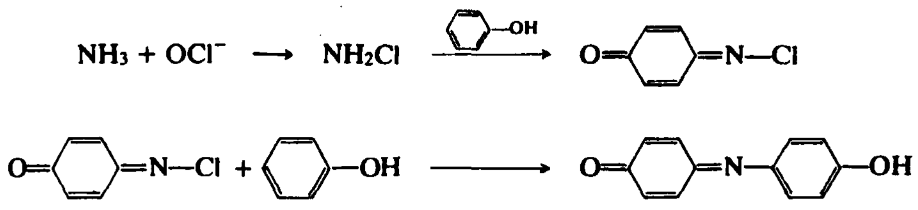
Active chlorine reacts in acid media with *o*-toluidine giving a yellow or even orange colour. The method is used for the determination of active chlorine at concentrations > 0.02 mg l^{-1}.

In the *iodometric determination* in the presence of acetic acid, chlorine releases an equivalent quantity of iodine from the solution of iodide: this is determined by titration with thiosulphate using starch as the indicator. The method is used for the determination of active chlorine at concentrations > 0.1 mg l^{-1} [13, 14, 32].

3.12.4.14 Ammonium ions and ammonia

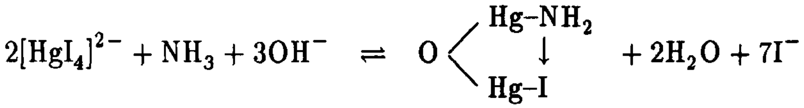
Ammonium ions and ammonia are mostly determined by photometry with phenol and hypochlorite [33, 34] or with Nessler's reagent [13–15, 32].

Ammonia reacts with *sodium phenolate* in an alkaline medium in the presence of *hypochlorite* to form a blue indophenol dye which is stabilized in the presence of Mn^{2+}:



The absorbance at 630 nm is measured. The method is used for the determination of ammonium ions and ammonia at concentrations > 0.02 mg l^{-1} (expressed as NH_4^+).

The photometric determination using Nessler's reagent (alkaline solution of a complex mercury-potassium iodide $K_2[HgI_4]$) is based on:



$$2[HgI_4]^{2-} + NH_3 + 3OH^- \rightleftharpoons O\left\langle\begin{matrix} Hg\text{-}NH_2 \\ \downarrow \\ Hg\text{-}I \end{matrix}\right. + 2H_2O + 7I^-$$

The precipitate formed is yellow-brown. At a low concentration of ammonia and ammonium ions a colloid solution is formed which is suitable for photometric measurements. Absorbance is measured at 400–425 nm (violet filter). The method is used for concentrations > 0.05 mg l^{-1} NH_4^+.

The *distillation method* [13–15] is based on the separation of ammonia from the sample by distillation from an alkaline medium, followed by volumetric or photometric determination of ammonia in the distillate. In the case of volumetric determination the separated ammonia trapped in a receiver with boric acid in the form of $NH_4H_2BO_3$ is titrated against standard H_2SO_4 using a mixed indicator (Methyl Red and Methylene Blue)

$$2NH_4H_2BO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_3BO_3$$

For the determination of ammonium nitrogen, ion-selective electrodes are increasingly used [3, 25, 26].

3.12.4.15 Calcium and magnesium

The total content of calcium and magnesium is determined by *titration with chelatone 3* (the double sodium salt of ethylene diaminetetraacetic acid) at pH 10 using Eriochrome Black T as an indicator (from wine-red to blue) [14, 32, 37]:

$$Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2H^+$$
$$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+$$

Chelatometric determination of calcium itself is carried out with chelatone at pH 12–13 using murexide as the indicator (from red to violet), or a mixture of murexide and fluoroexone and thymolphthalexone (from green to violet-pink). By this method it is possible to determine calcium at concentrations of 10–200 mg l^{-1} [13, 14].

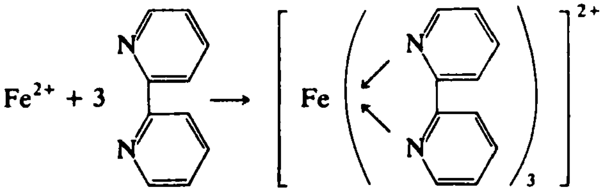
The content of magnesium is calculated from the results of chelatometric determination of the total content of Ca^{2+} + Mg^{2+} and chelatometric determination of calcium. The method is used for the determination of magnesium at concentrations of 5 mg l^{-1}. Magnesium can also be determined by *gravimetry* as magnesium-ammonium phosphate $MgNH_4PO_4$, and by chelatometry (after removal of calcium with oxalate, namely chelatone 3 in the presence of ammonia and ammonium chloride using Eriochrome Black T).

In many standards (e.g. [13]) the hardness of water is also included, defined as a property of water expressed by the sum of the concentrations of calcium, magnesium, strontium and barium.

Recently, the determination of calcium and magnesium by atomic absorption spectrometry is preferred; gravimetric and manganometric determinations after elimination of calcium in the form of calcium oxalate are losing their importance [14].

3.12.4.16 Iron

Iron is determined mostly by the *photometric method* using dipyridyl or thiocyanate [14]. At pH from 3.5 to 8.5 bivalent iron forms an intensively red, stable complex compound with 3 molecules of 2,2'-dipyridyl:



Absorbance is measured at 520 nm (green filter). The method is used for the determination of iron at concentrations in the range 0.05–2 mg l^{-1}.

For iron concentrations > 0.05 mg l^{-1} the *thiocyanate method* is also used with success. After oxidation to the trivalent form (with $KMnO_4$) iron reacts with thiocyanate in acid media forming a red complex $Fe[Fe(SCN)_6]$. Absorbance is measured at 500 nm (blue-green filter).

When determining iron (at concentrations > 0.05 mg l^{-1}) by *atomic absorption spectrometry* the absorbance of the line of iron at 248.3 nm is measured [13].

For the determination of higher quantities of iron (industrial wastewaters) *gravimetry* is used. Fe^{3+} iron is precipitated from ammonium solution in the form of $Fe(OH)_3$, and heated after filtration to form Fe_2O_3. $Al(OH)_3$ co-precipitates with iron. The mixture of Fe_2O_3 and Al_2O_3 is weighed (expressed as R_2O_3 — sesquioxides).

Iron can be determined together with manganese by *polarography*. Polarographic waves corresponding to the reduction of complexes of Fe^{3+} and Mn^{3+} with triethanol are measured [38].

3.12.4.17 Manganese

Manganese at concentrations > 0.02 mg l^{-1} is determined by *photometry* as permanganate after oxidation with peroxydisulphate in the presence of nitric acid and under the catalytic effect of silver ions

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^{-} + 10SO_4^{2-} + 16H^{+}$$

Absorbance is measured at 525 nm (green filter) [14, 32].

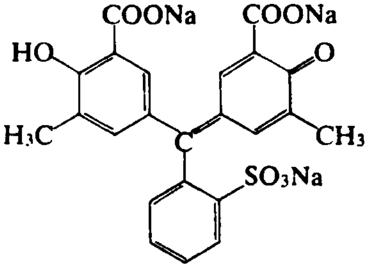
It is also possible to use the technique of *titration colorimetry*; in this case the colour of Mn^{2+} is compared with that of a $KMnO_4$ solution of known concentration which is added from a burette into treated distilled water [13, 14].

When determining manganese (at concentrations > 0.5 mg l^{-1}) by *atomic absorption spectrometry*, the absorbance of the manganese line is measured at 279.5 nm [13].

3.12.4.18 Aluminium

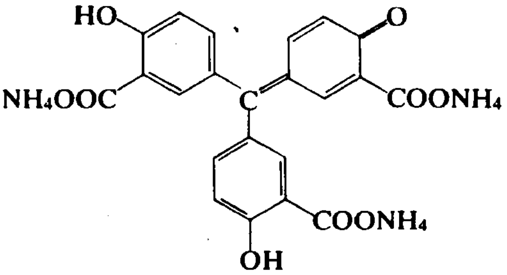
Aluminium is determined particularly in waters which have been treated with aluminium salts, and in the inspection of water station operation; it is determined by *photometry* with eriochrome cyanine R or with aluminon [13, 14].

Eriochrome cyanine R (sodium salt of 4-hydroxy-5, 5′-dimethylfuchson-3,3′-dicarboxylic-2″-sulphonic acid)



forms a violet complex with aluminium ions. Absorbance is measured at 535 nm. The method is used for the determination of aluminium at concentrations > 0.05 mg l^{-1}.

Aluminon (ammonium salt of auritricarboxylic acid)



turns red with aluminium ions at pH 4. The colloidal colour system is stabilized with gum arabic. Absorbance is measured at 525 nm (green filter). The method is used for the concentration range from 0.05 to 1 mg l^{-1} of Al without volume correction. In wastewaters aluminium is determined by *gravimetry.*

When using atomic absorption spectrometry the absorbance of the aluminium line is measured at 309.3 nm.

3.12.4.19 Copper

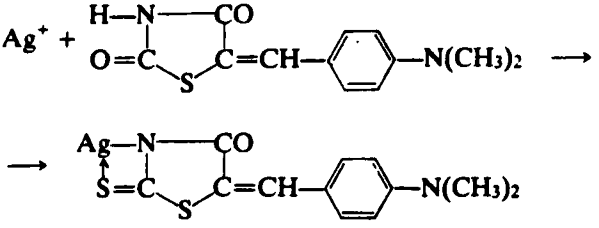
Copper is frequently determined by *photometry with dicupral* (tetraethyltiuram disulphide) $(C_2H_5)_2N-CS-S-CS-N(C_2H_5)_2$ with which Cu^{2+} forms a yellow or cinnamon brown complex. Absorbance is measured directly or after extraction of the complex into chloroform at 435 nm using a violet filter. The method is used for concentrations of copper > 0.01 mg l^{-1} [14, 15].

For waters with disturbing effects, atomic *absorption spectrometry* is recommended (at concentrations > 0.01 mg l^{-1}); absorbance is measured at 324.7 nm [13].

Polarography is recommended for the determination of copper when accompanied by other metals [39].

3.12.4.20 Silver

Silver is determined by *photometry* with *p*-dimethylaminobenzylidene rhodanine



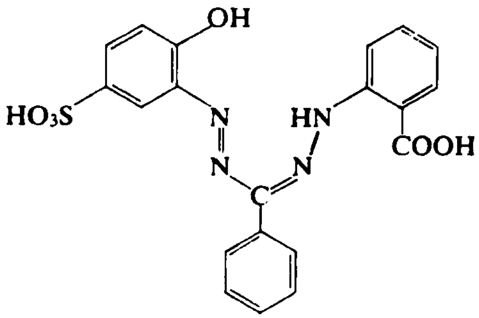
to form a red colloid-dispersed precipitate. Absorbance of the colloidal solution is measured at 530 nm (green filter). This method is used for the determination of silver at concentrations > 0.03 mg l^{-1} [14, 32].

When using *atomic absorption spectrometry* (for concentrations of Ag > 0.01 mg l^{-1}) silver is concentrated by evaporation or extraction. The absorbance of the silver line is measured at 328.1 nm [13].

3.12.4.21 Zinc

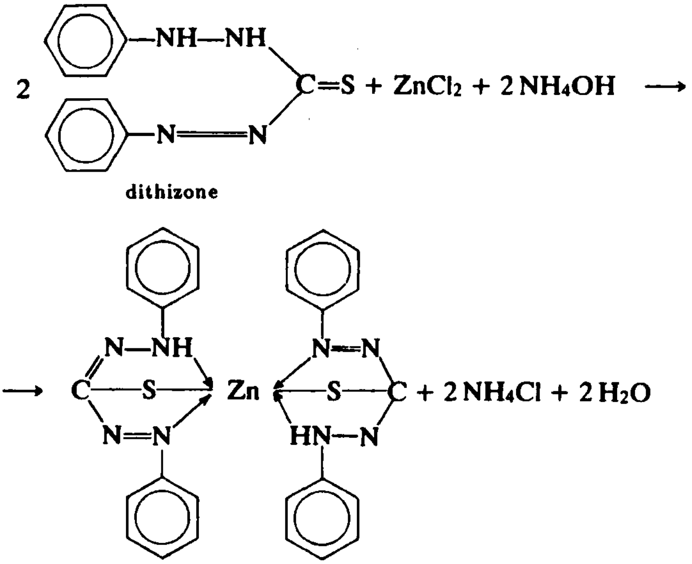
Zinc is determined by *photometry with zincon* (2-carboxy-2′-hydroxy-5′-sulphoformazyl benzol) or *dithizone.*

When using zincon for the determination, zinc is retained on a strongly basic anion exchanger (e.g. Dowex II), and it is then determined by photometry with zincon at pH 8.5–9.5:



— a blue complex is formed, and the absorbance is measured at 625 nm (red filter). The method is used for the determination of zinc at concentrations > 0.1 mg l^{-1} [15, 40].

When determining zinc with dithizone (diphenylthiocarbazone) red zinc dithizonate is formed:



Absorbance is measured at 538 nm. The method is used for the determination of 0.005–0.030 mg l^{-1} of zinc [15].

Polarography is used for zinc concentrations of 1 mg l^{-1} [15]. In this case, zinc(II) ions are reduced to the metal on a dropping mercury electrode.

For concentrations of zinc > 0.010 mg l^{-1} *atomic absorption spectroscopy* is used (the zinc line absorbance is measured at 213.9 nm) [13].

3.12.4.22 Cadmium

For the determination of cadmium at concentrations > 0.005 mg l^{-1} the *photometric method* with dithizone is used. The Cd^{2+} ions are extracted in the presence of potassium sodium tartarate (Seignett's salt) from a strongly alkaline medium with a solution of dithizone in tetrachloromethane. The extract of cadmium dithizonate is red. Absorbance is measured at 518 nm (green filter) [13].

The method of *atomic absorption spectrometry* is very convenient for concentrations ~ 0.002 mg l^{-1}. Cadmium is concentrated by evaporation or extraction in the form of a complex salt of 1-pyrrolidine dithiocarboxylic acid into methyl isobutyl ketone. The absorbance of the cadmium line is measured at 228.8 nm [13].

Polarography can be used for the determination of cadmium with other metals (Cu, Ni, Zn) at concentrations of tenth and even hundredths mg l^{-1}.

3.12.4.23 Mercury

When using *atomic absorption spectrometry* the compounds of mercury are reduced to mercury, which is then expelled by an air stream. Absorbance of the mercury line is measured at 253.7 nm. The method is used for the determination of mercury at concentrations > 0.0002 mg l^{-1} [13].

In the case of *photometric techniques* for the determination of mercury (at concentrations from 0.05 to 1.0 mg l^{-1}) primarily the dithizone method is used (chloroform extract of dithizonate becomes orange) [13].

Organic compounds of mercury must be degraded prior to mineralization.

3.12.4.24 Lead

For the determination of lead in drinking and surface waters *photometry* is preferred. Lead ions form a colourless compound extractable with tetrachloromethane with diethyldithiocarbamate $C_5H_{10}NS_2Na$ at pH 11–12.5, which reacts with copper ions to form yellow-brown copper diethyldithiocarbamate. Absorbance is measured at 435 nm (violet filter). The method is used for the determination of lead at concentrations of > 0.01 mg l^{-1} [13].

When using *atomic absorption spectrometry* lead is concentrated in the form of a complex salt of 1-pyrrolidine dithiocarboxylic acid in methyl isobutyl ketone. Absorbance of the lead line is measured at 283.8 or 217 nm. The method is used for concentrations of lead > 0.01 mg l^{-1} [13].

For the determination of lead in all types of waters *polarography* is recommended for concentrations of 0.05–1.0 mg l^{-1} of Pb.

3.12.4.25 Chromium

For the determination of hexavalent chromium (at concentrations > 0.01 mg l^{-1}) a *photometric method* with diphenylcarbazide (C_6H_5–NH–NH–CO–NH–NH–C_6H_5) is used (red-violet colour). Absorbance is measured directly or after extraction into amyl alcohol at a wavelength of 540 nm (green filter) [19, 41].

For higher concentrations of chromium (1–40 mg l^{-1}) iodometric titration can be used (CrO_4^{2-} and $Cr_2O_7^{2-}$ oxidize iodide to iodine in acid media, the latter being determined by titration) [19].

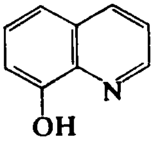
For all types of waters *polarography* can be used. For the determination of Cr^{6+} *atomic absorption spectrometry* can also be used [13].

3.12.4.26 Barium

Barium at concentrations > 1 mg l^{-1} is determined by *flame spectrometry* (emission is measured in the region of 489 nm) after being first concentrated by precipitation with calcium in the form of carbonate [16].

3.12.4.27 Vanadium

Vanadium at concentrations > 0.002 mg l^{-1} is determined *photometrically*. The determination is based on the reaction of vanadium with 8-hydroxyquinoline



in an acid medium to form a yellow-brown or even black complex extractable into chloroform. Absorbance is measured at 550 nm [42].

3.12.4.28 Selenium

In the *photometric determination*, tetravalent selenium reacts with 3,3'-diaminobenzidine in the acid medium to produce yellow piazoselenol, extractable into toluene. Absorbance is measured at 420 nm (violet filter). The method is used for determination of selenium at concentrations > 0.005 mg l^{-1} [13].

3.12.4.29 Arsenic

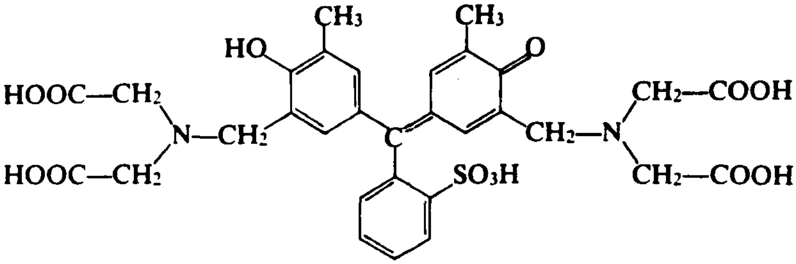
In the *photometric determination* of arsenic, arsenic trihydride formed by reduction of the compounds of arsenic (mostly of arsenate) with nascent hydrogen reacts in the medium with pyridine with silver diethyldithiocarbamate to produce a red colour. Absorbance is measured at 560 nm. The method is used for concentrations of arsenic > 0.05 mg l^{-1}. For the determination of lower concentrations the sample should be first concentrated by evaporation [13].

3.12.4.30 Fluorides

Fluorides are determined primarily by *photometry* using *zirconium alizarine* or *Xylenol Orange*.

Fluorides with zirconium ions form a colourless complex $[ZrF_6]^{2-}$ which is more stable than Zr^{4+} with alizarine (red), therefore, an equivalent amount of this dye is destroyed when F^- solutions are added. Reduction of the intensity of the solution colour measures the concentration range from 0.05–2.5 mg l^{-1} [14, 15].

Zirconium ions form a red chelate with Xylenol Orange



(medium: 0.1–3 mol l^{-1} HCl) which is decolourized with F^- ions to form fluorine-zirconium-xylenol orange. Absorbance is measured at 540 nm against a reference solution. The method is used for the determination of fluorides at concentrations > 0.02 mg l^{-1} [43].

The *ion selective membrane electrode* (the membrane is of lanthanum fluoride) is becoming more widely used for the determination of fluorides at concentrations > 0.02 mg l^{-1} [13, 14, 43–46].

Fluorides can also be determined by *titration* with thorium nitrate using sodium alizarinsulphonate as an indicator [45].

3.12.4.31 Chlorides

Chlorides are determined in all types of waters particularly by *argentometry* or by *mercurimetry.* For turbid or intensively coloured solutions, a potentiometric indication of the end point is used.

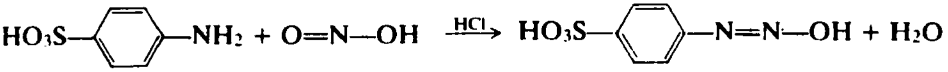
The *argentometric determination* involving titration against $AgNO_3$ is carried out in neutral or slightly alkaline media (pH 6.5–10.5). The end point is indicated visually with formation of the red-brown precipitate of Ag_2CrO_4 which is more soluble than the precipitate of AgCl, or potentiometrically (silver indication electrode, calomel reference electrode). The method is used for the determination of chlorides at concentrations > 4 mg l^{-1} [13, 14].

The *mercurimetric determination* with $Hg(NO_3)_2$ titrant is carried out at pH 2.5 ± 0.1 using diphenylcarbazon as the indicator of the end point, forming a violet compound with excess of mercury ions. The method is used for the determination of chlorides at concentrations > 4 mg l^{-1} [13, 14].

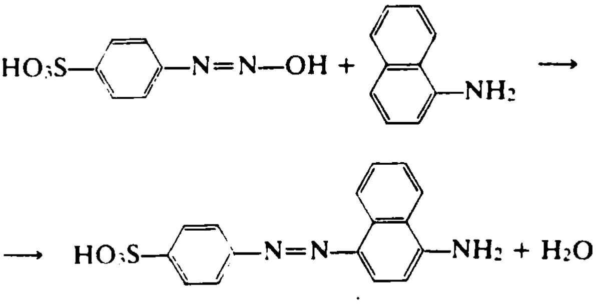
3.12.4.32 Nitrites

Nitrites at concentrations of 0.002–0.6 mg l^{-1} are determined *photometrically with sulphanilic acid and α-naphthylamine.*

The determination is based on diazotization of sulphanilic acid

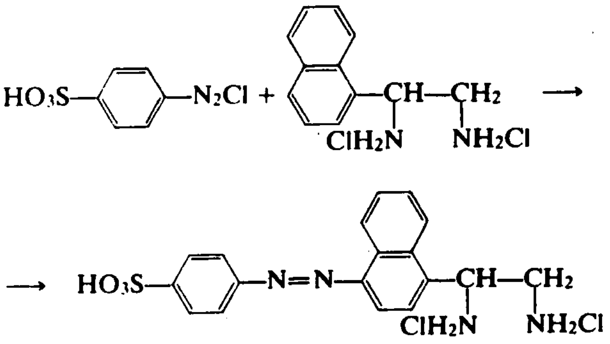


and on coupling of the diazonium salt formes with α-naphthylamine to form a red-violet azo dye suitable for photometry



Absorbance is measured at 550 nm (green filter) [13, 14, 73].

At present, the most widely used method is that which employs *N*-(1-naphthyl)ethylenediamine dihydrochloride

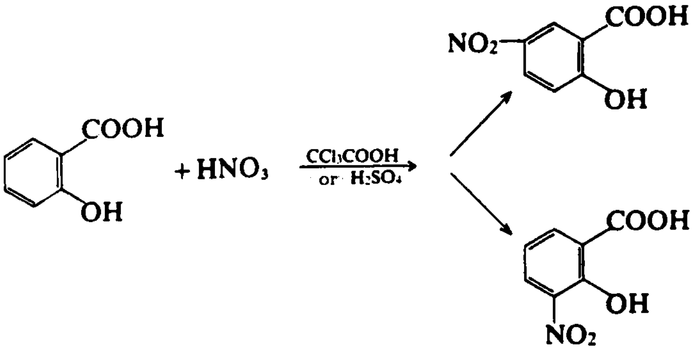


as the coupling agent, which gives rise to a red azo dye.

The intensity of the colour produced is proportional to the concentration of nitrites in the sample. Without dilution, the method is suitable for the determination of nitrites at concentrations from 0.05 to 0.5 mg l^{-1} [13, 14, 16, 36].

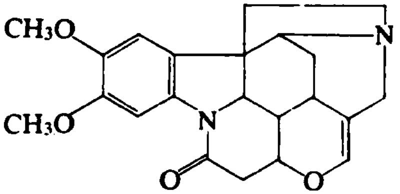
3.12.4.33 Nitrates

For the determination of nitrates at concentrations > 0.5 mg l^{-1} the *photometric method with sodium salicylate* is used. It is based on the reaction of NO_3^- with sodium salicylate in the presence of trichloroacetic or sulphuric acid. After alkalization yellow salts of nitrosalicylic acid are formed:



Absorbance is measured at 410 nm (violet filter) [14, 48].

For the photometric determination of nitrates their reaction with *brucine*



can also be used, in the presence of H_2SO_4, to form yellow nitro compounds. The range of the detectable concentration without sample dilution is 1–20 mg l^{-1} of NO_3^-.

The standard methods of water analyses used in various countries employ other agents for direct spectrophotometric determination of nitrates, for example, chromotropic acid (4,5-dihydroxy-naphthalene-2,7-disulphonic acid) [13] or 2,6-dimethylphenol and *p*-fluorophenol [49]. As well as the method with salicylate the method with chromotropic acid is also used in the standard methods.

In addition to the absorption photometric determination of nitrates in the visible region, absorption spectrophotometric methods in the UV region are also used. This method is one of the standard methods, e.g. [13, 32], but it is recommended only for very pure waters (drinking or unpolluted natural waters) [50, 51].

Nitrates can also be determined after their reduction with zinc or cadmium amalgam to nitrites, employing *photometry with sulphanilic acid and α-naphthylamine*. In the case of polarographic determination nitrates are reduced on the mercury droping electrode in a weak acid medium under catalytic effects of uranyl ions.

For pure waters a potentiometric method for the determination of nitrates is coming more into use, with a nitrate ion-selective electrode [13, 15, 35, 36, 43, 44, 52].

3.12.4.34 Carbon dioxide and carbonates

The quantity of *free carbon dioxide* in water can be calculated from the determination of basic neutralization capacity up to pH 8.3 ($BNC_{8.3}$, total acidity). In this case, free CO_2 reacts with an alkaline titrant to form hydrogen carbonate ($CO_2 + OH^- \rightarrow HCO_3^-$). Provided that the whole basic neutralization capacity up to pH 8.3 consists only of free carbon dioxide, its weight concentration ($c(CO_2)$) can be calculated from the following equation:

$$c(CO_2) = BNC_{8.3}.44 \qquad (\mathrm{mg\ l^{-1}}) \qquad (3.121)$$

where $BNC_{8.3}$ is the basic neutralization capacity of water up to pH 8.3 ($\mathrm{mmol\ l^{-1}}$).

Determinaaleadtion of *carbonates and hydrogen carbonates* is based on the assumption that the acid neutralization capacity is formed only by ionic forms of CO_2, or hydroxide ions. The content of HCO_3^-, CO_3^{2-} and OH^- is calculated from the results of the determination of acid capacity (alkalinity) by titration to pH 4.5 and 8.3 using the relationships presented in Table 3.75 (the numbers 61, 60 and 17 are the molar weights of HCO_3^-, CO_3^{2-} and OH^-, respectively) [13, 14, 21].

Table 3.75. Relationships for calculation of the concentration of HCO_3^-, CO_3^{2-} and OH^- ions in water

Ratio of acid capacity of water to pH 4.5 (m) and to pH 8.3 (p)	HCO_3^-		CO_3^{2-}		OH^-	
	$\mathrm{mmol\ l^{-1}}$	$\mathrm{mg\ l^{-1}}$	$\mathrm{mmol\ l^{-1}}$	$\mathrm{mg\ l^{-1}}$	$\mathrm{mmol\ l^{-1}}$	$\mathrm{mg\ l^{-1}}$
$p = 0$	m	$m.61$	0	0	0	0
$2p < m$	$(m - 2p)$	$(m - 2p).61$	p	$p.60$	0	0
$2p = m$	0	0	p	$p.60$	0	0
$2p > m$	0	0	$(m - p)$	$(m - p).60$	$(2p - m)$	$(2p - m).17$
$p = m$	0	0	0	0	p	$p.17$

The content of aggressive CO_2 can be determined by the *Heyer marble test.* In this case aggressive CO_2 dissolves calcium carbonate (marble) to form hydrogen carbonate and thus the acid neutralization capacity of water increases up to pH 4.5 (total alkalinity). The increase of the acid neutralization capacity is proportional to the content of the originally present aggressive CO_2 [14, 21].

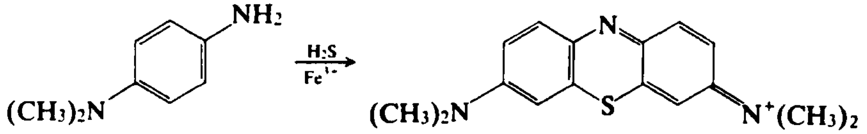
3.12.4.35 Sulphates

Sulphates (at concentrations > 50 $\mathrm{mg\ l^{-1}}$) are determined by *titration* with lead(II) nitrate. The end point is indicated with dithizone (from green to violet-red) [14, 32].

For the determination of higher quantities of sulphates a *gravimetric method* is used (weighable form of $BaSO_4$) [13, 14, 32]. In the case of lower concentrations *polarographic* [54] or *nephelometric methods* are used [13].

3.12.4.36 Sulphides and hydrogen monosulphide

Sulphides and hydrogen monosulphide at concentrations > 0.05 mg l^{-1} are determined *photometrically* with N,N-dimethyl-p-phenylenediamine. A sensitive and selective determination is based on the production of Methylene Blue during the reaction of hydrogen monosulphide with the above reagent in the presence of Fe^{3+}



Absorbance is measured at 600 nm (red filter) [13, 14].

For the determination of higher amounts of hydrogen monosulphide (0.5–20 mg l^{-1}) and sulphides a *iodometric method* can be used. In this case sulphides and hydrogen monosulphide are separated in the form of a mixture of insoluble CdS and $Cd(OH)_2$. The precipitate is separated, and known amounts of iodine and HCl are added. Iodine required for oxidation is determined from the difference between the added and remaining quantity of iodine, by titration with thiosulphate [13, 14].

For the determination of sulphides thin-layer chromatography [55, 56] is used, as well as spectrophotometry in the IR region [57], AAS [58], and a sulphide ion selective electrode [59–61].

3.12.4.37 Phosphates

The most important forms of phosphorus are inorganic orthophosphates which are determined *photometrically with molybdenum.* Orthophosphates react with ammonium molybdate in the presence of sulphuric acid and antimony ions to form heteropolyacids — phosphomolybdic acid. By reduction with ascorbic acid the yellow complex of phosphomolybdic acid changes into a solution of Phosphomolybdic Blue which can be determined photometrically:

$$PO_4^{3-} + (NH_4)_2MoO_4 \rightarrow H_4P(Mo_{12}O_{40}) \rightarrow \textit{Phosphomolybdic Blue}$$

Absorbance is measured at 690 nm (red filter). The method is used for the determination of soluble inorganic orthophosphates at concentrations > 0.05 mg l^{-1}. For low concentrations (> 0.005 mg l^{-1}) the extraction of Phosphomolybdic Blue into butyl alcohol can be used [14, 16, 62].

In a similar way hydrolysable polyphosphates and total phosphorus can also be determined after being first treated. Total quantity of phosphorus can be determined by gravimetry after mineralization of the sample in the presence of MgO by precipitation of ammonium molybdate in the form of ammonium molybdate phosphate, $(NH_4)_3PO_4.12MoO.2HNO_3.H_2O$. The form for weighing (after heating at 400°C) is $P_2O_5.24MoO_3$.

3.12.4.38 Cyanides

The total quantity of cyanides can be determined by their *distillation* from water containing diluted sulphuric acid. In this way, it is possible to degrade even the most stable ferri- and ferrocyanides. Released HCN is trapped in a solution of alkaline hydroxide and the determination of cyanides in the distillate can be carried out either *photometrically*, or by *argentometric titration.*

In *photometric titration* cyanide ions are transformed into cyanogen chloride in the course of the reaction with chloroamine to form a red-violet compound in the presence of pyridine and barbituric acid at pH 4–5. Absorbance is measured at a wavelength of 580 nm. The method is suitable for the determination of cyanides at concentrations > 0.002 mg l^{-1} [14, 19, 63, 64].

Free hydrogen cyanide, CN^- ions and complex cyanides of cadmium, zinc, copper and part of complex cyanides of nickel can be determined by a photometric method directly in a water sample without distillation.

For the determination of higher quantities of cyanides (2–40 mg l^{-1}) *titration against silver nitrate* can be used. After transforming all cyanides into the complex $[Ag(CN)_2]^-$ the excess of silver ions is indicated by *p*-dimethylbenzilidene rhodanine which reacts with silver to form a red precipitate [14].

Cyanides can also be determined by membrane ion-selective electrodes using direct potentiometry (argentoiodide electrode or an electrode with a mixture of $AgI–Ag_2S$). The principle of the response to cyanides in the case of the most frequently used ion-selective electrodes for CN^- ions consists in the dissolution of AgI according to the following reaction:

$$AgI(s) + 2CN^- \rightarrow [Ag(CN)_2]^- + I^-$$

The electrode potential is determined by the activity of iodides released from the surface of the membrane electrode [65].

3.12.4.39 Extractable substances

The term “extractable substances” denotes those substances which are extracted under certain conditions by an organic solvent from a sample of sludge (or water), and which then remain after elimination of the solvent and drying. This group includes oils (both mineral and plant), fats, soaps, waxes, heavy hydrocarbons, tar, etc. The results of the determination of extractable substances are given in mg kg^{-1} or mg l^{-1} in liquid samples (it is necessary to state the method used).

Since no selective organic solvents exist into which particular types of substances would be transferred, their mixture is used for determination. For the determination of total amount of extractable substances, *weighing* and *pycnometric methods* are frequently used, employing tetrachloromethane as the extraction agent. Since the extractable substances are determined by the various recommended weighing methods after elimination of the solvent and drying at 80°C (except the determination of tar and mineral oils with a high boiling point, when drying takes place at 105°C), the extractable substances with a lower boiling temperature or the volatile substances are not included in these results.

For the determination of extractable substances *chromatographic methods* are becoming ever more important, particularly *gas chromatography* or gas chromatography with *mass spectrometry* [14].

3.12.4.40 Oil and oil products

The determination of oil products in waters can be classified into weighing, volumetric, spectrophotometric and chromatographic methods [14].

The *weighing methods* belong to the oldest and most frequently used techniques in the past. They are based on the extraction of oil products from a sample of water with a solvent and the subsequent determination of the weight of extracted substances after distillation [13–15, 66]. The *volumetric methods* are based on distillation of the volatile oil substances from water and measuring their volume after condensation [67, 68].

Recently, *thin-layer* and *gas chromatographies* are becoming more and more used for the determination of oil products in waters [15, 66, 69–71].

Oil and oil products are commonly determined *spectrophotometrically* in the IR and UV regions [14].

Spectrophotometry in the IR region is based on the extraction of oil products in the sample using a suitable solvent, separation of the extracted polar substances from the extract and recording of the spectrum within the frequency range 3.150 to 2.750 cm^{-1}. To evaluate the record a calibration graph of the substance separated from a sample of standard oil substance and a mixture of hydrocarbons is used. Often, also calculation is used. The method can be used for the determination of oil substances at concentration > 0.1 mg l^{-1} in the UV region; absorbance of extracted polar substances is measured at a wavelength of 270 nm [14, 15].

3.12.4.41 Phenols

Monovalent phenols are separated from water by distillation with water vapour. At higher concentrations (> 50 mg l^{-1}) they are determined by *bromometry* based on the production of tribromo derivatives. The non-reacted residue of the brominating agent is determined by *iodometry* [14, 49]. When determining low concentrations, *photometric methods* with 4-aminoantipyrine are applied (for concentrations > 0.002 mg l^{-1}), or those using *p*-nitraniline (for concentrations > 0.03 mg l^{-1} and concentration range from 0.005 to 0.050 mg l^{-1}).

The determination with *4-aminoantipyrine* is carried out in alkaline media in the presence of hexacyanoferrate(III) and after extraction of the dye into chloroform. Absorbance of the extract is measured at 460 nm (blue filter) [13, 15, 72].

Photometric determination with diazotized *p-nitraniline* in an alkaline medium is carried out either directly (for higher concentrations) or after extraction of the dye into butyl alcohol (for lower concentrations). In the case of the direct determination absorbance is measured at 470 nm (blue filter) and in the case of the extraction, determination at 530 nm (green filter) [14, 37, 49, 73].

Multivalent phenols are relatively non-volatile when compared with the monovalent one. The method for the determination of pyrocatechol by Fe^{2+} ions has found wider application possibilities. The reaction of pyrocatechol with Fe^{2+} in acid medium in the presence of sulphite and tartrate gives a violet complex. Without dilution 1–7 mg l^{-1} of multivalent phenols can be determined, expressed as pyrocatechol [14].

3.12.4.42 Tensides

Lower concentrations of *anion tensides* (i.e. alkylsulphates, alkylsulphonates and alkylarylsulphonates) are determined by *photometry with Methylene Blue*. The complex of Methylene Blue–tenside is extracted with chloroform in an alkaline medium. The absorbance of the chloroform extract is measured at 610 nm (red filter). This is the method for the determination of anion tensides at concentrations from 0.01 to 0.8 mg l^{-1} [14, 74].

For the determination of higher concentrations of anion tensides (more than 3 mg l^{-1}) the volumetric method by double phase titration using a visual indicator has been suggested [75, 76]. Potentiometric titration as well as ion selective electrodes are also used [77].

The main types of *non-ionic tensides* are adducts of higher alcohols, alkylphenols and aliphatic acids with ethylene oxide. They are determined mostly by photometry, e.g. by using tungstic-phosphate acid and hydroquinone. Non-ionic tensides are precipitated in the presence of calcium chloride with 2% tungstic-phosphate acid. After centrifuging, the dried precipitate is dissolved in concentrated H_2SO_4 and the red-brown colour caused by addition of hydroquinone is measured at 500 nm [14, 15, 21].

3.12.4.43 Humic substances

For the determination of humic matters *oxidimetric* (non-specific) and *spectrophotometric methods* in the visible and UV regions are recommended. In particular, the spectrophotometric method employing extraction of humic substances at a low pH values into pentanol and reextraction from pentanol with NaOH is recommended [14, 32].

The humic substances can also be determined by *gravimetry*, e.g. after precipitation with lead(II) nitrate, by determination of the weight of the precipitated humins and subtraction of the separately-determined content of the heavy metal [78].

3.12.5 Automated monitoring of waters

Automated analysis of waters can be performed either by *contact* or *contactless measurements.*

A contactless system is based on the measurement of electromagnetic radiation from the water surface caused by the component to be determined. This method can be used for the determination of temperature, turbidity, chlorophyll, oils, etc.

The *contact measurements* can be carried out using both *in situ* and *on line* methods. The difference is that whereas in the case of the *in situ* measurement the sensors are immersed directly in the investigated water, in the case of the *on line* measurement the sample of water is transported by a pump into a building sited on the bank or to a sensor situated in another place.

The *in situ* method is used to measure water temperature, electrolytic conductivity, dissolved oxygen, pH and some other components which can be determined by ion-selective electrodes (e.g. chlorides, ammonium ions).

The *on line* system measurements can be divided into the following two groups:

(1) a water sample reaches the sensors *without preliminary treatment.* This system is used as in the case of the *in situ* sensors, and can involve apparatus for the measurement of turbidity, absorption of UV radiation, fluorescent oil indicators, etc.

(2) a water sample is taken continuously and reaches the sensor *after being treated.* This group includes colorimetric or photometric analysers and the majority of ion-selective electrodes.

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4 Biology of water

4.1 Foundations of the ecology of aquatic organisms

The need for water is a common feature of all living organisms since water represents the only and indeed the essential environment in which the processes of life can take place. A cell as the fundamental and functional unit of living mass cannot grow and develop without a supply of water. In the case of actively growing cells, this amount is only rarely lower than 80% of live weight, regardless of whether it concerns microbes or multicellular macroorganisms. In this sense, water is a unifying component. However, there is a considerable versatility with respect to the relationship of living organisms to water as a component of the environment, particularly the nature and extent of the water in which the organisms live. Some organisms require water for their existence as the predominating environmental factor, others are satisfied just with a short contact with water, and some are able to utilize water in a mostly dry environment. As well as purely aquatic or land organisms, species with various transition positions between these two extremes also exist in nature. Many live in water only in a certain zone of the transition from aqueous to land environment all their life. If a specialization to the aqueous environment appears, it is the more strict the more the organism is at a higher stage of development. And still, among microorganisms receiving nutrients only from water and aqueous solutions and therefore unable to reproduce on the land and to grow without a direct contact with water, there are also species which are in some ways adapted to the life on land. On the other hand, among the typical and specialized aquatic animals such as fish, primitive species occur sporadically, which are even able to survive temporary periods of drought in swamps.

The fact that many organisms are not explicitly aquatic or terrestrial corresponds to the present konwledge of the evolutionary changes in Nature.

Life originally existed in the sea, and only at a certain stage of evolution land started to be inhabited, including adaptation to the life in fresh waters. Afterwards, however the evolution did not continue only in the direction from water to land, but also to some extent vice versa. Some of the present fresh water species comes directly from the sea and others come from land organisms which again adapted to the life in water. It is assumed that the evolution of some species was continued by their return to the sea.

4.1.1 Characteristics of the aqueous environment

In common with all the habitats of living organisms, also the aqueous environment can be characterized by its physical and chemical properties; the main aspects are now discussed in some detail.

4.1.1.1 Temperature

Aquatic organisms are mostly exposed to smaller temperature changes than the land organisms. The fact that water in Nature undergoes much smaller temperature deviations than the air is primarily due to specific physical properties of water (anomalies; see Section 3.2).

One crucially important factor for aquatic life in large enclosed areas of water such as lakes or reservoirs is that they do not freeze to the bottom, particularly because of the anomalous changes in the density of water when its temperature approaches zero.

4.1.1.2 Concentration of oxygen and carbon dioxide

Oxygen is required for breathing of aerobic organisms which eliminate CO_2. Oxygen enters water via diffusion from the atmosphere, or is released from photosynthesizing aquatic organisms binding simultaneously CO_2, and its reduction to organic compounds. Thus, both gases appear in two fundamental processes of life. The concentration of dissolved oxygen, which is of special importance for aquatic organisms, depends on both physical and biological factors.

Physical factors are the water temperature and partial pressure of oxygen in the atmosphere. These change quite markedly due to the effect of climatic and physical conditions but their mutual dependence is well known and can be determined quite simply. Figure 4.1 illustrates the relationship between the concentration of dissolved oxygen and water temperature at normal atmospheric pressure; it is evident that with increasing water temperature the amount of dissolved oxygen decreases significantly. The

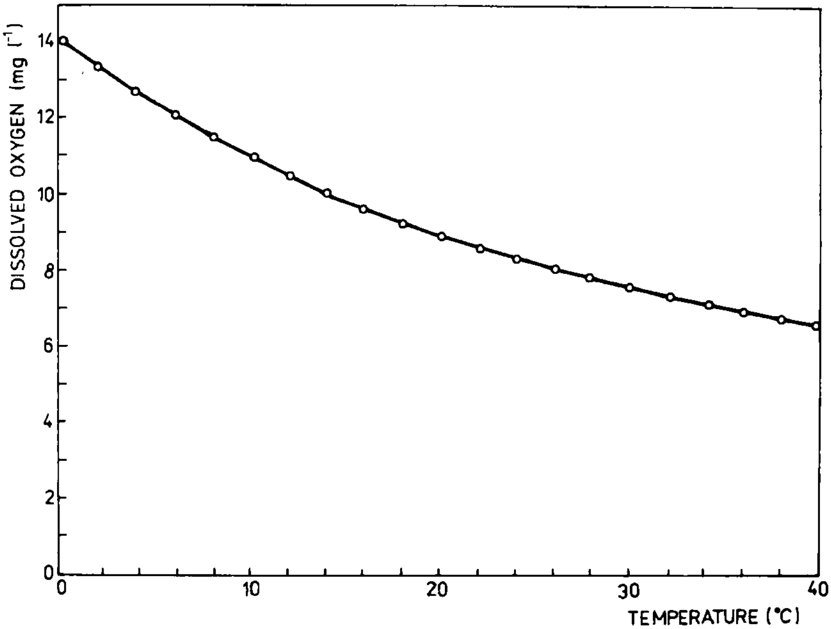

Fig. 4.1. Dependence of dissolved oxygen content on water temperature

oxygen content decreases with a decrease in atmospheric pressure, which changes in dependence on the climatic conditions and altitude. If the content of dissolved oxygen is in equilibrium with the atmospheric oxygen, then the water is saturated with oxygen. Under natural conditions the content of O_2 in saturated water ranges from 7 to 15 mg O_2 l^{-1} of water.

A more complicated situation is encountered in water containing living organisms; the O_2 concentration can be remarkable increased or decreased due to the biological activity. The amount of oxygen from photosynthesis depends particularly on the amount of photosynthesizing organisms, intensity and duration of allumination, and water temperature. Biologically, oxygen is consumed primarily during breathing and microbial degradation of organic matter. The rate of consumption of oxygen depends primarily on the content of well-degradable organic matter in water.

The CO_2 content in water is influenced by the same microorganisms as in the case of O_2 but in an opposite direction. Free CO_2 is present in water mostly as a dissolved gas. Only a small fraction (0.7%) reacts with water to form carbonic acid which dissociates to ions H^+ and HCO_3^-. Carbonic acid converts difficultly soluble carbonates of calcium and magnesium into readily soluble bicarbonates. Thus, so-called *bonded* (*carbonate*) CO_2 is transformed into a *semi-bonded* (*bicarbonate*) form which is utilizable for aquatic organisms via photosynthesis. Free carbon dioxide can be present in water in markedly varying amounts: 1–100 mg CO_2 l^{-1} depending on whether its biological production or its consumption prevail. Usually, it ranges from a few to 20 mg l^{-1}. (In mineral waters the content of non-biological origin CO_2 can exceed 1000 mg l^{-1}.)

4.1.1.3 Light radiation

Adequate intensity of light radiation at suitable wavelengths together with sufficient quantity of CO_2 is an essential condition of photosynthesis; the intensity, duration and wavelength of illumination are also important. If illumination gradually decreases, it is obvious that the intensity of photosynthesis decreases as well. This results in lower CO_2 bonding and less intensive oxygen release. At a certain level of illumination the quantity of CO_2 consumed by photosynthesis equals the quantity of CO_2 released by respiration. This is the so-called *light compensation point* and its value also depends on the water temperature [1, 2]. If the intensity of illumination continues to decrease, the CO_2 release ever more outweighs the bonding until photosynthesis stops. The relationship between the intensity of photosynthesis and the intensity of illumination is not linear, it is more logarithmic in character (Fig. 4.2). Too high an intensity of light can also reduce the photosynthetic activity [3]. The overall relationship corresponds to a more generally understood law of minimum [4], formulated by Liebig for the relationship between the growth and concentration of nutrients. The inhibition effect on photosynthesis of too intensive illumination is, for example, that on bright sunny days the maximum photosynthesis is achieved at a certain depth below the water surface. On account of this, some algae move from the surface layer into the deeper layers.

An important, sometimes even limiting, factor is the duration of illumination. Some plant species require for their proper development a certain number of hours of sunshine. For example, increasing the light intensity under the conditions of a short day cannot satisfy the requirements of plants requiring a long day. Other species require a certain minimum period of dark. However, many plants develop well under the conditions of both short and long days. This phenomenon of dependence on light duration, termed *photoperiodicity*, has nothing to do with photosynthesis but is concerned with the production of hormones controlling the development of an individual [5, 6]. It is quite well studied in the case of land plants, but certainly it is important for the development of aquatic species (for example, fish farms can regulate their stocks of juvenile fish by imposing an artificial photoperiod).

Along with its quantitative properties, the quality of light is of great importance. Of the total energy of sunshine impinging on the earth's surface, approximately 10% is UV radiation, 45% visible light and 45% infrared light. These components have different effects on living organisms. For photosynthesis particularly the visible light of the spectrum is used, but not evenly in its whole width, and also the individual species of photosynthesizing organisms may differ in the utilization of various parts of the spectrum. This depends on their photosynthetic, and to a certain degree on other colour pigments. The most important photosynthetic pigment is chlorophyll, present in plants and algae. In cyanobacteria (blue-green algae) it is phycocyan. It is typical of aquatic autotrophic organisms that they often contain other dyes which complete and extend their capability to utilize the spectrum of the sun. In plant, green and brown algae one can find carrotenoids playing this role, in cyanobacteria and red algae it is phycoerithrin.

In general, however, one can state that the maximum intensity of photosynthesis is achieved in red light with a wavelength of about 650 nm and usually also another maximum appears in the blue region at about 440 nm. In some species of red algae the green region around 560 nm has a similar effect [7, 8].

Even more complicated is the situation in the utilization of non-visible parts of the sun's radiation. Some plants, algae and cyanobacteria have a certain photosynthetic activity also in the upper part of the UV region, for green plants the maximum is at about 360 nm, for brown and red algae it is around 340 nm. Infrared radiation cannot be utilized by green organisms, but some brown and red algae are able to utilize the shortwave part of infrared spectrum quite well. The purple phototrophic bacteria also possess a similar ability [9, 10].

A variety of assimilation pigments is especially convenient particularly in the aqueous environment since the incident light is often impoverished due to varying absorption and shading in some wavelengths. This is caused primarily by the effect of soluble and insoluble admixtures. The upper water layers filter most of the red and blue region from the incident light. Therefore, combinations with pigments which enable the photosynthetic use, e.g., of orange or green parts of the spectrum are important here.

The ultraviolet and infrared regions of sunlight are also important, particularly in the upper water layers [8]. These layers become warm by absorption of the infrared rays, and shortwave ultraviolet radiation hinders

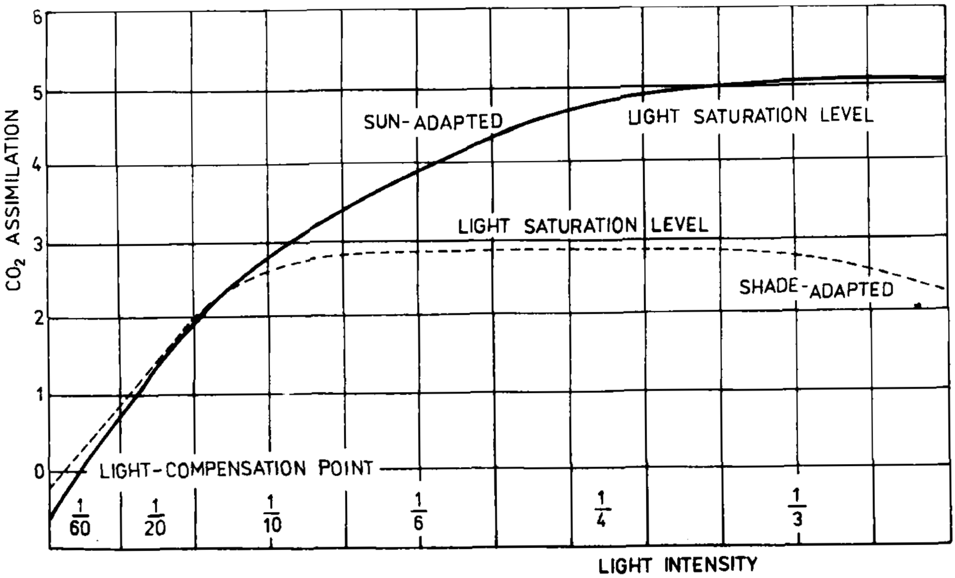

Fig. 4.2. Dependence of photosynthesis intensity on light intensity for sun-adapted and shade-adapted plants. At the beginning, CO_2 consumption is less than the amount released by respiration. At certain intensity of illumination the compensation point is achieved when the CO_2 assimilation is equal to CO_2 production. Photosynthesis is accelerated only up to optimal intensity of illumination; over-intensive light can inhibit photosynthesis

the development of more sensitive species, particularly of some algae and small bark beetles in the vicinity of the water surface.

With increasing depth the light intensity in water decreases, its spectrum changes and the length of a light day becomes shorter. However, for organisms, that part of radiation which can reach them is important [9]. Due to the high adaptability of aquatic organisms the limit of the compensation point is near to the depth into which only 1% of impinging sunlight penetrates. For the assessment of the absorption and dispersion properties of water, *water transparency* has been used since the middle of the last century. It is most often determined according to the depth at which the contours of submerged Secci board (a white standard-size disk) are just visible. Since the light dispersion affects transparency more than absorption, no exact conclusions on the light conditions in water can be drawn from such results. More accurate data can be obtained by the use of photoresistors, for example.

4.1.1.4 Concentration of hydrogen ions

The concentration of hydrogen ions is expressed in pH units, defined as the negative decadic logarithm of the concentration of hydrogen ions H^+ although they are in fact hydroxonium ions H_3O^+. The pH value determines the degree of acidity or alkalinity of water and its solutions (Fig. 4.3).

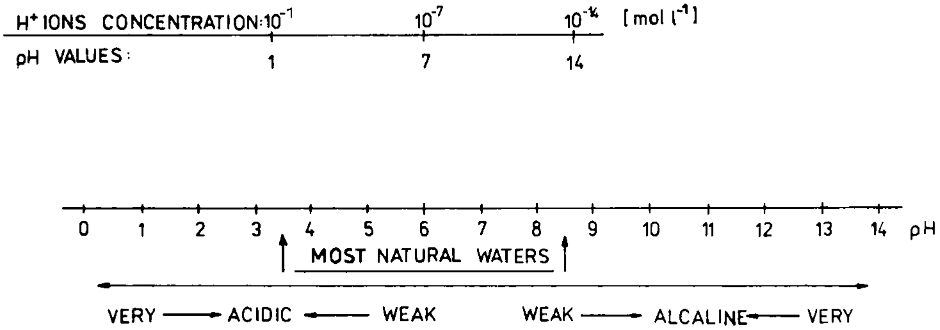

Fig. 4.3. Relationship between hydrogen ion concentration, pH value and water acidity (alkalinity)

This value is important for aquatic organisms for two particular reasons:

(1) The activity of the environment influences the course of life processes in living cells.

(2) The effect and biological utilizability of the substances present often depends on the pH of water.

Taking these two aspects together, their physiological effects often overlap. The basis of the life activity of each organism involves enzymatic reactions which take place only within certain pH limits. The optimum is usually in the neutral region. Under normal conditions the pH of natural, not too polluted water is about 7, and usually the deviations of water reaction are within the range pH 5–8 even on very different mineralogical bases. However, cases do occur when water has extreme pH values due to non-biogenic and biogenic factors. Mineral waters with CO_2 sometimes have a pH as acidic as 3.5–4, as also have water of mountain peat moors. Intensive biological activity of microorganisms can cause water to become alkaline, and the pH can increase to 10 [11].

Cells have a certain ability to keep the pH of their inner liquid within necessary limits, but if the reaction of the environment is too far outside these limits, they cannot defend themselves against unfavourable changes. Also their inner pH changes, which results in serious metabolic disorders.

The ability of cells to take up nutrients is dependent on the pH of the environment. On the other hand, the presence of certain cations changes the physiological effect of the environment reaction. Especially calcium ions and ions of some other metals decrease the unfavourable effects of high water acidity, even though they are not nutrients of particular importance for the organism in question. Cells in acid environment take up practically no ammonia nitrogen, whereas in the alkaline environment it enters their cells in excessive amounts. The dependence of nitrate nitrogen uptake on pH has almost an opposite character. No harmful effects were observed due to the lack of calcium at pH above 4.5 in the algae of the *Chlorella* genus, but in a more acid environment calcium eliminates the unfavourable effects of hydrogen ions quite efficiently. These, as well as other relationships, are of special importance for some aquatic organisms since they are in a permanent contact with the electrolytes present [10]. Sometimes, however, it is difficult to say whether the unfavourable effect is a direct consequence of incorrect pH or of the presence of other harmful ions.

4.1.1.5 Content of dissolved substances

Water lacking a certain content of foreign substances would be inconvenient and even harmful for most aquatic organisms. The only exceptions are some undemanding photoautotrophic organisms which are satisfied with water containing a minimum amount of mineral nutrients, oxygen and carbon dioxide. Other species require higher amounts of dissolved substances which, according to chemical composition and quantity, determine several important properties of water, especially the content of nutrients, pH value and osmotic pressure.

As regards the content of nutrients, a sufficient condition is the presence of biogenous elements. Such elements which are present in living mass in an amount of 1% or more are called *macrobiogenous* elements; they include C, H, O, N, P, Ca. The elements which make up 0.05–1% of living mass are called *oligobiogenous*; Mg, Na, K, Fe, S, Cl. The biogenous elements are completed by a group of trace elements occurring in all organisms in amounts lower than 0.05%; Cu, Co, Zn, Mn, F, I, Mo. These are the *microbiogenous* elements. Some organisms require several other elements, others do not. In natural waters the majority of elements of the Periodic Table is present including all biogenous elements, but not necessarily at the required concentrations [12]. The critical requirements are those of autotrophic organisms, utilizing entirely mineral nutrients for the production of organic matter. At the same time, it is necessary to bear in mind that not only the quantity is important, but also the mutual ratio of the elements present. Whereas in organic matter the relative representation of elements is quite constant, it varies quite widely in water and is completely different from the composition of the elements in organisms. One of them may occur in insufficient amounts and according to the law of minimum it then becomes the limiting element. This disproportion has remarkable effects in the case of macroelements: carbon, nitrogen and phosphorus. It seems that the most convenient ratio C:N:P in water is 106:16:1, but the actual range of these elements is much wider. The limiting element is phosphorus followed by nitrogen; rarely, it is carbon. Of the other elements, calcium is particularly significant [13].

The content of dissolved substances is determined by the chemical composition of rocks and gases with which water is in contact. If allowed by other conditions, the basic chemistry of water undergoes marked biologically conditioned changes. Aquatic organisms incorporate a part of nutrients into their organic matter. The biological bonding of limiting elements is often so intensive that they hardly occur in the dissolved state. However, even during the life of an organism a part of nutrients returns in the form of excreted metabolites and the remaining amount returns in the form of dead organic matter. A part of the returned organic matters is again mineralized by destructive agents, others remain in the form of original or simpler organic compounds and can be utilized. Thus, in life-bearing water nutrients are present in both mineral and organic form. Elements in short supply are immediately picked up almost quantitatively after being released and are incorporated into newly originating organisms. The total quantity of nutrients in water is sometimes significantly enriched by substances released from organic matter of foreign (allochthonous) origin, for example leaf waste. Organisms are able to adapt quite easily to this natural cycle of nutrients in spite of variations caused, for example, by the climate. Therefore, dynamic equilibrium is quite quickly established in the balance of bound and released nutrients and life-bearing water is thus adequately stabilized. In polluted natural water the content of nutrients is mostly very low, and therefore only a limited amount of micro- and macroorganisms are able to live in it. Much more serious problems are caused by artificially induced access of substances of anthropogenic origin caused, for example, by sewage waters and particularly by highly polluted wastewaters from industry and agriculture. They often represent a shock supply of excessive quantities of foreign substances which can completely upset a stabilized aquatic biocenosis.

We now consider in turn the most important biogenous elements.

(1) *Phosphorus.* The sustenance capacity of natural water is limited mostly by a low content of phosphorus [13]. This is not because it is scarce

element. The concentration in the earth's crust is approximately 12 times greater than in living matter. However, it occurs mostly in the form of compounds which dissolve in water to a very limited extent and therefore, most of phosphorus remains bonded in rocks and sediments. Dissolved phosphorus of inorganic origin, and also phosphorus originating from organic matter, is almost exclusively in the form of the phosphate ion which readily associates with Fe, Al and Ca, forming simple salts or complexes whose solubility changes according to pH and water saturation with oxygen. Solubility of phosphates in very slightly acidified water, with an almost neutral reaction, is very low. Clean water, especially from springs and brooks, does not contain more than 0.1 mg of PO_4^{-3} l^{-1}; usually, the content of PO_4^{-3} is below 0.03 mg l^{-1}. At present, the number of cases of clean waters without the presence of sewages, fertilizers or industrial wastes, which carry an increased amount of phosphorus, is decreasing. Concentrations exceeding 0.1 mg PO_4^{-3} l^{-1} give reason to suspect water pollution. In water poor in oxygen the content of dissolved phosphates increases, particularly due to reduction of non-dissolved ferric phosphate to the more soluble ferrous phosphate. In such water, for example in peat moors, more than 0.1 mg l^{-1} of dissolved phosphate ions can be present. In some waters natural concentrations of phosphates can be as high as 0.5 mg l^{-1} even under the effect of favourable chemical properties of rocks. In such cases the increased content of phosphorus is permanent, whereas polluted water is characterized by continual changes in the content.

The most readily biologically utilizable ions are $H_2PO_4^-$ originating from the salts of monovalent and bivalent cations [14, 15]. However, their concentration in water usually decreases fairly rapidly since they are very unstable. They very frequently come into contact with bicarbonates and in neutral media they are transformed into a less accessible hydrogenphosphate form:

$$(H_2PO_4^-)_2 + (HCO_3^-)_2 \rightarrow (HPO_4^{2-})_2 + 2H_2O + 2CO_2$$

If they are not utilized by organisms the reaction goes further, and transformation to insoluble phosphate takes place:

$$(HPO_4^{-2})_2 + (HCO_3^-)_2 \rightarrow (PO_4^{-3})_2 + 2H_2O + 2CO_2$$

Usually, calcium participates in the reactions with bicarbonates. The effect of iron cations on the utilizability of phosphate ions was discussed above. Phosphorus in precipitates is also partially utilizable. Plants and microorganisms are probably able to resorb phosphorus from precipitates of colloid size. Aquatic animals which filter water actively can also utilize phosphorus in finely suspended particles.

Biologically bound phosphorus takes part in metabolic processes again in the form of phosphate. It returns to water via excreted metabolites or as a part of dead organic matter. In water with intensive microbial activity several times higher amounts of phosphorus in released organic compounds can be found than that in dissolved minerals. Phosphorus bound in organic compounds can be again biologically utilized, but its uptake is somewhat slower than that of soluble inorganic phosphate ions. It must be first enzymatically detached from micro- and macromolecular organic compounds and it enters the cells in the form of a phosphate ion [16].

(2) *Nitrogen.* Of the three main macrobiogenous elements, nitrogen occupies the second place when considering deficiency factors. Usually, it occurs in water in slightly higher amounts than with phosphorus, but in some cases it can be a limiting factor. This situation is usually caused artificially by an increased supply of phosphorus from municipal and industrial wastes, less from fertilizers. Nitrogen present in water is bound in various compounds or in its molecular form as dissolved gas, which enters water from the atmosphere, or it is released from nitrogen compounds by denitrification bacteria. The compounds include primarily nitrates, nitrites, ammonia nitrogen and organically bound nitrogen [17].

Like phosphorus and other nutrients, nitrogen present in the form of dissolved substances is also taken up from water by microorganisms and plants. Generally, the complex cations NH_4^+ and anions NO_3^- are readily utilizable although not always to the same degree. Many fungi, especially of the yeast-type, some bacteria, algae and colourless flagellata usually utilize ammonia cations as the source of nitrogen. In other species utilizing both types of compounds there is some selectivity, which changes during individual developmental stages. Some plants prefer ammonia ions at younger stages, and when they become older they prefer nitrate ions. This selection is also influenced by other chemical properties of water. A certain role is played by the fact that nitrate nitrogen must be first reduced in the organisms to ammonia and only then it is bound to organic compounds. Similarly, also nitride, which can be well utilized by some plants, must be reduced. In other cases it is toxic even at low concentrations. Molecular nitrogen can be utilized in water only by some species of autotrophic and heterotrophic procaryotic microorganisms; others, also autotrophic organisms, are not able to utilize it. As an important macroelement, nitrogen easily becomes deficient [18].

In water, sometimes a significant portion of nitrogen is present in organic compounds. Nitrogen compounds in the bodies of living or dead organisms are, for the majority of higher animals, the only utilizable form of nitrogen. During the decomposition of organic residues, molecules of nitrogen compounds of different size are released into water, and many are excreted as metabolites. They can form regular or colloidal solutions and mostly plants and microorganisms utilize them more intensively [19].

(3) *Carbon.* Apart from organic matter, for which carbon is the essential component, inorganic carbon compounds are also present in water. Of these CO_2 and the carbonates are of the greatest importance. The relationship of organisms with various carbon compounds is so basic that it is considered to be the criterion for categorization of organisms according to nutrition. Only photosynthesizing organisms are able to utilize CO_2 as a source of carbon. The majority of plants and other aquatic autotrophic organisms is able to utilize not only dissolved CO_2 but also bicarbonate HCO_3^- anion. This is of great importance because the higher the content of HCO_3^-, the higher the content of free dissolved CO_2. In stagnant waters with a low amount of bicarbonates and intensive growth of algae and cyanobacteria the rate of consumption of CO_2 can equal its rate of supply into water in warm summer period due to intensive photosynthesis. Under these conditions carbon becomes temporarily a deficient element [20].

(4) *Other biogenous elements.* Of the other macrobiogenous elements, probably only *calcium* can be considered to be limiting. It maintains the elasticity of cell surface, activates some plant and animal enzymes, it is an important structural element of skeleton and sometimes also of animals' shells. In some waters, such as water from peat moors or water on an extremely calcium-poor subsoil, the calcium content is so low that it becomes deficient for the majority of aquatic species [21].

As regards the oligobiogenous and microbiogenous elements, in exceptional cases a deficiency of sulphur (which is so important particularly for the synthesis of proteins) can occur [21]. All other biogenous elements are present in water in lower or higher amounts, but are not considered limiting, as a general rule.

4.1.1.6 Other chemical properties of water

The effect of dissolved substances on the quality of the water environment cannot be individually assessed just from the viewpoint of the content of available nutrients because at the same time all biological effects of present elements and compounds play a combined role. Some substances have a favourable effect on aquatic organisms, others have adverse and even toxic effects, depending on the species and sensitivity of organisms, on the properties and concentration of the substance and on other ecological factors [22]. Since natural water is a solution as well as a mixture of a greater number of substances, their effects do not always depend on their individual properties. Many of them infuence and change the interactions of other species of substances. If they weaken or interfere with such effects we speak about *antagonistic activity*; if they intensify their effects so that the overal result is the sum of their effects, we speak of *synergism*. Antagonism and synergism concern both elements and compounds. The terms can refer to favourable and adverse effects, but due to general worsening of the environment the attention is focused more on the harmful effects of chemical substances.

One of the first pieces of evidence on the existence of the antagonistic relationships among elements, including biogenous ones, came from experiments with algae. Whereas pure solutions of NaCl and KCl had inhibitory or even toxic effects on their growth, they became harmless after addition of a small amount of $CaCl_2$. Antagonistic relationships, influencing several physiological functions, which prevail between Ca^{2+} and K^+ or Mg^{2+} or among other elements are also known. A synergic effect was observed in the case of joint effect of B and Zn or Cu and Zn. These elements form cations, but similar relationships were also observed between anions: SO_4^{2-} decreases unfavourable affects of SeO_4^{2-}, NO_3^- weakens adverse effects of ClO_3^-, PO_4^{-3} reduces the effect of AsO_4^{-3} [23].

Soluble substances influence the course of physiological phenomena also by changing the osmotic value of water and its capability to absorb gases. Substances which are unimportant from the viewpoint of biochemistry or toxicology also participate in these effects since they do not metabolize at all or only slightly.

All aquatic organisms tolerate only a certain range of osmotic values of neighbouring water, which means that they tolerate only certain limited concentrations of dissolved substances, particularly salts [24]. At a higher concentration (hypertonic) the osmotic value of the environment increases and the organisms are damaged or die because of the loss of water drawn from their cells. At too low concentration (hypotonic) the net osmotic flow of water is reversed and water endeavours to overfill and swell the cells, even to bursting point.

In fresh waters the content of salts does not exceed 0.5‰ and the osmotic pressure is considerably lower than the osmotic pressure in the cells. Therefore, aquatic organisms must be adapted to life in a distinctly hypotonic environment. Bacteria, fungi, algae and plants have strong cellular walls, mostly constructed from polysaccharides. Such a wall is readily permeable to water, but due to its mechanical strength it prevents excessive swelling of the cells. Organisms without cellular walls must control their osmosis in such a way that excessive water penetrating into their body is somehow eliminated. Fish have kidneys for this purpose, and in protozoa a pulsating vacuole fulfils this function. The effect of dissolved salts on the content of dissolved gases has been mentioned in connection with the favourable effect of bicarbonate ions on the content of CO_2. Generally, the content of free O_2 slightly decreases with increasing salinity of water, however, the changes in the solubility of gases due to increased salinity are not so serious as the changes in the osmotic value.

The effect of toxic substances is very destructive. Some are of natural origin in the sense that they enter the water from dissolved rocks, or are products of the metabolism of aquatic organisms. Examples of such toxic substances are heavy metals, hydrogen monosulphide, ammonia and some poisonous organic compounds. Compounds of heavy metals and in some mineral waters also H_2S are of mineral origin. In most cases H_2S is formed in water by microbial reduction of sulphates, but it is also released during anaerobic decomposition of dead organic matter, particularly of its protein components. During the decomposition of proteins ammonia is also released, in quantities much higher than to that of hydrogen monosulphide. Poisonous metabolites (toxins) are produced by some cyanobacteria. In the case of their over-reproduction, known as lake water bloom, the concentration of toxins can be so high that water becomes poisonous especially for higher animals. However, all these toxic substances can accumulate in significantly high amounts under natural conditions only in stagnant waters [25–27].

4.1.1.7 Motion of water

Both regular and irregular motion of water is an important ecological factor since it significantly influences the distribution of salts, gases, suspended solids and small organisms. Intensive motion limits the possibilities of fixation of plants and animals to a firm base, and it washes off smaller or larger pieces on the bottom, which can have serious impact on some organisms. A stronger water stream also transports higher organisms able to move by themselves. There is thus a great difference between the biological habitat of running and stagnant waters. However, the effect of the motion of water is observed in both types of waters although the causes of the motion and its character are different. Unidirectional motion of running water driven by gravitational force is — except the period when the stream is frozen — continuous. The fairly irregular motion of stagnant waters is caused primarily by differences in the temperature, and by wind.

4.1.2 Categorization of water in the environment

The categorization of water in the environment is discussed in detail in Section 3.5. Here, it is sufficient to use the simple and convenient categorization of natural waters:
— water of oceans and seas,
— terrestrial water,
— water in the atmosphere.

Naturally, the water on the continental surface is the richest in organisms; it is noted for its great variety of ecological factors and the intensity of their changes. Its salinity also varies; however, only in certain parts of the total amount. The majority of terrestrial water is fresh, the natural content of salts usually ranging from 0.5 to 3‰, only rarely does it exceeds 5‰. Such water is therefore characterized by typical fresh-water organisms. However, some surface water in relatively few and isolated water bodies is salty. In some smaller localities the salt concentration reaches extreme values which markedly exceeds the sea water salinity. In these waters a small amount of halophilic, mostly lower species can be found, particularly bacteria and cyanobacteria. The water of oceans and seas covers 70% of the earth's surface, and its salinity is quite constant — about 35‰. However, the concentration of nutrients is lower than that of terrestrial waters, and thus the habitat and biological production per volume unit is also lower [28]. On the other hand, due to their extensiveness, the total productivity of seas is higher than the total biological productivity of terrestrial waters.

For the sake of completness we should mention brackish waters which are somewhere between terrestrial waters and seas. They are "semi-closed water areas", freely connected with open sea, in which sea water is mixed with fresh water coming from the land. Therefore, their salinity varies quite remarkably. From the ecological viewpoint they should be considered as an independent type of water with its own particular character of biological habitat [28].

4.1.3 Terrestrial waters

There is a range of conditions for the development of the life in terrestrial waters. From the viewpoint of hydrology and ecology the marked boundary is their classification into ground- and surface waters. Their more detailed classification has already been mentioned. In terms of quantity, groundwaters prevail (see Table 4.2) which — together with soil moisture and surface waters — is of special importance for the development of life. However, the groundwater itself is rather poor as regards the quantity and diversity of biological habitat. Naturally, the best life conditions are on the earth's surface, and thus also in surface waters. Surface waters can be divided into *running* and *stagnant waters*, which represent two different types of aquatic environment from the viewpoint of ecology.

4.1.3.1 Stagnant (lentic) waters

In stagnant waters, by definition, there is no unidirectional flow of the water body. However, the stagnant waters need not be absolutely motionless, so there is no strict boundary between stagnant and running waters. However, the criterion for stagnant water is that the eventual flow of the body of water must not influence its typical characteristics. In limnology, an ecological criterion has been adapted according to which the flow of water should not significantly disturb normal development of the aquatic plankton. Therefore, a water of 1 cm s^{-1} is generally considered to be the limiting rate for stagnant waters.

Stagnant waters are categorized into several types taking into consideration primarily morphometric requirements, such as depth, size, shape and volume. Other data concerning the characteristics of stagnant waters, its origin and/or purpose for which it is used are also important. According to these criteria stagnant waters can be categorized as follows:
— lakes,
— ponds,
— valley dams,
— special types of stagnant waters.

Furthermore, within these main types various more detailed classifications have been elaborated, taking into consideration different criteria. In general, physical, chemical and biological parameters are combined, such as content of oxygen, content of nutrients, colour and water transparency, and the richness and diversity of biological habitat.

Lakes are steady (eustatic), natural, mostly enclosed (isolated) reservoirs of stagnant waters. They are usually quite deep with low amounts of aquatic plants. Their characteristic feature is that they become gradually old, and at the same time they become shallower and overgrown. This process terminates with a total covering of soil, i.e. the disappearance of the lake. The current lakes are thus quite young geological formations.

Ponds are artificial, rather shallow and sometimes emptied (astatic) water reservoirs. Generally, they are more rich in nutrients and are more biologically alive than the lakes, and they are liable to faster changes. Often intensive care is paid to them and thus their natural development is artificially changed.

Valley dams are also of artificial origin. They are built across water streams for water accumulation, however, they are through-flowing with a possibility of controlled flow-off. They are used for the control of the through-flow regime, for energy supply, for the improvement of water properties, as a source of water for man, industry and agriculture, and for aquatic environment creation. The valley dams combine the properties of stagnant and running waters. The flowing water stream and the dam water have a considerable mutual interaction.

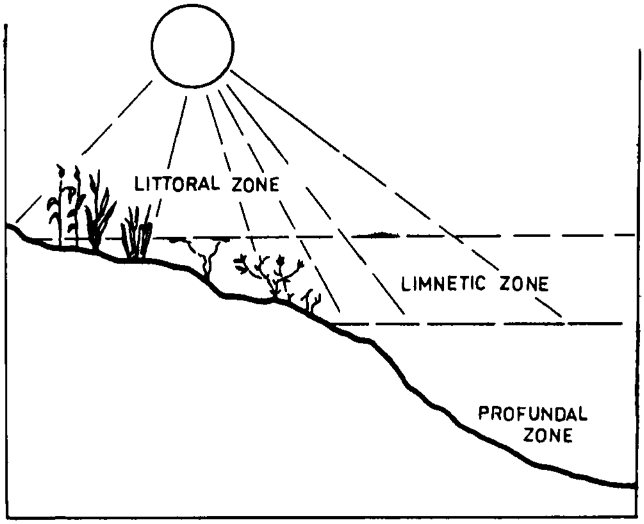

Fig. 4.4. The three major light-dependent zones in stagnant water (lakes and ponds)

In *stagnant waters* some common characteristics determine the life conditions in a dam. They concern primarily light and thermal conditions, content of oxygen, and the distribution of suspended and soluble substances.

Important characteristics also include changes of these conditions related to regular or irregular water motion.

Light conditions. For the light conditions, three main zones can occur in stagnant waters (Fig. 4.4):

Littoral zone: a zone of shallow water where practically all the light penetrates to the bottom. In natural reservoirs this zone is usually overgrown with root-bearing plants, in controlled ponds it need not be overgrown.

Limnetic zone: a zone of free, well transilluminated water. The lower boundary is limited by the compensation depth at which photosynthesis equals respiration, which corresponds approximately to the depth to which 1% of the total sunlight penetrates.

Profundal zone: the bottom and the region of deep water below the level of the compensation depth. This practically non-transilluminated zone is missing in shallow ponds and other shallow reservoirs.

All the transilluminated waters of the limnetic and littoral zones are sometimes called *euphotic zones.* Each main zone can be, if necessary, subdivided into several sub-zones. Various more detailed categorizations are used in special ecological studies, however, a certain disagreement prevails.

Water temperature

The main source of water heating is sunshine, the intensity of which sharply decreases with increasing depth of water. For heating, the infrared component of total spectrum is important, however, this is absorbed by water very quickly, and thus only a thin surface layer is warmed thoroughly. At a depth of more than 1 m, warming of water by sunshine is practically of no account. Thus, one might expect that stagnant water will be warmest in the shallow upper layer and that with increasing depth the water temperature would decrease quickly and steadily till it reaches the minimum value. In fact, the course of temperature changes with depth is completely different (Fig. 4.5). In the upper part water has approximately the same temperature to a depth of several metres from the surface, then the temperature rapidly decreases and density of water increases. This layer, characterized by a sharp change and rapid temperature decrease is called "jump layer" (*thermocline, metalimnium*). After several metres this layer terminates and water temperature decreases only slowly [29].

The even temperature of water above the jump layer is due to mixing of water in this zone. The motion is brought about by wind, or by the night cooling of water. Density of water increases proportionally with decreasing temperature in the jump layer towards the bottom, therefore the warmer upper layer does not become mixed with the more viscous and cooler water

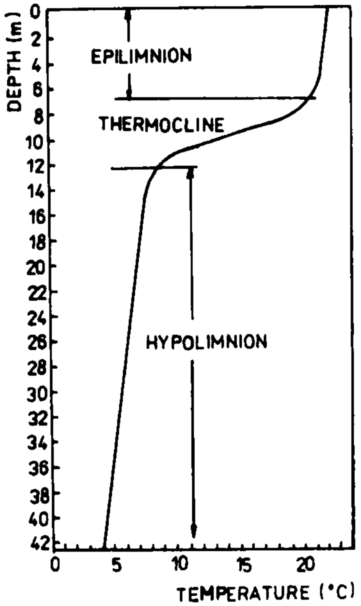

Fig. 4.5. An example of a temperature vs. depth curve in a deep lake during the summer stagnancy

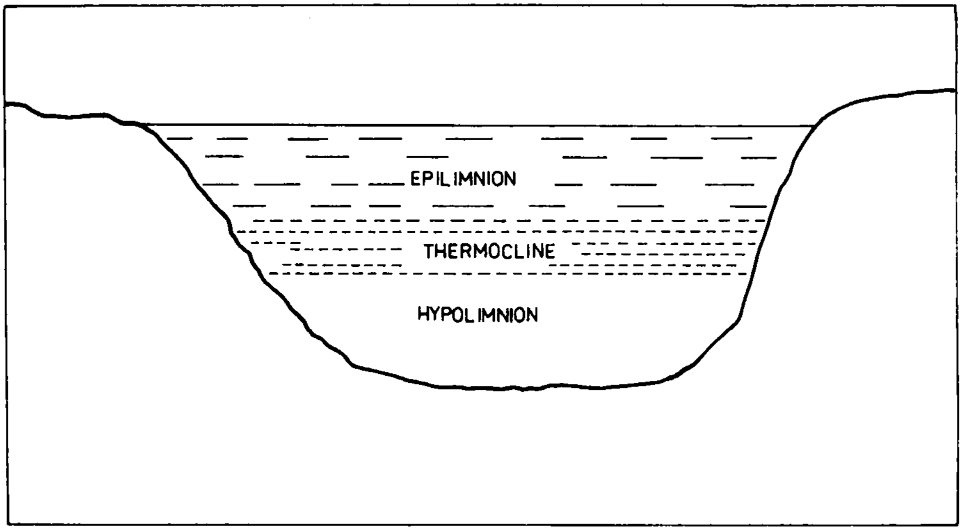

Fig. 4.6. Thermal stratification in a deep lake

below. The zone above the separating jump layer is called the *epilimnium*, the zone below, down to the bottom, is the *hypolimnium*. All three zones occur primarily in deep reservoirs (Fig. 4.6). It was found that in deep lakes two or three jump layers can be formed simultaneously (primary through tertiary). On the other hand, the thermocline can be completely missing in shallow waters. This can be observed, for example, in shallow ponds. Thus, depending on circumstances, the following variations of thermal stratification can occur in stagnant waters:

— the thermocline is at the surface and the epilimnium is missing;
— thermal stratification is not marked or is completely missing (for example a shallow reservoir);
— thermocline is at the bottom, stratification is formed only in cambers above which a common epilimnium is present.

During the course of the year the depth of the jump layer as well as total character of thermal stratification change due to climatic alterations. The following seasonal cycle is typical for stagnant waters in the Temperate Zone: At the end of spring when the temperature of the top layer of water is about 10°C a slight jump layer is formed near the surface. The thermocline can be considered to be formed when the drop of temperature per m of depth exceeds 1°C. In summer, the thermocline shifts to deeper layers and at the same time it becomes more marked. In some cases distinct thermal gradients have been measured in which the temperature difference per 30 cm was greater than 8°C. The epilimnium is increasing whereas the hypolimnium is isolated by the jump layer from the conditions at the surface, and the water remains motionless. This is the period of summer stagnation. In autumn, cooling of water surface by air and also by evaporation begins. Cooled water of epilimnium drops to deeper layers, the jump layer is moved to the bottom and at the same time it becomes less distinct. When the temperature in the epilimnium drops approximately to 10°C, the thermocline disappears. The temperature of the epilimnium and hypolimnium is balanced and due to autumn winds all water layers are mixed, down to the bottom. This is the start of autumn circulation which lasts until the water temperature drops to 4°C. During further decrease in temperature the water becomes cooler because of the lower density in the upper layers. Circulation in the reservoir ceases and gradually new temperature stratification with a reverse (inverse) gradient is formed. Water at the bottom has a temperature of 4°C and the temperature decreases towards the surface even to negative values. This is the period of winter stagnation whose length depends on the degree of the water surface freezing. In spring, first the ice melts and then the water temperature at the surface begins to increase. Warmer water drops to the bottom until the temperature in the whole reservoir is 4°C. It can be again mixed in the whole volume and the period of spring circulation starts, which is terminated by formation of the jump layer and thermal stratification [30, 31].

In shallow reservoirs a copy of the seasonal cycle can take place during one day. However, the jump layer cannot be permanent. It is formed only in the afternoon when the top water layer is suitably warm. The thermocline is at first near the surface, during afternoon and evening it moves to the bottom. In the night, water becomes cold and in the morning, after balancing of the temperatures, circulation starts in the whole reservoir. The jump layer in this case is not marked, but is sufficiently stable since the differences in the density of water are greater in the region of higher temperatures.

Content of oxygen

In stagnant waters the content of oxygen depends on the depth [16]. This is due to temperature stratification in water, when the water rich in oxygen at the surface cannot be mixed with deeper layers. The most marked differences appear during the summer stagnation when the hypolimnium is oxygen-deficient. There are two opposing biological processes contributing to this state: photosynthetic assimilation, and degradation of organic matter. Whereas in the top zone water can be oxygen-oversaturated due to the assimilation activity of photosynthesizing organisms, oxygen in the hypolimnium is consumed for degradation processes [32, 33]. At the same time, CO_2 is released, with which the hypolimnium is strongly saturated, whereas in the epilimnium it is consumed and its temporary deficiency can appear. These differences are not so marked in winter since the biological processes then slow down. The situation is changed after surface freezing. Photosynthesis under snow and ice is either limited or non-existent, but respiration and degradation continue even though very slowly. In reservoirs with intensive life, rich in nutrients (eutrophized) the oxygen-free layer becomes too extensive and at the end of winter a serious loss-rate of fauna and flora might appear. If the ice is transparent, water can be oversaturated with oxygen due to the photosynthesis of algae even after the surface layer is frozen.

The differences in oxygen stratification disappear in the period of spring and autumn circulation. Providing that there is thorough mixing, oxygen is evenly distributed in the whole volume of water. In the time of spring circulation the concentration of dissolved oxygen is higher since the water temperature is lower than in autumn [29, 31, 34].

Direct diffusion of oxygen from the atmosphere would not be sufficient in shallow reservoirs, particularly in the surface layer. The oxygen concentration increases due to the motion of the surface, and particularly due to photosynthetic activity. Therefore, one might expect that the oxygen concentration under the surface would evidently decrease in agreement with the light absorption and thus, with decreasing intensity of assimilation. In fact, due to the circulation of water there is approximately the same concentration of oxygen in the whole epilimnium provided the jump layer is not below the compensation point. If water is exceptionally clean, phytoplankton can also photosynthesize in the jump layer, rarely also in the upper zone of hypolimnium. In such a case, since it concerns cooler layers, the oxygen concentration in these layers is higher than that in the warmer epilimnium [16]. The euphotic zone, which depends on the light penetration, need not necessarily be limited to the epilimnium determined by temperature stratification of the water.

Distribution of dissolved and suspended substances

Stratification of oxygen has already been mentioned. However, temperature stratification also influences the distribution of other substances. During stagnation, gases are accumulated at the bottom, formed during the degradation of organic matter. Such gases are mainly CO_2, CH_4, H_2S and NH_3. In deeper waters stratification of electrolytes can also appear with the highest concentration at the bottom, from where they diffuse slowly [35].

Suspended substances include organic and inorganic detritus (i.e. products of degradation), as well as living and dead microorganisms. They either slowly drop to the bottom or float in a certain layer of corresponding viscosity and density. A dense suspension is formed at the bottom [36]. All these stratifications are maintained only during stagnation. During the spring and autumn circulations the stratification disappears and all dissolved and suspended substances are evenly dispersed in the whole volume of the reservoir.

The stratification described and its changes are typical of deep and little overgrown reservoirs of stagnant water. This refers particularly to lakes. The situation is reversed in the shallow and densely overgrown ponds which are usually transilluminated to the bottom, thus providing suitable conditions for the intensive development of higher forms of vegetation. The water temperature in a shallow pond usually changes in step with the temperature of the air. Motion of water in densely overgrown ponds is limited by wind. In young ponds with a mud-free bottom the content of oxygen is sufficient all the year round; the situation gradually deteriorates with the ageing of the pond. The quantity of available nutrients increases and so does the density of living organisms and the quantity of degraded organic matter, particularly on the bottom. The turbidity formed also increases water warming by sunshine. The end result is that in old ponds the reserves of oxygen are often completely exhausted in the night or in winter under ice [37].

As already mentioned, in shallow ponds a certain temperature stratification can also occur which is usually less marked and short.

Of course, intermediate types exist between both extremes, such as deep lakes with clean water and constant surface height and shallow turbid ponds sometimes completely emptied. In the total scheme of stagnant waters, river lakes occupy a special position, and particularly valley dams. In many of their properties they resemble typical lakes, but the fact that water flows through them gives them some of the characteristics of running waters. The degree to which these conditions differ depends on the ratio between the volume of water in the reservoir and the quantity of water flowing through. If the daily flow-rate is high, the water becomes relatively less stagnant in character. Another important factor is the bottom run-off of water from the dam and frequent changes in the flow-rate according to the regulation schedule. River lakes have both surface inlet and outlet. In a through-flow reservoir a certain gradient of changes from the tributary mouth to the outflow is seen. As opposed to the lakes, water in the lowest layers is not motionless but it moves at the bottom in the direction of the original river bed to the outflow. The jump layer is usually formed, but due to the mentioned disturbing effects the total temperature stratification is more irregular and less distinct [38, 39] particularly in shallow reservoirs and those with intensive through-flow. These particularities are also reflected in the chemical stratification. In deep valley dams, marked temperature and chemical stratification usually occur, and also a regular seasonal circulation takes place there which is analogous to that in the lakes. Generally one can state that the properties of running waters are more or less applicable to those of the valley dams [20, 40].

A special environment is that of smaller stagnant waters with very particular characteristics, such as peat bogs, moorlands or saline meadows. Moorlands and peat bogs are often formed in the last stages of ageing of lakes and ponds and their covering with soil. In alkaline moorlands (bogs) peat is formed from decaying plant residues without access of air. Conversely, a strong acid reaction is typical for high peat bogs. There are various intermediate stages between both types since many bogs with permanent piling of pure organic matter on poor impermeable layers gradually change into high bogs. Saline meadows are small areas with a high content of salt. They are formed in the vicinity of sea shores and inland on places with significant deposits of rock salt in the subsoil [20, 24, 28].

4.1.3.2 Flowing (lotic) waters

Flowing waters differ from the lentic waters in that that in the former, the water flows in the whole volume in one direction. As already emphasized, there are gradual intermediate stages between the stagnant and flowing waters. Lotic waters are those in which unidirectional flow becomes the characteristic and limiting factor. It is usually so strong that, among the aquatic organisms, only fish are able to move upstream. In spite of this, the flow may become so low especially in the lower sections of rivers that it has a character of stagnant water. However, this is only a temporary state which does not change substantially the general properties of the lotic environment predominating along the whole course of the river [41].

Other marked features of flowing waters are their long bank line and restricted depth of water. Due to this the lotic environment is strongly influenced by the neighbouring land and the atmosphere with which it is in a closer contact. Therefore, it represents a more open ecosystem than do the stagnant waters. This ecosystem is more responsive to the effects of the environment. Flowing waters are noted for distinct zone formation, arising from the gradient of conditions from the spring to the mouth. Sections with fast disturbed and even cascade-like flow (torrential) alternate with sections of slow peaceful flow (fluviatile). Torrential zones occur particularly in the upper parts of the river.

Flowing waters have a great ability to take eroded material from the bottom and the banks, which is then transported and gradually accumulated in the lower flow. Therefore, the bottom of the upper flow is mostly stony, and that of the lower parts flowing through plain landscape is covered with mud from sediments. Also in flowing rivers, ageing takes place, which is evident from the gradual shortening of erosion sections and elongation of the sections with predominating sedimentation. However, this process is never terminated by complete covering with soil as in the case of stagnant waters.

In lotic water usually no temperature and chemical stratification exists in the direction from the surface to the bottom [22]. Due to the permanent flow, small depth, large contact area with atmosphere and considerable turbulence both the oxygen and temperature regimes are quite simple.

Oxygen content is constant over the whole cross-profile and is usually sufficient for organisms. Temperature is also equal at all depths, however, a greater tendency to remain in balance with the air temperature can be observed. Symptoms of certain stagnation appears only in extremely slow sections with deep river beds, and even here they last only for a short time.

Turbidity caused by eroded particles and microorganisms is negligible in the upper sections, it gradually becomes more distinct and the highest values are obtained in the slow plain sections of the river flow. Thus, the light conditions under the surface are limited in these sections. Differences in the saturation with oxygen and in water temperature occur mainly in the direction of flow. Lower sections with a slow flow of deep water are sometimes warmer, and poorer in oxygen.

Generally, one can state that in running waters natural zoning is manifested by a more or less gradual change in the physical, chemical and biological properties in the direction of flow. The greater the distance from the spring to the mouth the more marked are the differences [41, 42].

4.1.3.3 Groundwater and springs

Part of the water falling on the earth's surface in the form of atmospheric precipitation penetrates into deeper layers of the earth's upper crust. At a certain depth it encounters the impermeable subsoil, above which a continuous level of groundwater is formed. Under the surface level, water fills all capillary and non-capillary pores and larger free spaces, if any. In compact rocks, cracks or cavities can form due to tectonic processes or weathering, in which crack water accumulates. Some cavities are very large. In soluble rocks, such as limestones and dolomites, the underground spaces are continually being enlarged due to the chemical activity of crack water, giving rise to the well-known karst formations. Groundwater can appear on the earth's surface in the form of various natural springs. Groundwaters represent a special type of the environment with some characteristic features [22, 35, 43]. They are characterized especially by light deficiency, quite constant temperature and typical, quite constant chemical composition. Total light deficiency is common. If groundwater has some connection with the surface, sunshine is significantly reduced and also time limited. Groundwater temperature is usually low, corresponding approximately to the annual temperature of the locality in question. However, thermal groundwaters with extremely high temperatures also exist. As regards chemical aspects, groundwater is strongly influenced by the structure of rocks through which it flows. It is often rich in carbonates and sulphate. Unpolluted groundwater is characterized by a low content of organic substances. The oxygen content is usually lower than the saturation value. This is due to its lower quantities in the soil air, as well as oxidation processes taking part in water. The water springing out to the surface has the same properties as the underground source. However, there are no light limits in the case of springs and also the conditions for water oxygenation are improved.

4.1.4 Trophies and saprobes

In the previous sections the most important factors influencing the quality of water from the viewpoint of the environment were discussed. However, it is necessary to emphasize two facts:

(1) These factors act together, and the resultant effect is decisive for the development of life.

(2) An aquatic environment is created and changed by the aquatic organisms themselves.

In general, the better are the overall conditions provided by water, the more rich is the life it sustains. Conversely, the more intensive is the biological activity, the more influence it has on the quality of water.

The ability of water to provide necessary conditions of life can be called trophy. This ability depends mainly on the content of mineral substances, the temperature and the light conditions necessary for biological production. Several categorizations have appeared, but the most frequently used one in practice is [43–45]:

— *oligotrophic*, with low amounts of nutrients and low biological production;

— *eutrophic*, with high amount of nutrients and high biological production [46, 47].

Since water temperature and light conditions are determined by climatic conditions which are difficult to influence, a change in the trophy of waters reflects a change in the content of available nutrients. There is continuing and increasing discussion of the unfavourable impacts of water eutrophication, caused by a continuously increasing supply of nutrients, particularly of phosphorus and nitrogen. High amounts of phosphorus come from the residues of washing agents in sewage waters. Nitrogen comes from various organic wastes and fertilizers. Due to eutrophication a gradual deterioration of all types of surface waters takes place. Their high nutritional ability results in increased production of organic matter and its subsequent intensive decomposition, which brings about further adverse phenomena, such as oxygen-deficiency and enrichment with ammonia, hydrogen monosulphide and other products of anaerobic decomposition. Exceptionally intensive growth of algae and cyanobacteria results in the production of water bloom. The water assumes the colour of vegetation, its utility and aesthetic properties are considerable worsened. Strongly eutrophized waters cannot be used in industry and/or agriculture, nor can they be used for recreational purposes.

The converse of organic matter production is its degradation. The term "saprobe" relates to the intensity of the degradation processes in water and changes of ecological indicators evoking these processes. *Water saprobe is a biological state caused by pollution from biologically degradable organic matter.* It changes the water quality as well as the composition of aquatic habitats. *Saprobiology* deals with the relationships between organic pollution and corresponding biological response. Its aims are to determine the differences in the biological habitats of waters differing in the content of degradable organic matter, and to apply the knowledge obtained to the evaluation of the quatility of water on the basis of biological analysis. Utilization of saprobe as a criterion of purity offers several advantages in comparison to the chemical and biological criteria, but since it concerns complex ecological relationships it is quite difficult in application. The most important advantages of saprobiological indication are concerned with the fact that a biological analysis provides data on the average state of the aquatic environment over a longer period of time. It records the effect of short-term intensive pollution which is already over but whose ecological consequences persist for a certain time. The chemical approach would require numerous chemical analyses in short time intervals. However, saprobe can only prove pollution by putrefactive organic matters, it is not convenient for the determination of the presence of difficult-to-degrade or distinctly toxic substances. Problems still remain over the method of the biological analysis, selection of the organisms to be studied, evaluation of qualitative and quantitative data and proper interpretation of results. Therefore, the saprobiological categorization of waters in an intensively studied and also intensively discussed topic, and it is being continuously developed with increasing precision [46–51]. Several systems for saprobic assessment of waters have been elaborated in Czechoslovakia and other countries. Some of them are rather complex and laborious, others are simple but usually less objective. Often the following 5-stage categorization of the saprobic state of water is used:

(1) *xenosaprobes* — the purest waters,
(2) *oligosaprobes* — very pure waters,
(3) *beta-mesosaprobes* — the maximum natural pollution,
(4) *alpha-mesosaprobes* — medium pollution with wastewaters,
(5) *polysaprobes* — serious pollution with putrefactive wastewaters.

For all these stages of organic pollution different types and proportions of residential organisms are characteristic.

4.1.5 Ecological categorization of aquatic organisms

Taxonomic classification alone is not sufficiently realistic for describing the communities living in a certain environment. A better picture of the character of their habitat is provided by categorization based on some of the ecological aspects. The following criteria are commonly used:

(1) *Position in the food chain* (*trophy*)

(a) *Producers* — autotrophic organisms: green plants, photosynthesizing microorganisms. These are able to utilize light or chemical energy and inorganic nutrients to produce organic substances. They are direct nourishers of all other organisms.

(b) *Macroconsumers* — phagotrophic organisms: primary, secondary, etc. heterotrophs feeding on other organisms, especially animals such as herbivora, predatory animals, parasites and the like.

(c) *Microconsumers* — saprotrophic organisms: decomposers, particularly bacteria and fungi. They degrade the dead matter, consume part of the degraded substances and change the residue into mineral forms available to producers (both of the last groups are heterotrophic).

(2) *Life style*

(a) *Benthos*: organisms fixed to the bottom or resting on the bottom, or living in the sediments on the bottom.

(b) *Periphyton*: plant or animal organisms living on the stems and leaves of plants having roots in water or in the sediment.

(c) *Plankton*: tiny organisms floating in water whose motion is more or less passive and depends on the flow. Some members of zooplankton make active movements to maintain their position, but plankton as a whole cannot move against the stream. That part of the plankton which can be trapped by a fine plankton netting is called netting plankton; the part consisting of the smallest organisms passing through the meshes of the netting is called nanoplankton.

(d) *Nekton*: larger organisms actively swimming at will, such as fish, amphibians, larger insects, etc.

(e) *Neuston*: Organisms floating or swimming in surface water, or inhabiting the surface film.

(3) *Region or sub-biotope of the aquatic environment*: generally two zones are recognized in running waters:

(a) *Rapids* (*torrential waters*): sections with shallow but rapid water. The bottom is stony, free from fine sediments. In this zone only specific benthic and periphytic organisms can live which are able to fix firmly to the basis, and those which are good swimmers such as fish.

(b) *Calm waters* (*fluviatile*): deeper and slower water with sediments on the bottom. A soft bottom is not good for surface benthic organisms, however, it is convenient for organisms which bury themselves into the bottom sediments. In stagnant water, as already mentioned in more detail, four zones of water are distinguished:

(a) *littoral zone*: inhabited by plants rooted to the bottom;
(b) *limnetic zone*: inhabited by plankton, nekton and sometimes neuston;
(c) *euphotic zone*: inhabited by organisms of both above-presented zones;
(d) *profundal zone*: inhabited by benthic and some plankton organisms with heterotrophic nourishment [37, 46, 52, 53].

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4.2 Microbiology of water

Water is a typical habitat of microorganisms. Microorganisms that can be found in various kinds of waters belong to two basic categories: (a) typical aquatic microorganisms, and (b) microorganisms that get into water secondarily. A representative of the former category is, for example, *Thiovulum* sp., a chemotactic organism living at the boundary sulphides/oxygen and participating in the sulphur cycle. A well known representative of the latter category is *Escherichia coli*, an intestinal organism that gets into water via faecal pollution. Many terrestrial and airborne microorganisms get into water via rain, snow, air currents, etc.

The microbiological quality of water and wastewater is one of continuing and increasing concern, and is of great importance. Microorganisms serve as indicators of quality of water; water-borne pathogens represent a serious health hazard; finally, aquatic microorganisms play an important part in the biogeochemical cycles of matter and energy. The importance and principles of water treatment are discussed in Section 4.5 of this book.

4.2.1 Survey of aquatic microorganisms

Representatives of all the major categories of microorganisms can be found in various types of water. They include viruses, prokaryotic bacteria and cyanobacteria, and eukaryotic algae, fungi and protozoa.

4.2.1.1 Viruses

In the aquatic environment, viruses pathogenic to man, animals, plants and microorganisms (especially bacteriophages) can be found. The greatest attention is given to viruses pathogenic to man. Wastewater can be most frequently contaminated by viruses which may penetrate also surface water and even drinking water. Water can be most often contaminated by viruses excreted in faeces (enteroviruses, adenoviruses, rheoviruses and probable hepatitis viruses).

In most cases, water is contaminated by *enteroviruses* pathogenic to man and belonging to the picornaviruses (Greek pico = very small, rna = RNA-containing). They include poliovirus, *Coxackie* virus group A and B as well as echoviruses. Their viability in contaminated water is prolonged by decreasing temperature and increasing organic and bacterial pollution [1]. A common treatment of wastewater reduces the concentration of enteroviruses, which are found in wastewater mostly in summer and autumn periods. A contamination of surface water by enteroviruses is presumed if there is an inflow of untreated or treated wastewater [2]. Epidemics caused by enteroviruses present in bathing pools have also been reported.

Adenoviruses are found less frequently in water as compared with enteroviruses. Sporadic findings have been reported in wastewater by Askew et al. [3], in rivers by Grinstein et al. [4] and in bathing pools by Bell et al. [5].

Rheoviruses have been found in wastewater [6] and also in river water.

Data are available which show that *viral hepatitis* can be acquired from contaminated water. Fifty references dealing with epidemics of hepatitis were reviewed [7]. Enterovirus 72 (hepatitis A virus) is frequently implicated as the aetiological agent of outbreaks of water-borne disease, and the non-A-, non-B-hepatitis virus may also follow a similar pattern of spread. It is also thought that the largest single water-borne outbreak of viral hepatitis (Delhi, India, approximately 30,000 cases in 1955–1956) was caused by this agent [8].

Wastewater is known as an abundant source of bacteriophages, with plaque counts on *Escherichia coli* host strains normally ranging between 10^3 and 10^4 plaque forming units (pfu) per ml. The consistent presence of F-specific RNA bacteriophages in a variety of wastewaters was demonstrated by Havelaar [8].

4.2.1.2 Bacteria

A variety of physiological groups of bacteria are of importance for water quality. They participate in various natural processes in water. In addition, other bacteria are introduced from the environment, indicating general and faecal pollution. They include conditionally pathogenic and pathogenic bacteria.

Bacterial indicators of general pollution include saprophytic mesophilic, psychrophilic and anaerobic bacteria. Indicators of faecal pollution include coliform bacteria, enterococci and clostridia.

Coliform bacteria, belonging to the family of Enterobacteriaceae, are represented mainly by the genera *Escherichia* (*E. coli*), *Citrobacter* (*C. freundii* and *C. intermedius*) and *Enterobacter* (*E. cloaceae* and *E. aerogenes*).

Among *enterococci*, *Streptococcus faecalis* and *S. faecium* are of greatest importance.

Anaerobic sporulating *clostridia* (*Clostridium perfringens*) are much less frequent as compared with the coliforms.

Faecal pollution may be responsible for spreading of intestinal pathogens. Taxonomically, the most important group of bacteria indicating water pollution are facultative anaerobic Gram-negative fermenting rods of the family Enterobacteriaceae with the following 12 genera: *Escherichia, Edwardsiella, Citrobacter, Salmonella, Shigella, Klebsiella, Enterobacter, Hafnia, Serratia, Proteus, Yersinia* and *Erwinia*. Another important family, Vibrionaceae, comprises five genera as follows: *Vibrio, Aeromonas, Plesiomonas, Photobacterium* and *Lucibacterium*. The group of non-fermenting Gram-negative rods includes the genera: *Acinetobacter, Pseudomonas, Xanthomonas, Chromobacterium, Alcaligenes, Flavobacterium* and their species. The remaining pathogenic and conditionally pathogenic bacteria comprise staphylococci and micrococci (the genera *Staphylococcus* and *Micrococcus*), mycobacteria (the genus *Mycobacterium*), and spirochaetes and leptospires of the order *Spirochaetales* (especially the genus *Leptospira*).

In testing water quality in bathing pools, micrococci and staphylococci are of special importance.

In addition to pathogenic and occasionally pathogenic bacteria, various other types of aquatic bacteria are known. They have characteristic morphological features and some of them are of importance in the biogeochemical cycles of elements and energy (Fig. 4.7).

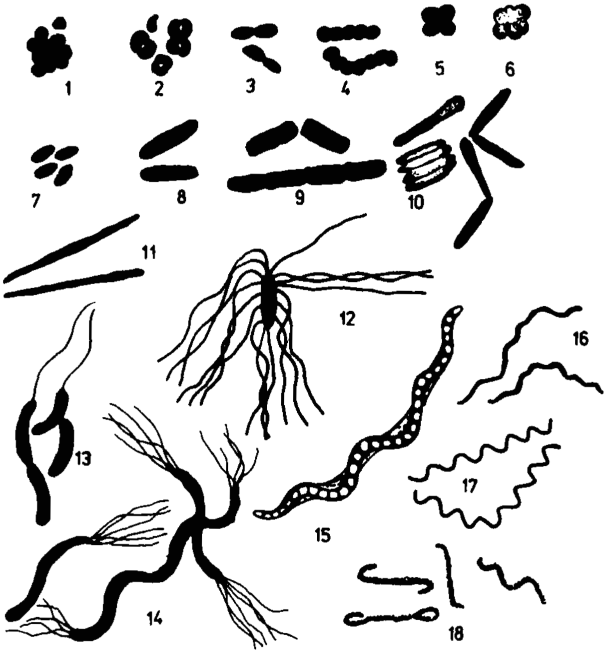

Fig. 4.7. Morphological forms of bacteria drawn to approximately the same scale. Spherical bacteria: 1 — *Staphylococcus*, 2 — diplococci (e.g. *Neisseria*), 3 — diplococci (e.g. *Diplococcus pneumoniae*), 4 — *Streptococcus*, 5 — micrococci (e.g. *Micrococcus tetragenus*), 6 — *Sarcina*. Rod-shaped organisms: 7 — small rods (e.g. *Serratia marcescens*), 8 — larger, round-ended rods (e.g. *Escherichia coli*), 9 — flat-ended rods, both single and in chains (e.g. *Bacillus anthracis*), 10 — clubbed bacilli arranged singly, in palisades and at various angles to one another (e.g. *Corynebacterium diphteriae*), 11 — fusiform bacilli (e.g. *Fusobacterium fusiforme*), 12 — flagellate rod (e.g. *Salmonella typhi*). Spirillar organisms: 13 — vibrios with single polar flagellum (e.g. *Vibrio cholerae*), 14 — spirilla with tufts of polar flagella (e.g *Spirillum*), 15 — *Cistispire*, 16 — *Borrelia*, 17 — *Treponema*, 18 — *Leptospira*. (Modified from L. E. Havker and A. H. Linton (eds), Microorganisms: Function, Form and Environment. Edward Arnold, London 1971, p. 309.)

Filamentous *Actinomycetales* belong to the important aquatic microflora. In addition to the above-mentioned genus *Mycobacterium*, most aquatic actinomycetes belong to the families Streptomycetaceae and Micromonosporaceae. Most of the aquatic actinomycetes are saprophytic. They can be isolated from rivers, lakes, ponds and also from sources of drinking water. Some of them are responsible for unpleasant odours and taste. Others are known as producers of antibiotics.

In recent years there has been a growing awareness of the potential value of marine and river sediments as sources of actinomycetes that produce useful metabolic products. Approximately 16% of the strains obtained from marine sediments displayed antimicrobial activity, consisting primarily of the inhibition of Gram-positive bacteria [9]. Actinomycetes were also isolated from sediments obtained from the Hudson River. Of 165 isolates obtained, 22 exhibited significant antifungal activity. All but three of the active substances contained polyene antibiotics and most of the bioactive actinomycetes were identified as streptomycetes [10]. These observations of the production of antibiotics resulted from laboratory cultivation; it is not known whether the bioactive actinomycetes are also capable of producing antibiotics in the aquatic environments.

The members of the *Sphaerotilus* group are motile rods, which bear a polar tuft of 10 to 20 flagella. Their distinguishing structural feature is the formation of a tubular sheath, which encloses the rods in loose chains. Reproduction occurs by the liberation of motile cells from the open ends of the sheath. The typical habitat is fresh water. *S. natans* develops abundantly in streams that are polluted with organic wastes. It grows as long, slimy tassels attached to submerged plants and stones. It is also a conspicuous component of the microflora in aerobic sewage treatment plants using the activated sludge process. This organism can be regarded as one of the best biological indicators of the pollution of water by organic wastes. *S. discophorus* belongs to the group of iron bacteria, usually having thick and golden brown sheaths, as a result of incrustation with iron and manganese oxides. These forms are sometimes in a separate genus, *Leptothrix*.

Beggiatoaceae are able to live both in an aquatic and a terrestrial habitat. They belong to filamentous non-photosynthetic gliding organisms. The non-photosynthetic filamentous gliders are strict aerobes, dependent on reduced inorganic or organic compounds as energy sources. *Beggiatoa* and *Thiothrix* are chemoautotrophs, which can use H_2S as an energy source, but most members of the group are chemoheterotrophs. Certain strains of *Beggiatoa* are facultative chemoautotrophs. The chemoautotrophic members of the group are aquatic organisms. They occur in streams, ponds and sea water containing dissolved H_2S of either geochemical or microbial origin and they grow at or near the air–water interface. Growths of *Beggiatoa* and *Thiothrix* have a characteristic appearance under microscope, since their filaments are packed with highly refractile inclusions of elementary sulphur. In the absence of H_2S they gradually loose their stored sulphur as a result of its oxidation to sulphuric acid.

The members of the gliding cytophaga group (genus *Sporocytophaga*) are widely distributed in fresh water, the sea and soil. Many marine cytophagas can grow at the expense of agar, a polysaccharide constituent of the red algae. Some cytophagas are facultative anaerobes. The aquatic cytophagas include pathogens of fish. *Cytophaga columnaris* is associated with massive epidemics in salmonid fishes.

The aerobic chemoheterotrophs of the genera *Leucothrix* and *Vitreoscilla* are similar in structure to *Thiothrix* and *Beggiatoa*, respectively. *Leucothrix* is a marine organism that grows abundantly in decomposing algal material; *Vitreoscilla* occurs in fresh water and soil.

The prosthecate bacteria are typical aquatic organisms. The genera *Caulobacter* and *Hyphomicrobium* are aerobic chemoheterotrophs, whereas *Rhodomicrobium* is a photosynthetic purple bacterium. Other peculiar aquatic bacteria have been described (see, e.g., ref. [11]).

4.2.1.3 Cyanobacteria

Cyanobacteria, formerly known as blue-green algae, are prokaryotic microorganisms that are widely distributed in water, icebergs, hot springs, etc. They have been defined by Stanier [12] as "microorganisms that harbor, within a typically prokaryotic cell, a photosynthetic apparatus similar in structure and function to that located in the chloroplast of phototrophic eukaryotes. Their traditional classification as algae was, accordingly, based on the resemblances between the cyanophytan cell and one constituent of the algal cells, its chloroplast. These organisms are in reality bacteria .... The cyanobacteria differ from the two other groups of phototrophic prokaryotes, which have always classified among the bacteria — namely, purple and green bacteria — in many respects: the mechanisms of photosynthesis; the fine structure and chemical composition of the photosynthetic apparatus; nutritional requirements and growth physiology."

The only form of cellular movement in cyanobacteria is gliding locomotion, it is widespread but not universal.

Cyanobacteria belong to the group of Gram-negative bacteria, as defined now by the fine structure and molecular composition of the cell wall.

The simplest cyanobacteria are unicellular rods or cocci, which reproduce by binary fission or budding (a few species). Many cyanobacteria have a filamentous structure. The filament of cells, called trichome, elongates by intercalary division and reproduces by breakage. The trichome can be composed only of vegetative cells. Some vegetative cells are converted into non-reproductive cells known as heterocysts with a special physiological function.

The photoautotrophic mode of life brings cyanobacteria into direct competition in natural environments with eukaryotic algae. No major group of algae has an ecological range as extensive and varied as that of cyanobacteria. The factors which lead to the predominance of cyanobacteria in some environments are now understood, the most important of them being temperature relationships, nitrogen fixation and facultative anoxygenic photosynthesis in particular ecosystems.

The upper temperature limit for the growth of phototrophic eukaryotes is 55–60°C. Certain cyanobacteria are thermophiles, with temperature maxima as high as 75°C. As a result, they constitute the dominant or almost the exclusive photosynthetic population of hot springs. Thermotolerance seems to be the major factor which makes cyanobacteria the most important agents of photosynthesis in deserts. They develop as a subsurface layer in desert rocks, in microfissures where water is trapped by condensation at night.

Many cyanobacteria can fix atmospheric nitrogen and dominate the microbial phototrophic population in environments where the supply of combined nitrogen is limiting. Until recently, heterocystous cyanobacteria were the only cyanobacteria known to fix nitrogen. Non-heterocystous cyanobacteria (e.g., *Gloeothece, Plectonema*, etc.) able to synthesize nitrogenase have since been recognized.

A mode of cyanobacterial photosynthesis which does not lead to oxygen production — anoxygenic photosynthesis — has been discovered as the outcome of an ecological analysis of a shallow hypersaline lagoon, the Solar Lake on the Gulf of Eilat [12]. In the winter, stratification produces an anaerobic layer with a steep H_2S gradient, inhabited by three populations of photosynthetic prokaryotes. In the upper parts of the anaerobic layer, purple and green sulphur bacteria form the largely distinct horizontal layers. Oscillatorian cyanobacteria are present at all levels, but form a dense mat at the bottom, where the H_2S concentration is maximal. It was accordingly hypothesized that the cyanobacteria in this particular ecosystem might be engaged in anoxygenic photosynthesis. The hypothesis was confirmed by isolating the predominant species, *Oscillatoria limnetica*, capable of performing both oxygenic and anoxygenic photosynthesis.

Cyanobacteria are very widely distributed microorganisms. They can be found in hot sulphur springs at temperatures as high as 70°C and in all soils and most aquatic environments, particularly in the tropics. Some planktonic cyanobacteria are buoyant and under calm conditions they float to the surface of lakes and ponds forming the so-called water blooms. This buoyance is associated with the presence in the cells of gas vacuoles. However, cyanobacteria are not very abundant in oceanic plankton. The symbiotic species *Richelia* (Fig. 4.8) occurs in the diatom *Rhizosolenia*. Symbiotic relationships of cyanobacteria are quite common in algae, ferns, liverworts, gymnosperms and angiosperms.

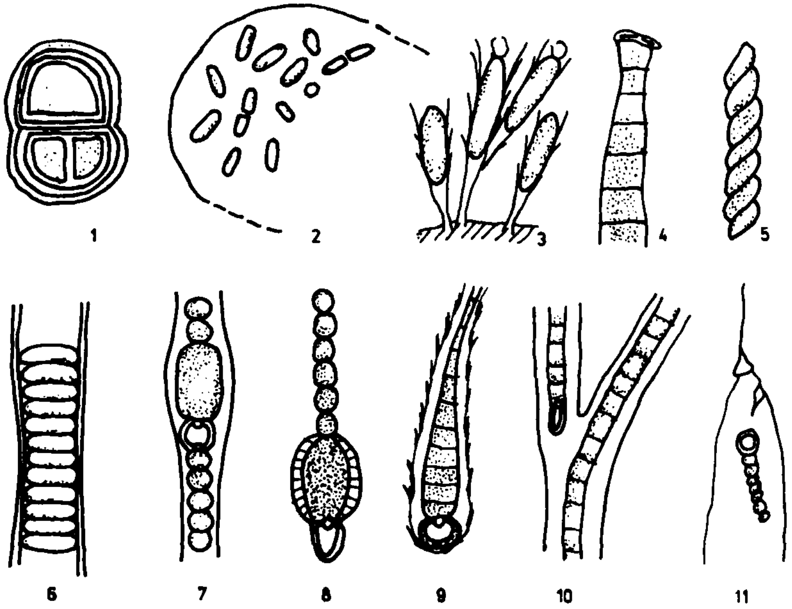

Fig. 4.8. Characteristic cyanobacteria: 1 — *Chroococcus*, 2 — *Aphanothece*, 3 — *Chamaesiphon*, 4 — *Oscillatoria*, 5 — *Spirulina*, 6 — *Lyngbya*, 7 — *Anabaena*, 8 — *Cylindrospermum*, 9 — *Calothrix*, 10 — *Tolypothrix*, 11 — *Richelia* inside a cell of the diatom *Rhizosolenia* (modified from ref. [13])

The aggregation of cells and filaments often yields macroscopic colonies which lie on lake sediments, float freely in the water, rest on soil or form blackish clusters on rock faces. Colonies of *Calothrix* (Fig. 4.8) often form a conspicuous zone on rocks in the upper inter-tidal zone, in some areas associated with other cyanobacteria which actively bore into the rock.

Many of the species living around thermal springs are involved in the precipitation of lime to form travertine. Filamentous species of *Anabaena, Oscillatoria* and *Spirulina* are frequently found both floating in water (planktonic) or moving freely over the surface of underwater sediments (epipelic) and high concentrations of filaments appear bluish-green or black.

Some species of cyanobacteria (e.g., *Anabaena, Microcystis* and *Aphanizomenon*) produce very potent toxins which have been responsible for death of cattle from drinking water containing these genera [13].

Several cyanobacteria are indicators of quality of the water. *Chamaesiphon fuscus* is characteristic to catarobic, *Oscillatoria* and *Nostoc* to oligosaprobic, *Aphanizomenon flos-aquae* and *Anabaena* to mesosaprobic water, and *Spirulina* occurs also in the polysaprobic zone of wastewaters.

4.2.1.4 Algae

The algae are eukaryotic organisms. They may be characterized as organisms that perform oxygen-generating photosynthesis and possess chloroplasts. Some of them are unicellular microorganisms; some are filamentous, colonial, or coenocytic; others have a plant-like structure that is formed through extensive multicellular development (with little or no differentiation of cells and tissues). Accordingly, by no means all of them fall into the category of microorganisms. The brown algae may attain a total length of 50 m.

The primary classification of algae is based on cellular properties: the nature of the photosynthetic pigments, the chemical composition of the cell wall, nature of reserve materials and the nature and arrangement of the flagella. In terms of these characters, the major groups of algae are arranged in Table 4.1.

Algae are mostly aquatic organisms that inhabit either fresh water or the oceans. Since 70 per cent of the global surface is water the importance of algal photosynthesis cannot be over-estimated. It is probable that at least as much carbon is fixed by aquatic algae as by the land plants. The aquatic forms are principally free-living, but certain unicellular marine algae occur in symbiotic relationships with specific marine invertebrates and grow within the cells of the host animals. Some terrestrial algae as epiphytes on trees, on bare rock surfaces moistened by sea-spray and on soils.

The great bulk of marine algae are unicellular floating (planktonic) organisms, predominantly dinoflagellates and diatoms. They are distributed through the surface waters of the oceans where they are maintained in circulation by the turbulent motion of the water. The most conspicuous

Table 4.1. Major groups of eucaryotic algae [11]

Group name	Pigment system		Composition of cell wall	Nature of reserve materials	Number and type of flagella	Range of structure
	Chlorophylls	Other special pigments				
Green algae: division *Chlorophyta*	a + b	—	Cellulose	Starch	Generally two identical flagella per cell	Unicellular, coenocytic, filamentous; plant-like multicellular forms
Euglenids: division *Euglenophyta*	a + b	—	No wall	Paramylum and fats	One, two, or three flagella per cell	All unicellular
Dinoflagellates and related forms: division *Pyrrophyta*	a + c	Special carotenoids	Cellulose	Starch and oils	Two flagella, dissimilar in form and position on cell	Mostly unicellular, a few filamentous forms
Chrysophytes and diatoms: division *Chrysophyta*	a ± c	Special carotenoids	Wall composed of two overlapping halves, often containing silica	Leucosin and oils	Two flagella, arrangement variable	Unicellular, coenocytic, filamentous
Brown algae: division *Phaeophyta*	a + c	Special carotenoids	Cellulose and algin	Laminarin and fats	Two flagella, of unequal length	Plant-like multicellular forms
Red algae: division *Rhodophyta*	a	Phycobilins	Cellulose	Starch	No flagella	Unicellular; plant-like multicellular forms

members of marine algae, the seaweeds, are attached to rocks in the intertidal zone and the shallow coastal waters of the continental shelves. Some species of algae coat the larger aquatic plants and also occur on many animals, particularly molluscs and hydroids. A marine algal community exists in and on the undersurface of sea ice and is of considerable importance in polar regions.

As diatoms are one of the major groups of algae in the oceans, large fossil deposits of diatom walls have accumulated in many areas. These deposits are known as diatomaceous earth.

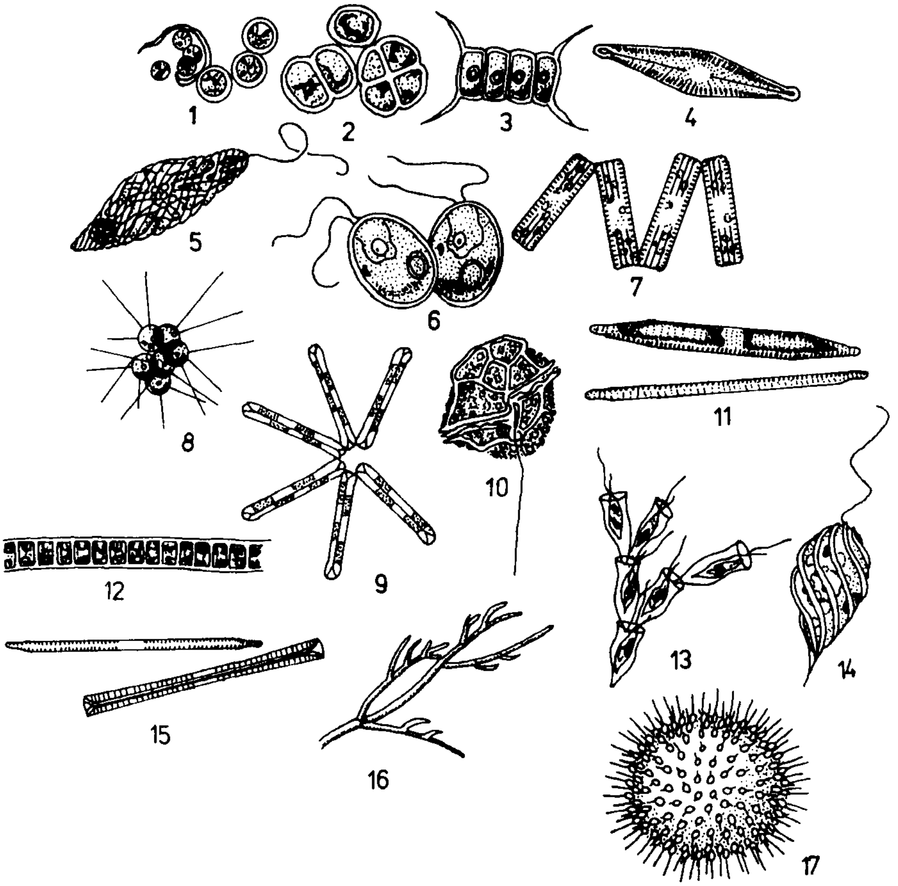

Fig. 4.9. Characteristic genera of aquatic algae: 1 — *Chlorella*, 2 — *Protococcus*, 3 — *Scendesmus*, 4 — *Navicula*, 5 — *Euglena*, 6 — *Chlamydomonas*, 7 — *Tabellaria*, 8 — *Micractinium*, 9 — *Asterionella*, 10 — *Peridinium*, 11 — *Nitschia*, 12 — *Ulothrix*, 13 — *Dinobryon*, 14 — *Phacus*, 15 — *Synedra*, 16 — *Cladophora* and 17 — *Uroglenopsis*

The aquatic algae occupy the water column only down to the limit where photosynthetically available light penetrates. Although the factors affecting their growth are similar in fresh water and marine habitats, the algae in the two environments are almost entirely distinct.

Characteristic genera of aquatic algae are shown in Fig. 4.9.

4.2.1.5 Fungi

Fungi are heterotrophic eukaryotic organisms. Some of the aquatic fungi show resemblances to flagellate protozoa, but most fungi have a biological organization which is well adapted to life in the soil, their most common habitat.

Except for the unicellular yeasts, most fungi are coenocytic organisms with mycelium as their vegetative structure. A mycelium normally arises by the germination and outgrowth of a single reproductive cell, or spore. The germinating fungal spore puts out a hypha which branches repeatedly as it elongates to form a ramifying system of hyphae which constitutes the mycelium. Reproduction of fungi is either sexual and/or asexual.

A simplified classification of fungi is as follows (Divisions end in "-mycota", sub-divisions in "-mycotina"; classes in "-mycetes"; sub-classes in "-mycetidae"; orders in "-ales"; families in "-aceae", but these are excluded. Some representative orders only are listed).

Fungi (Mycota)
I. *MYXOMYCOTA (Myxobionta)*
  (1) *Acrasiomycetes*
      Acrasiales
  (2) *Hydromyxomycetes*
      Hydromyxales
      Labyrinthulales
  (3) *Myxomycetes* (slime moulds)
  (4) *Plasmodiophoromycetes*
      Plasmodiophorales
II. *EUMYCOTA* (*Mycobionta; Eumycetes*)
  (1) *Mastigomycotina* (formely *Phycomycetes*)
    (a) *Chytridiomycetes*
        Blastocladiales
        Chytridiales (chytrids)
        Monoblepharidales
    (b) *Hyphochytridiomycetes*

            Hyphochytriales
        (c) *Oomycetes*
            Lagenidiales
            Leptomitales
            Perenosporales
            Saprolegniales
    (2) *Zygomycotina* (formerly *Phycomycetes*)
        (a) *Zygomycetes*
            Entomophtorales
            Mucorales
        (b) *Trichomycetes*
    (3) *Ascomycotina* (*Ascomycetes*)
        (a) *Hemiascomycetes*
            Endomycetales
            Taphrinales
        (b) *Euascomycetes*
            Protomycetidae (*Plectomycetes*)
            Eurotiales
            Unitumycetidae
        (c) *Laboulbeniomycetes*
    (4) *Basidiomycotina*
        (a) *Hemibasidiomycetes*
        (b) *Hymenomycetes*
        (c) *Gasteromycetes*
    (5) *Deuteromycotina* (fungi imperfecti)
        (a) *Coelomycetes*
            Melanconiales
            Sphaeropsidales
        (b) *Hyphomycetes*
            Hyphales (syn. *Moniliales*)
        (c) *Agonomycetes* (mycelia sterilia)
            Agonomycetales (syn. *Myceliales*)

A more detailed classification of fungi was described by Ainsworth [14].

Whether the *Myxomycota* are closely related to *Eumycota* is doubtful. Possibly they are more closely related to *Protozoa* [15]. The best known aquatic representative of the *Myxomycota* is *Labyrinthula* (*Hydromycetes*), species of which are parasitic on marine algae and angiosperms. *L. macrocystis* is a destructive parasite of sea grass, *Zostera marina*. Some aquatic fungi inhabit fresh water, some the sea. Most aquatic fungi belong to the *Mastigomycotina*, some are *Ascomycotina* or *Deuteromycotina.*

Aquatic *Mastigomycotina* (*Chytridiales, Blastocladiales, Saprolegniales*) are also known collectively as water moulds. They occur on the surface of decaying plant (e.g. leaves) or animal material in ponds and streams; some are parasitic and attack algae, protozoa or fish.

The developmental cycle of a typical simple chytrid is as follows. The flagellated zoospore settles down on a solid surface. As development begins, a branching system of rhizoids is formed, anchoring the fungus to the surface. Growth results in the formation of a spherical zoosporangium, which cleaves internally to produce many zoospores. The zoosporangium ruptures to liberate a fresh crop of zoospores.

Among the *Blastocladiales*, the aquatic *Allomyces* shows a well-marked alternation of haploid and diploid generations.

Monoblepharidales are represented by the aquatic genera *Monoblepharis* and *Gonapodya* which are to be found on submerged twigs and fruits in fresh water ponds and streams, especially in the spring.

Saprolegniales (the class *Oomycetes*) are the best-known group of aquatic fungi, often termed the water-moulds. Members of the group are abundant in fresh water, mainly as saprophytes on plant and animal debris, whilst some are marine. A few species of *Saprolegnia* and *Achlya* are economically important as parasites of fish and their eggs. Algae, fungi, rotifers and copepods may also be parasitized by members of the group and occasional epidemics of disease among zooplankton have been reported.

Most water-moulds of the family Saprolegniceae are less common in strongly eutrophic waters than in rather less productive ones, but the related *Leptomitus lacteus* ("sewage fungus") increases with the organic content of the water. It is common in water polluted with sewage or organic industrial effluents. There it may become a serious nuisance by mechanical blocking of channels and by exhaustion of the available oxygen supply.

Examples of fungi that may be found in aquatic environments are shown in Fig. 4.10.

Stems of some fresh water aquatic plants (*Phragmites, Scirpus*) are parasitized by aquatic *Ascomycetes*, including many *Discomycetes.* A few brown seaweeds are parasitized by species of *Mycosphaerella*, some other *Pyrenomycetes* and some *Deuteromycetes. Pyrenomycetes* (e.g. *Ceriosporopsis*) attack and erode wood submerged in the sea. Decaying leaves of deciduous trees in well-aerated streams and lakes support a characteristic flora of aquatic *Hyphomycetes*, which readily become entangled in submerged leaves which they colonize after germination.

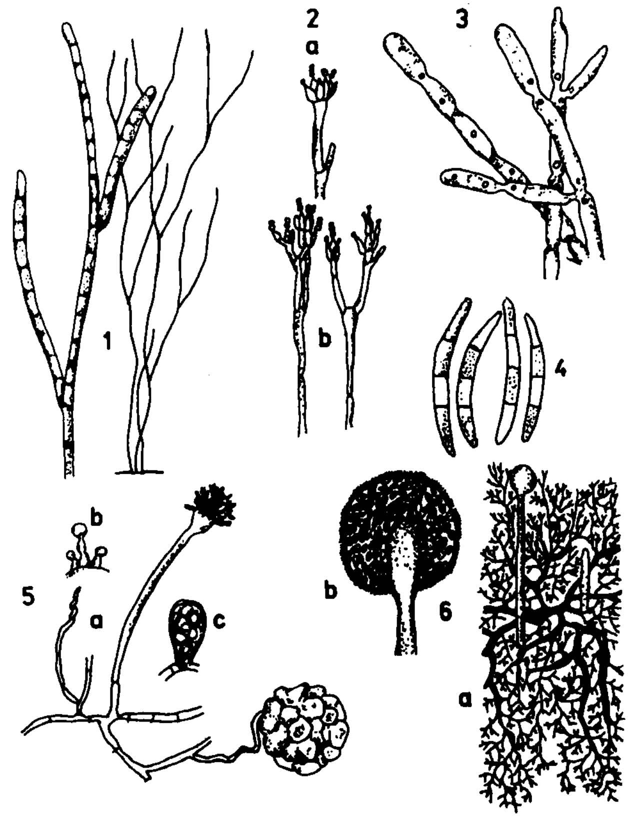

Fig. 4.10. Characteristic aquatic fungi: 1 — *Sphaerotilus dichotomus*, 2a — *Penicillium fluitans*, 2b — *P. glaucum*, 3 — *Leptomitus lacteus*, 4 — conidia of *Fusarium*, 5 — *Aspergillus glaucus*, a — conidiophore, b — ascocarps, c — ascospores, 6 — *Mucor mucedo*, a — mycelium, b — sporangium with sporangiospores

Where oxygen is scarce in water, as in deposits of organic matter at the bottom of stagnant ponds, the fungus flora is different from that of similar substrates in well-aerated waters. Certain *Hyphomycetes (Helicodendron, Clathrosphaerina)* produce their conidia only when removed from the water and placed in humid air. They are also described as "aero-aquatic" fungi.

4.2.1.6 Protozoa

The protozoa can be characterized as comprising a number of groups of non-photosynthetic, motile and eukaryotic unicellular protists. A complete account of the flagellate protozoa would necessarily include a number of autotrophic organisms that can justifiably be classified as algae (e.g. *Euglena*). Although the protozoa are regarded as unicellular, there are many species with two or more nuclei enclosed within a single membrane and

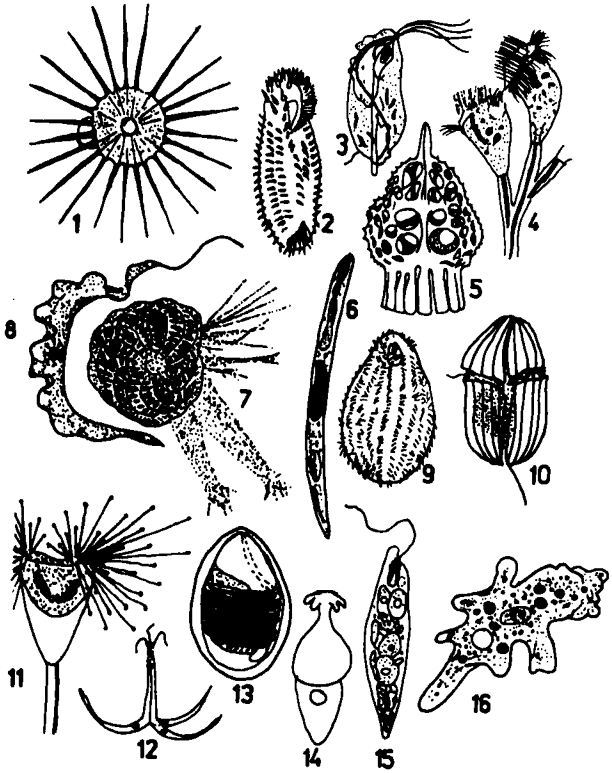

Fig. 4.11. Characteristic protozoa: 1 — *Actinophrys*, 2 — *Peraurostyla*, 3 — *Trichomonas*, 4 — *Carchesium*, 5 — *Sepalospyris*, 6 — *Plasmodium*, 7 — *Elphidium*, 8 — *Trypanosoma*, 9 — *Tetrahymena*, 10 — *Gymnodinium*, 11 — *Acineta*, 12 — *Triactinomyxon*, 13 — a spore of microsporidium, 14 — *Rhopalonia*, 15 — *Euglena*, 16 — *Amoeba*

many species have a colonial organization of interconnected individuals (Fig. 4.11).

The major sub-groups of the protozoa are classified on the basis of their locomotion and characteristics of their life cycles. The nutrition of some of the pigmented flagellates may be exclusively photoautotrophic, but the majority of the protozoa are heterotrophs; many of them, so-called phagotrophs, eat other organisms or large fragments of these by phagocytosis, taking the organic material into food vacuoles for digestion. Numerous protozoa (osmotrophs) feed saprozoically, absorbing soluble organic materials.

The primary subdivisions of the protozoa are as follows:

(I) *Mastigophora* — motile by one or more flagella; included here are the "phytoflagellates" (photosynthetic) and the "zooflagellates" (non-photosynthetic) protozoa, which in the main, are osmotrophs.

(II) *Rhizopoda* — the amoeboid protozoa motile by means of pseudopodia; phagotrophic.
(III) *Sporozoa* — parasitic immotile, osmotrophic protozoa.
(IV) *Ciliata* — protozoa motile by means of numerous cilia; phagotrophs.

Aquatic protozoa are common both in fresh and salt waters. One of the commonest of all fresh water flagellates is the osmotrophic crytomonad *Chilomonas*. The predominantly marine dinoflagellate group includes many species that are parasitic in animals or plants as well as free-living photoautotrophic forms and many phagotrophic forms with diverse body forms. The so-called collar-flagellates use the flagella to collect bacteria and organic particles from the water.

Protozoa pathogenic to man which can be transmitted by contaminated water (*Entamoeba histolytica, Giardia lamblia, Naegleria gruberi* and *Acanthamoeba*) are described in Section 4.2.7.

4.2.2 Source water

Water from artesian springs and wells usually does not contain microorganisms, due to filtration effects of earth layers through which it passes. Increasing urbanization and industrialization as well as increased use of recreation facilities have placed extreme pressure on the microbiological quality of both groundwater and surface water sources. Water transport systems and storage facilities en route to customers become the major foci of public health and management concerns. More and more reliance is being placed on water treatment to produce finished water of acceptable microbiological quality, regardless of source quality. Data collected in the USA in the 1970s showed that 67% of the largest water-borne disease outbreaks were due to source water contamination where treatment was either inadequate or non-existent [16].

The microbiological quality of source water has been assessed through the use of indicator microorganisms. Until recently, total coliforms have been most often used to determine the level of treatment required for a source water. Treatment strategies recommended by the US Public Health Service for source water are shown in Table 4.2.

In recent years, the use of coliforms as an adequate indicator of microbiological quality of water have been found to be insufficient. Newly discovered pathogens such as *Legionella*, or pathogens recently recognized as causing water-borne diseases, e.g. *Yersinia*, are able to multiply in water under certain circumstances. Other pathogenic agents, such as *Giardia*, have resistant life-stages that survive for longer periods in the environment.

Table 4.2. Recommended sanitary requirements for water treatment systems related to the quality of the source water [16]

Designation	Treatment required	Type of water	Level of sanitary contamination	Coliform count (per 100 ml per month)
Group I	None	Protected groundwater	None	≤ 1
Group II	Chlorination	Ground and surface	Low	≤ 50
Group III	Complete	Water requiring filtration for turbidity; waters polluted by sewage	Medium	≤ 5000 and 20% of samples exceeding 5000
Group IV	Complete plus auxiliary treatment to rapid sand filtration with continuous postchlorination	Polluted	High	≥ 5000 in more than 20% of the samples and $\geq 20{,}000$ in not more than 5% of samples

Thus, it has been shown that it is inadequate to relate pathogen occurrence in water to faecal contamination by traditional indicators [16].

In addition, interpreting the meaning of the presence of coliform bacteria in relation to faecal contamination of a source water continues to be difficult. Coliforms are able to regrow under a variety of conditions. Blooms of *Escherichia coli* have been reported in Lake Burragorang, the raw water source for Sydney. The blooms occurred at several locations simultaneously in this lake after spring rainfall and algal blooms. The same serotype of *E. coli* was found in several areas of the lake, which suggested regrowth as opposed to direct faecal contamination [17]. *E. coli* has been shown to survive and to grow in a warm 28.5–38°C monomictic reservoir which receives thermal effluent [18]. In the summer of 1983, a persistent coliform bloom was observed in an open finished water reservoir in California. The bloom, identified as *Enterobacter cloacae*, lasted for several weeks and it was found to be associated with a concurrent algal bloom and a resident frog population in the reservoir [16].

More detailed information on source water microbiology and protection can be found in Pojasek [19] or in [16].

Increasing interest in studying microorganisms in mineral water may be found in the literature. In a variety of European springs, the following bacterial genera have been found: *Pseudomonas, Xanthomonas, Flavobacterium, Arthrobacter* and *Achromobacter.* However, in Spain a predominance of appendaged and/or budding bacteria and of iron-related bacteria was found, with *Caulobacter* as the most frequently isolated genus [20]. It is surprising that samples of bottled Spanish uncarbonated mineral drinking water stored at 6°C showed a higher bacterial population than those stored at 20°C. This could possibly be because the low mean temperature of the spring (6–9°C) stimulates the multiplication of some bacteria, even though not all autochthonous bacteria adapted to this temperature are really psychrophilic. It is possible that bacterial growth in bottled mineral water could be prevented by pasteurization or sterilization. However, in countries such as France and Spain, where these and other treatments are not permitted because the mineral water is considered to have therapeutic properties, these populations are unavoidable. Moreover, their presence indicates that mineral water has not been sterilized and its therapeutic characteristics have been conserved. Furthermore, the absence of bacteria in any unsterilized, low nutrient water may indicate the presence of toxic substances [20].

In some countries, legislation concerning the hygienic quality of mineral waters employs specifications concerning the absence of *Pseudomonas* *aeruginosa*. In Spain, the absence of *P. aeruginosa* in 100 ml of water is an obligatory condition. According to the European Economical Community proposal for the legislation of the Member States, the absence of *P. aeruginosa* in 250 ml of mineral water at the spring and during marketing was recommended. The recommendation of the Coordinating Committee for Europe of the Food and Agriculture Organization/World Health Organization (FAO/WHO) is a similar proposal, but requires five 250 ml samples of each mineral water [21].

According to these documents, natural mineral water must be: (a) free from parasites and pathogenic microorganisms; (b) contain no *Escherichia coli* or other coliforms, faecal streptococci or *P. aeruginosa* in a sample of 250 ml; (c) contain no sulphite-reducing spore-formers in a sample of 50 ml, either at the spring or at the stage of marketing [22].

Aspects of the composition and quality of mineral waters may be found in Section 3.5.3.2.2.

4.2.3 Treated water

A variety of treatment schemes serve as the most important and direct means of controlling the microbiological quality of drinking water. They involve storage, pretreatment, coagulation and flocculation, filtration, and disinfection techniques. They are usually used for source waters. Groundwaters often receive no treatment or only disinfection because of the low levels of contaminants.

Storage serves to reduce organic matter, and also the numbers of microorganisms [23]. However, storage can also result in the degradation of water quality by pollution from water fowl and by algal growth which can promote growth of bacteria and actinomycetes, resulting in taste and odour problems [24].

The occurrence of blooms or dense growths of cyanobacteria in water storage bodies is of increasing importance and is related to the problem of eutrophication of rivers and streems. Many of these blooms are toxic and have caused significant deaths of livestock and wildlife, as well as being implicated in human illnesses. Although the distribution of freshwater cyanobacterial blooms is worldwide, most toxic species occur in temperate rather than tropical waters (for recent literature see e.g. [25]).

Certain treatment processes are less effective in reducing enteric viruses and protozoan cysts than enteric bacteria. Different treatment processes are differently able to remove and to inactivate viruses, bacteria, actinomycetes, algae, protozoa, filamentous fungi and yeasts in drinking water.

Virus removal and inactivation have been reviewed by several authors [23, 25–27]. It is generally accepted that conventional water treatment practices can reduce viral levels by a factor of 10^6 to 10^8 in the finished water. Disinfection, mostly in the form of chlorination, has been the main method of virus inactivation in drinking water. Viruses seem to be considerably more resistant than coliforms, thus requiring higher doses and longer contact times (for ref. see [16]).

The effectiveness of removal of various bacterial pathogens or indicators by treatment processes has been reported and discussed by several workers.

The effects of three pretreatment types can be summarized as follows. Microstraining does little to remove bacteria but it does remove larger particles and certain types of algae [28]. Roughing filtration removes larger suspended solids or filamentous algae. Biological sedimentation is effective in removing ammonia [29].

Slow sand filtration has been the classical form of biological treatment and it has been used as a means to reduce water-borne outbreaks of typhoid and cholera [30]. A biofilm is formed on the surface of the filter, which removes bacteria, protozoa, viruses and also organic nitrogen. The mechanical process of filtration of the water through the sand bed increases removal of microorganisms as well as various chemical constituents.

Coagulation and sedimentation, used to treat surface water sources, greatly reduce indicator bacteria. Removal rates for *E. coli* and coliforms by aluminium sulphate range from 75 to 99.4% [16].

Among disinfectants, such as inorganic chloramines, chlorine and chlorine dioxide, the latest is the most efficient disinfectant for bacteria, having both the lowest effective dose and the shortest contact time [16], but human health problems can arise with its use [31]. Increasing pH increases the bactericidal activity of chlorine dioxide [32]. However, at higher pH values (> 7.0) chlorine becomes less effective because hypochlorite ions are formed. Increased pH levels (> 7.5) also convert dichloramines to monochloramines which are less bactericidal [16]. On the other hand, monochloramines are more efficient viricides than dichloramines [33].

Filtration results in a comparatively small reduction (50–90%) in actinomycete colony-forming units (CFUs) [34] which is attributed to the presence of actinomycetes in the natural flora of the filters [35]. The vegetative or the spore forms of actinomycetes are more resistant to chlorination than are coliform bacteria, and chloramines are even less effective [34, 35].

Yeasts and filamentous fungi are generally more resistant to chlorine and ozone than are coliforms [36, 37]. Water treatment generally results in a 100 times reduction in filamentous fungi CFUs [34, 38].

Algae are an important factor in surface water treatment because they frequently clog slow and rapid sand filters and can reduce the duration of filter runs [39, 40]. Usually, the greatest clogging occurs in the late summer months [41]. Silica shells of diatoms frequently clog filters even after the inactivation of the protoplasm inside. Algae and cyanobacteria can cause taste, odour and toxicity problems [25, 39, 42]. Coagulation and filtration can remove varying levels of algae from water [39, 40] but copper sulphate, chlorine and chlorine dioxide are also used and are relatively effective in controlling algal levels in raw and finished water. However, the chlorination of algal blooms increases levels of trihalomethanes or their precursors, which may result in the formation of carcinogenic substances. Another cousequence can be a release of nutrients which may be utilized by aftergrowth bacteria (for references and discussion see ref. [16]).

Protozoa may become another problem of water treatment. Usually, removal or inactivation of *Entamoeba* has been the central problem, but recent investigations also concerns *Giardia* [43]. Proper coagulation, flocculation, sedimentation, and filtration can remove up to 99% of protozoan cysts; slow sand filtration can remove *Giardia* cysts [16]. Improper operation of treatment facilities can cause outbreaks of water-borne illnesses caused by protozoa [44]. Chlorination and disinfectants such as chloramines and ozone can further reduce levels of protozoa [45–47].

4.2.4 Distribution systems

The possibility of contamination of the distribution system by microbial aftergrowth was suggested in the literature as far back as the 1920s [48] but the problem received more attention in the early 1970s when certain principles from microbial ecology were adapted and applied to drinking water distribution systems [16].

Viruses can be isolated from improperly treated or contaminated drinking water. The presence of viruses in drinking water samples has been reported from France [49] and USA [50]. Viruses present in drinking water due to improper treatment or distribution can cause serious outbreaks such as gastroenteritis and infectious hepatitis [51]. However, unlike other microbes, it is highly improbable that in a well-functioning distribution system virus levels would increase as the water moves from treatment plant to the consumer [16].

Olson and Nagy [16] reviewed observations, beginning by the early 1920s, that bacterial levels in drinking water increase due to passage through distribution systems. In the 1940s, American researchers have carried out comprehensive bacteriological analyses of drinking water and in addition to coliforms, they have isolated several other genera such as *Salmonella, Flavobacterium, Achromobacter, Pseudomonas, Alcaligenes* and *Proteus*. Research conducted in the 1970s have been based on a better understanding of the need to integrate physical, chemical and engineering data in such studies. In evaluating data reported mostly in the early 1980s, Olson and Nagy [16] concluded that among bacterial genera occurring in a variety of water supply systems, *Acinetobacter* and *Alcaligenes* were isolated from 73% of the systems, while *Flavobacterium* and *Pseudomonas* occurred in 90 and 100% of the systems, respectively. Gram-positive or Gram-variable genera were found to occur less frequently, but were present in 27 and 36% of the systems sampled, respectively. Coliforms were frequently identified in 58 and 83% of the systems examined, and were represented respectively by *Klebsiella* spp. and *Enterobacter* spp. *Staphylococcus saprophyticus* and *S. aureus* have been reported, and *Aeromonas* spp. have been isolated from all groundwater systems.

In the early 1980s, *Legionella pneumophila* has been detected, in addition to natural habitats, within the plumbing systems of homes, hospitals, and other buildings. *Legionella* sp. has been shown to be capable not only of surviving in this environment, but also of multiplying in warm water, especially under conditions typical of those found in the hot-water systems of hospitals. In some cases the occurrence of *Legionella* sp. has been associated with disease, while in other cases it has not. It has been suggested that this bacterium survives much of the drinking water treatment process now in use across the United States. It has further been hypothesized that *Legionella* sp. may be introduced via the municipal water supply and that this supply seeds the hot water and cooling systems of these buildings. These suggestions are supported to some extent by earlier findings that *L. pneumophila* is more resistant to chlorine than are coliforms, the group commonly used to indicate the sanitary quality of potable water. References to the literature may be found in a recent paper by States et al. [52]. These authors have conducted studies to investigate the survival and multiplication of *Legionella* spp. in public drinking water supplies. An attempt was made, over a period of several years, to isolate legionellae from a municipal system. Sampling sites included the river water supply, treatment plant, finished water reservoir system, mains, and distribution taps. *Legionella* spp. could not be detected in any of the samples other than those collected from the river. It was hypothesized that this was due to the maintenance of residual chlorine throughout this system. To investigate the potential for *Legionella* growth, additional water samples, collected throughout the system, were dechlorinated, pasteurized and inoculated with *Legionella pneumophila.* Subsequent growth indicated that many of these samples, especially those collected from areas affected by an accumulation of algal materials, exhibited a much greater ability to support *Legionella* multiplication than did river water prior to treatment. Correlation of chemical data and experimental growth results indicated that the chemical environment significantly affects the ability of the water to support multiplication, with turbidity, organic carbon, and certain metals being of particular importance. These studies indicate that the potential exists for *Legionella* growth within municipal systems and support the hypothesis that public water supplies may contaminate the plumbing systems of hospitals and other large buildings.

Bacteria of public health importance isolated from drinking water systems will be discussed in Section 4.2.8.

Actinomycetes are frequently found in drinking water distribution systems. Their levels are usually in the range of 10^0–10^2 CFU/100 ml. The genus *Streptomyces* is probably most frequently represented in drinking water, although *Nocardia* and *Micromonospora* species have also been reported [35]. *Actinomycetes* are microorganisms primarily responsible for taste and odour problems in drinking water [34] but they may also contribute to the degradation of the system [53].

Yeasts and filamentous fungi have received less attention in drinking water systems than bacteria. Yeasts have been isolated from regular drinking water [54]. Rosenzweig et al. [37] identified three species isolated from drinking water as *Cryptococcus laurentii, Rhodotorula glutinis* and *R. rubra.* The occurrence of yeasts on the surface of drinking water pipes was reported by Olson and Nagy [16] who identified *Cryptococcus albidus, C. laurentii, Rhodotorula minuta, R. glutinis, R. rubra* and *Sporobolomyces salmonicolor* as frequently occurring species.

Filamentous fungi isolated from drinking water generally belong to the *Deuteromycotina* with genera such as *Cephalosporium, Verticillium, Trichoderma, Penicillium, Sporocybe, Acremonium, Fusarium, Alternaria* and *Epicoccum.* Filamentous fungi have also been noted on, or isolated from, the surface of drinking water reservoirs, drinking water tanks, drinking water pipes, and pipe joints. Genera identified have included *Penicillium, Cladosporium, Cephalosporium, Verticillium, Trichoderma, Fusarium, Alternaria* and *Epicoccum* (for references see [16]). The possible public health importance of filamentous fungi is discussed in Section 4.2.7. They also contribute to taste and odour problems [55].

Algae and cyanobacteria are present in drinking water, particularly if light is available. Most of the widespread occurrence of these organisms results from the use of uncovered finished water reservoirs within the distribution system [56]. Frequently observed genera are *Schizothrix* (cyanobacteria); green algae such as *Chlorella, Ankistrodesmus* and *Scenedesmus*; and the diatom *Glenodinium*. Of these, *Chlorella* appears to be particularly widely distributed in finished drinking water reservoirs [56, 57]. Water from reservoirs frequently carries with it an algal load, and despite chlorination, the algae often survive passage through the distribution system [57]. Diatoms have often been observed in encrustations on the surface of drinking water pipes [58].

Since most protozoa feed on detritus and bacteria, their occurrence in drinking water is not unexpected [45]. Ciliate and amoeboid forms are commonly observed in uncovered finished water reservoirs [59] and amoebae have also been observed in uncontaminated distribution systems especially the genera *Hartmanella, Naegleria, Echinamoeba* and *Acanthamoeba* [45].

Among genera observed in slime or biofilm on finished water reservoirs, *Bodo, Vorticella, Uronema* and *Euplotes* have been reported [60]. Although most protozoa in drinking water have little public health importance, species such as *Giardia lamblia, Entamoeba histolytica, Balantidium coli, Naegleria floweri*, and the genus *Acanthamoeba* are regarded as protozoan pathogens [16].

To sum up, the microbiological quality of water may change during distribution to the consumers. This may be due to many factors and can present health problems. Factors responsible for microbial deterioration of water quality are summarized in Table 4.3.

4.2.5 Microorganisms as indicators of water quality

The incidence of microorganisms in waters gives a biological indication of their quality. This indication can be used practically to evaluate potable, industrial and wastewaters. Microorganisms present in water samples indicate the degree of their purity or pollution. Pollution can be caused by organic or inorganic substances. Organic pollution is generally due to proteins and polysaccharides. Inorganic pollutants include primarily the salts of iron, manganese and calcium. Microorganisms may also be indicators of salinity, pH and other qualities of water.

Table 4.3. Microbial deterioration of water quality during distribution [61]

Stage of supply	Problem encountered	Organisms involved	Significance
Distribution pipelines	Corrosion	(a) Sulphate-reducing bacteria *Desulfovibrio vulgaris* *Desulfotomaculum nigrificans*	Internal pitting and nodule formation in iron mains. Loss of carrying capacity
		(b) Nitrate-reducing bacteria *Micrococcus* *Bacillus* *Pseudomonas*	Odour of H_2S
		(c) Bacteria which alter pH and redox	Loose iron deposits
	Dirty water	(a) True iron bacteria *Gallionella and Leptothrix*	Consumer complaints with laundry and sanitary ware
		(b) Organisms which adsorb ferric iron — most microorganisms	Blocked filters and meters
		(c) Organisms which utilize iron humic complexes *Arthrobacter* *Siderocapsa*	Deposits in drink manufacture Formation of iron/organic slimes with loss in carrying capacity. Entrainment of algae. Animals graze any slime or deposit
	Depletion of oxygen	Many common heterotrophs, e.g. plate count bacteria	Putrefaction leading to offensive taste and odours
		Flavobacterium spp. Yeasts	Spoilage in food processing

Table 4.3 (continued)

Stage of supply	Problem encountered	Organisms involved	Significance
		Mycobacterium spp. *Klebsiella*	Some species are potential pathogens
		Amoebic cysts:	
		Entamoeba histolytica	Amoebic dysentery
		Naegleria sp.	Amoebic meningitis, i.e. in head swimming pool waters
		Giardia lamblia	Intestinal disorders
Possible hazards	Biological slime growths in medical and ancillary equipment, e.g.	Non-specific heterotrophic bacteria	
	(a) Dentists drills		Direct application to open wound, therefore potentially dangerous
	(b) Renal dialysis units		Danger of toxin formation and leakage to bloodstream when large volumes of tap water are incubated at 37°C in the presence of organic nutrients in dialysis fluid
	(c) Air conditioning plant		Can cause allergies
	(d) Water softeners		There is a danger of bacteriological contamination if not periodically sterilized
	Reduction of nitrates	Denitrifying bacteria	Nitrite formation Ammonia formation Possible production of chloramines and odour

Table 4.3 (continued)

Stage of supply	Problem encountered	Organisms involved	Significance
	Biodeterioration of materials	Many species of bacteria *Nocardia* Some fungi	Biodeterioration of tank sealants Biodeterioration of rubber sealing rings
Domestic or industrial plumbing	Microbiological growth on materials, e.g. tab washers, fibre seals, 'O' rings, hemp yarn and sealant pastes, tallow, fluxes, joint lubricants, plastic, components	Coliforms Pseudomonads, including *Ps. aeruginosa* *Mycobacteria, Nocardia* Yeasts Fungi and actinomycetes give high plate counts at 22 and 37°C *Flavobacterium* spp.	Complicates interpretation of microbiological tests Potential pathogens Potential pathogens Taste and odours produced Deterioration of water quality. Spoilage of food and manufacturing processes
	Biological slime growths in header tanks and water softeners	Various fungi, bacteria and actinomycetes derived from the water or surrounding environment and growing on volatile organic solvents	Water becomes jelly-like and unusable Large numbers of bacteria may be harmful
Final water	Organisms surviving treatment	Spore-forming bacteria, e.g. *Clostridium perfringens*, and *Bacillus cereus*	Metabolically active in nitrate-reduction and putrefaction. These two species can form enterotoxins if allowed to contaminate and grow in food

4.2.5.1 Indicators of organic substances

The decomposition of organic substances in waters is caused mostly by bacteria. In municipal wastewaters, the biodegradation caused by bacteria concerns proteins, sugars, fats, plant residues containing cellulose, pectins and lignins, etc. The process is terminated by the production of gases (hydrogen, carbon dioxide, ammonia, hydrogen sulphide, etc.), water, inorganic compounds and humus.

The chief decomposers of proteins are saprophytic bacteria such as *Bacillus subtilis, B. mesentericus, Escherichia coli, Pseudomonas fluorescens*, anaerobic clostridia and facultative anaerobic *Proteus vulgaris.*

Hydrogen sulphide, a product of protein decomposition, is mineralized by sulphur bacteria. Urea is metabolized by bacteria such as *Bacillus pasteurii, Sarcina ureae*, and by numerous fungi and algae. Starch and fats are decomposed by various heterotrophic bacteria. Anaerobic decomposition of cellulose is performed by the genus *Clostridium*; the genus *Cytophaga* participates in its aerobic decomposition. Methane production under anaerobic conditions is caused by methane-producing bacteria such as *Methanococcus* or *Methanosarcina.* Chitin is hydrolysed by *Bacterium chitinovorum* and by numerous fungi.

From the amino acids, resulting from the decomposition of proteins, ammonia is liberated, and it is oxidized to nitrites and nitrates by nitrifying bacteria *Nitrosomonas* and *Nitrobacter.* Denitrifying bacteria produce molecular nitrogen from nitrates. Nitrogen fixation is performed by nitrogenic bacteria (*Azotobacter*) and cyanobacteria (*Nostoc*).

Microorganisms which serve as indicators of water quality, are classified according to self-purification processes taking place in mineralization of proteins as follows:

polysaprobic — morphologically well-defined bacteria (*Sarcina, Spirillum*, purple bacteria of the genus *Chromatium*, chlorobacteria *Chlorobium*, filamentous hydrogen sulphide oxidizing bacteria *Beggiatoa* and *Thiothrix*), hydrogen sulphide indicating cyanobacteria *Oscillatoria* and *Anabeana*, algae *Polytoma, Carteria* and *Chlamydomonas*;

α-mesosaprobic — filamentous bacteria *Sphaerotilus*, cyanobacteria *Oscillatoria* and *Phormidium*, filamentous fungi *Mucor, Fusarium* and *Penicillium*;

β-mesosaprobic — green algae, diatoms and cyanobacteria (*Microcystis, Anabeana, Aphanizomenon*);

oligosaprobic — green algae, diatoms and cyanobacteria.

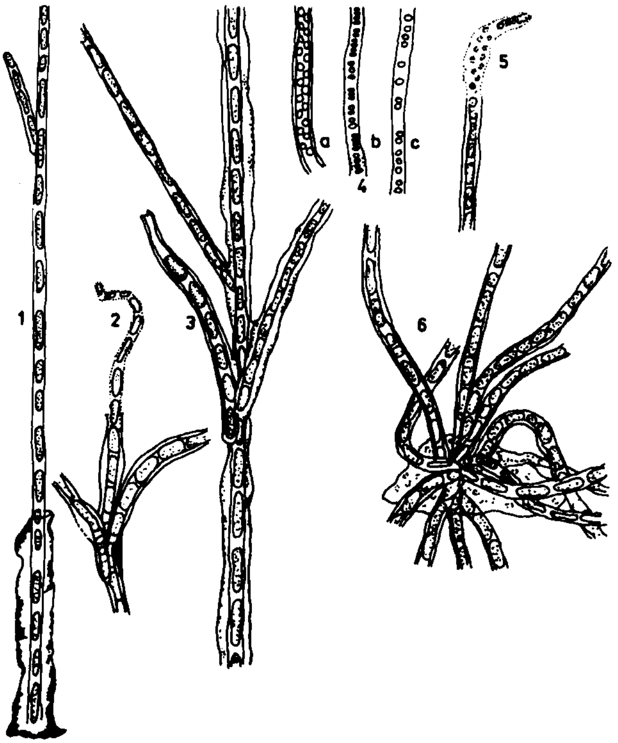

Fig. 4.12. Iron and manganese bacteria: 1 to 3 — parts of filaments, 4 and 5 — formation of gonidia, 6 — *Clonotrix fusca*, a bunch of filaments on a stratum of spores

4.2.5.2 Indicators of iron and manganese

In waters, iron is present as iron(II) hydrogen carbonate, sulphate or it is bound to humic acids. Manganese is present in its oxides and carbonates. The oxidation of iron(II) and manganese(II) compounds is performed by chemoautotrophic iron and manganese bacteria. The oxidation is possible under aerobic conditions in which bacteria utilize the liberated energy and the oxidized compounds are precipitated. Because in the oxidation of manganese less energy is liberated, more material must be oxidized and more serious damage can result in comparison with that resulting from the oxidation of iron.

The process of oxidation can be explained as follows. Fe^{2+} and Mn^{2+} compounds enter bacterial cells under alkaline conditions, they are oxidized inside the cells to neutral organic salts. These coagulate at the cell surface and are gradually changed to solid hydroxides or oxides.

The best known types of iron- and manganese-oxidizing bacteria are shown in Fig. 4.12. Filamentous oxidizers of iron and manganese are members of the genera *Leptothrix, Crenothrix, Clonothrix* and *Gellionella.* As a result of their massive growth, coatings up to 1 cm thickness may be formed.

Iron and manganese are also precipitated by the rod-shaped bacteria *Siderobacter* and coccoid *Siderocapsa*, by the flagellate *Anthophysa* vegetans and various *Rhizopoda.* The fungus *Papulospora manganica* is known to produce the "brown stone"; *Sideromyces siderophilus* liberates ferric oxide.

4.2.5.3 Indicators of calcium

The formation of calcium sinters on sand filters is partially a result of the activity of bacteria. Bacteria capable of precipitating calcium salts inside or on the surface of their cells are represented by sulphur, cellulolytic; sulphate reducing or molecular nitrogen fixing bacteria *Micrococcus, Desulphovibrio* and *Siderobacter.* Green algae *Chaetophora elegans* and *Cosmarium quadratum* are present in calcium-rich brooks. Stalks of *Vaucheria* are frequently covered by layers of calcium salts. The diatoms *Cymbella* and *Epithemia* are calcium-philic, as also are the cyanobacteria *Rivularia* and *Scytonema* and the alga *Haematococcus.*

4.2.5.4 Indicators of salinity

The salinity of seas, oceans, hypersaline lakes and the Dead Sea is represented mostly by chlorides; inland waters contain mostly carbonates and hydrocarbonates. Salts present in industrial wastewaters can influence the quality of underground and surface water. A variety of microorganisms indicate the presence of salts in water. For example, the diatom *Thalassiosire fluviatilis* is an indicator of potassium salts in wastewaters.

The occurrence of microbial groups in waters of various salinities is presented in Table 4.4.

As salinity of waters is mostly caused by chlorides (NaCl), the organisms which are able to live in hypersaline environments are named halophilic [62] or halotolerant [63]. Mechanisms of halotolerance have been reviewed recently [63].

Sea water contains about 3.5% of salts (mostly NaCl). Hypersaline waters which have an ion concentration similar to sea water are called thalassohaline. Such waters are typically chloride types. In general, the diversity

Table 4.4. Occurrence of microbial groups in waters of various salinities (adapted from ref. [62])

Group	Fresh water	Brackish water	Sea water	Hypersaline water
Prokaryotes				
Cyanobacteria	+++	++	+	+
Bacteria	+++	+++	+++	+
Algae				
Flagellates	+++	++	+++	±
Dinoflagellates	++	+	+++	0
Silicoflagellates	0	+	+++	0
Coccolithophores	±	+	+++	0
Diatoms	+++	+++	±	±
Conjugales — Desmids	+++	±	0	0
Siphonales	+	+	+++	0
Characeae	+++	+	0	0
Phaeophyceae	±	+	+++	0
Rhodophyceae	±	+	+++	0
Fungi				
Phycomycetes	+++	±	±	0
Myxomycetes	++	0	0	0

of organisms is greater in thalassohaline than in athalassohaline waters, and densities of organisms also seem to be higher. For example, the diversity of microbial flora is considerably higher in the Great Salt Lake, which is thalassohaline, than in the Dead Sea, which is much higher in magnesium and lower in sodium [62].

Two distinct types of purple sulphur bacteria were found in Great Salt Lake samples, one which resembled *Ecothiorhodospira*, the other *Amoebobacter*. *Ecothiorhodospira halochloris* was isolated from saline and alkaline soda lakes of Egypt. Cultures of non-photosynthetic *Halobacterium* have been isolated from the Dead Sea. *Halobacteria* have also been found in many brine pools and saturated lake waters. Non-photosynthetic bacteria, other than *Halobacterium*, isolated from hypersaline waters include chitin-digesting bacteria, denitrifying bacteria, *Halococcus*, *Vibrio*, *Achromobacter*, and sulphate-reducing bacteria [62].

"At salinities of less than 10%, a variety of cyanobacteria can be found and cultured from closed-basin lakes, including *Phormidium*, *Oscillatoria*, *Microcoleus* and *Aphanothece*. As salinities are increased above 10%, most of these cyanobacteria disappear, and only a single organism is found, which has been given the name *Aphanocapsa halophylica*. In the Great Salt Lake, this phototrophic organism is always a minor component of the saturated brines, apparently because it does not grow planktonically, but only attached to rocks and submerged structures. ... Most rapid growth of the *Aphanocapsa* occurred at NaCl concentrations between 16 and 23% NaCl, slow growth occurred at 7% NaCl, and no growth occurred at 3.5% NaCl, sea water salinity. At 30% NaCl growth was extremely slow. ... This cyanobacterium can thus be considered to be an obligate halophile, perhaps the only truly halophilic cyanobacterium" [62].

Halophilic yeasts were isolated from the Antarctic lake, Don Juan. Halotolerant yeast species, *Debaryomyces hansenii*, and osmotolerant *Saccharomyces rouxii* are known. A hyphomycete, *Cladosporium* sp., was found to grow in wood panels submerged in north-end water from the Great Salt Lake. Because of the extensive development and the fact that the salinity remained at 29% or higher, it seems clear that this fungus developed under extremely halophilic conditions [62].

The presence of protozoa in Dead Sea water has been reported. The development of both flagellate and amoeboid protozoa in an aquarium charged with Great Salt Lake water which became heavily colonized with bacteria and algae has also been reported, although no protozoa were seen microscopically in north arm water or sediment samples [62].

4.2.5.5 Indicators of peat-bog and underground waters

Peat-bog waters have a great insufficiency of calcium, they are strongly acidic and contain mostly humic substances and carbonic acids. In such waters, algae (*Desmidiaceae*), less frequently cyanobacteria (*Chroococcus turgidus*) and protozoa (*Rhizopoda*) can be found.

In underground waters, mostly in caves, red algae, diatoms and cyanobacteria are present at the deepest levels. Green algae (*Chara, Vaucheria*) are more dependent on light. Findings of photosynthetic organisms in underground and source waters indicate a lack of complete isolation from their environment. Slowly cooling underground waters may contain iron bacteria, *Clonothrix fusca.* Another group of iron bacteria, *Leptothrix*, from iron-manganese deposits on cave walls. Iron and manganese fungi, such as *Mucor* or parasitic *Saprolegnia* (in dead insect larvae) also occur in underground waters.

4.2.6 Microorganisms and sewage treatment

In water streams, spontaneous self-purification processes take place with an active participation of microorganisms. By the metabolic activities of these, wastewater organic and inorganic substances are gradually changed and the level of the dissolved oxygen increases. Figure 4.13 represents schematically the course of self-purification and the participation of bacteria, algae and protozoa in the process.

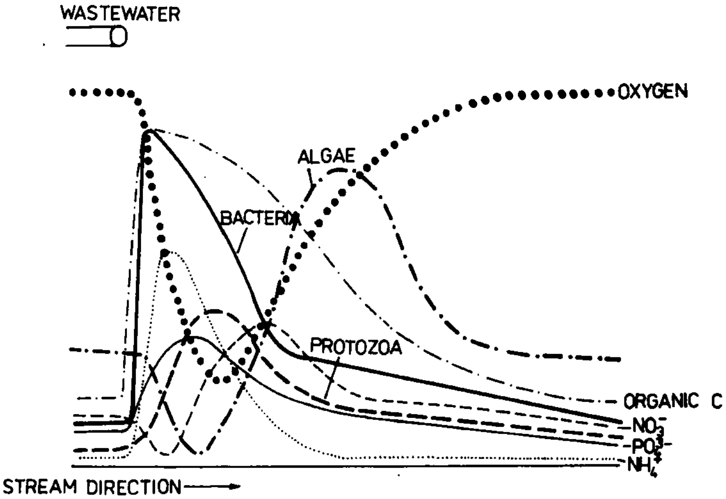

Fig. 4.13. Self-purification processes in a water stream (schematically)

Problems and techniques of the treatment of domestic and industrial wastewaters are described in Section 4.5.2. Some microbiological aspects of the processes are considered here.

In open sewage oxidation ponds, green flagellates and coccoid algae grow in distinct sequence and are essential, by the supply of oxygen for bacterial growth, to the purification process. The algae are to be removed and can be processed into cattle food by dilution with other feeds. It has been calculated that in the United States a total of six million acres of such ponds will be needed to deal with the water-borne wastes of that country by 1990 and that recovery of the algae from such systems would feed a quarter of the country's livestock [64]. There is little information on the bacterial flora, although *Alcaligenes, Flavobacterium, Pseudomonas*, other Gram-negative and some Gram-positive organisms may be present [61].

The activated sludge process is used at large sewage works and consists of running the sewage into tanks where it is aerated for 5 to 15 hours, and during this time flocculation of the organic matter takes place. The effluent is subsequently run into settling tanks, where the sediment is recycled back to provide an inoculum for the incoming sewage, whilst the water is sufficiently pure to be discharged into a river.

The chemical and microbiological changes that take place in activated sludge are not fully understood. In the microbial population heterotrophic bacteria dominate and these, with the saprobic protozoa, constitute the basic trophic level. Holozoic protozoa feeding on bacteria are also present. Fungi are present in low numbers, but algae are usually absent.

The majority of bacteria are Gram-negative organisms and the coli-aerogenes group account for only a small fraction. *Bdellovibrio bacteriovorus* which attacks bacteria reduces the bacterial numbers. Antibiotic-resistant aeromonads have been isolated from some samples. *Nitrosomonas* spp. are also present and are responsible for nitrification of ammonia.

The bacterial population may vary with the waste being treated. In antibiotic wastes *Pseudomonas* may be dominant. With fellmongery and tannery effluents, the activated sludge was dominated by *Pseudomonas* and *Acinetobacter*.

Protozoa are present in large numbers and may influence positively the quality of the effluent and may also play a part in flocculation (Fig. 4.14).

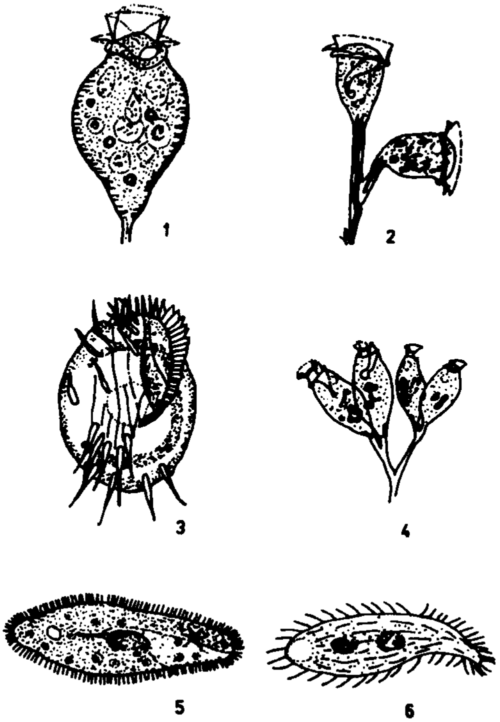

Fig. 4.14. Protozoa found in wastewaters and activated sludge: 1 — *Varticella*, 2 — *Carchesium*, 3 — *Euplotes*, 4 — *Opercularia*, 5 — *Parameccium*, 6 — *Trachelophyllum* (modified from ref. [61])

Filamentous fungi, and to a lesser extent yeasts, can be isolated from activated sludge. The following genera have been reported: *Cephalosporium, Cladosporium, Penicillium, Zoophagus* and *Arthrobotrys*.

It was considered that a single bacterial species, *Zooglea ramigera*, was responsible for flocculation but it has been shown that a wide variety of bacteria isolated from activated sludge flocks are able to flocculate. The microbiology of activated sludge bulking has also been studied. More than 25 different filamentous bacteria have been found and also some fungi and cyanobacteria which can cause bulking under certain conditions.

The activated sludge process is effective in reducing the number of coliform organisms, *Salmonella, Shigella* and *Mycobacterium tuberculosis* by 85 to 99%, polio virus type I by 90% and *Coxsackie* A9 virus by 98%. The process does not have a great effect on the cysts of parasitic protozoa.

When biological filtration with trickling filters is used, the bacterial *Zooglea* spp. often predominate together with *Pseudomonas, Flavobacterium* and *Alcaligenes*. Nitrifying bacteria are also present. Algae are abundant and include the genera *Stigeoclonium, Ulothrix, Phormidium, Euglena, Chlorella*, and others. There are also yeasts and moulds present including *Aureobasidium pullulans, Subbaromyces splendens, Fusarium aquaeductum* and other deuteromycetes.

The active film consists of an outer layer that is largely composed of fungi, a middle layer of fungi and algae and an inner layer of fungi, bacteria and algae. In contrast to activated sludge, fungi and algae comprise the greater part of the biomass [61].

The biological filter reduces the level of *Salmonella paratyphi* B84 by 99%, *Mycobacterium tuberculosis* by 66%, total coliforms by 85 to 99%, enteric virus by 40 to 60% and cysts of *Entamoeba histolytica* by 88 to 99%.

The microbiological aspects of sewage treatment have been considered in more detail in [61].

4.2.7 Water-borne pathogens and health hazards

Outbreaks of gastrointestinal illness of unknown aetiology can arise from drinking sewage-contaminated water or the use of untreated groundwater. Among the many biological agents present in streams, lakes and the marine environment likely to be of public health importance are those pathogenic organisms present in sewage, and particularly in wastewater discharged without treatment or with partial treatment, into rivers and coastal waters. Other sources of pathogens, besides sewage, are wastes from domestic animal farms, slaughter-house wastewaters, and rodents living in sewers. The main microbial agents of health significance include viruses, bacteria and protozoa [61, 64].

Pathogenic microorganisms live for a certain time after their discharge in the marine environment. Some disappear sooner than others, as is the case for those responsible for dysentery. Another important factor is concerned with the presence of other biological agents. The role of bacteriophages in the destruction of a number of bacteria is well known. Other organisms also feed on bacteria, flagellates, amoebas and other organisms living in the bottom sediments. Some microorganisms infested by these predators are destroyed, others are concentrated, so that the predators become carriers and reservoirs of agents which may be pathogens. For example, consumption of shellfish grown in polluted water has long been recognized as an important cause of typhoid fever and other enteric diseases. Evidence is also available that infectious hepatitis can be transmitted in this way. In the Mediterranean basin, because of the large consumption of shellfish, epidemic of enteric diseases from this cause still occur [64].

Cases and deaths from selected water-borne infectious diseases in the Mediterranean countries are summarized in Table 4.5. Microorganisms which can be pathogenic to man and which are transmitted by contaminated water are discussed below.

Theoretically, faecally polluted water may harbour a great variety of pathogenic viruses originating primarily from the human gastrointestinal tract. From an epidemiological point of view, the most important types present are the hepatitis and the gastroenteritis viruses. According to a recent review [66], enterovirus 72 (hepatitis A virus) is frequently implicated as the aetiological agent of outbreaks of water-borne disease, and evidence indicates that the "non-A-non-B" hepatitis viruses may also follow a similar pattern of spread. It is thought that the largest single water-borne outbreak of viral hepatitis in Delhi (India) in 1955–1956, involving approximately 30,000 cases, was caused by this agent.

Viral agents of gastroenteritis have been discovered in the examination of diarrhoeal stools. In this respect, the rotaviruses, the group of Norwalk-like viruses, the enteric adenoviruses types 40 and 41 and an undefined group of "Small Round Viruses" (SRVs) have been mentioned. Gastroenteritis of unknown aetiology is the most frequent illness spread by the water route and it is increasing rapidly, implicating the Norwalk-like viruses in particular [67]. Further examples of water-borne infections of viral origin are discussed in ref. [61].

Table 4.5. Cases (C) and deaths (D) from selected water-borne infectious diseases in Mediterranean countries [65]

Diseases		1970	1971	1972	1973	1974	1975
Cholera	C	1,023	139	399	280	21	56
	D	118	0	12	23	0	5
Typhoid and	C	36,752	25,731	27,076	36,646	16,400	19,698
paratyphoid	D	700	686	679	337	59	140
Bacillary dysentery	C	45,375	44,307	40,449	44,402	29,956	44,656
of amoebiasis	D	81	56	42	31	17	1
Infectious	C	85,685	88,978	84,785	112,953	37,944	74,411
hepatitis	D	1,529	1,586	1,698	1,224	538	89

The statistics are based on official information supplied to WHO by the following countries: Algeria, Morocco, Tunisia, Egypt, Cyprus, Israel, Syrian Arab Republic, Turkey, France, Gibraltar, Greece, Italy, Malta, Monaco, Spain, Yugoslavia. Not all countries have reported cases and deaths for all years from 1970 to 1975. Not all countries are reporting for all diseases recorded in this table.

Table 4.6. Relative sensitivity of enteric viruses to disinfection (highest sensitivity at top of the list) [67]

Cl_2	ClO_2	PAA	O_3
Human rota	Human rota	Echo	Human rota
f_2	*Coxsackie*	Human rota	Polio
Coxsackie	Echo	Polio	SA11
Echo	Polio.	*Coxsackie*	Echo
Polio	f_2	f_2	*Coxsackie*
SA11	SA11	SA11	f_2

Cl_2 — chlorine, ClO_2 — chlorine dioxide, PAA — peracetic acid, O_3 — ozone.

Table 4.7. Bacteria which can be pathogenic to man and are transmitted by contaminated water (adapted from ref. [61])

Organisms	Disease	Principal side affected
Salmonella typhi[a]	Typhoid fever	
Salmonella choleraesuis[a]	Enteric fevers	Gastrointestinal tract
Salmonella enteritidis and other serotypes[a]	Gastroenteritis	
Shigella sp.[a]	Dysentery	Gastrointestinal tract
Vibrio cholerae[a]	Cholera	Lower intestine
Enteropathogenic *Escherichia coli*[a]	Gastroenteritis	Gastrointestinal tract
Francisella tularensis	Tularaemia	Respiratory tract, gastrointestinal tract, lymph nodes
Leptospira icterohaemorrhagiae	Leptospirosis	Generalized
Mycobacterium tuberculosis	Tuberculosis	Lungs and other organs
Legionella pneumophila	Legionnaires disease	Lungs
Campylobacter fetus	Gastroenteritis	Gastrointestinal tract

[a] More commonly occurring infections.

There is a considerable degree of ambiguity and contradiction in views on the efficacy of various wastewater disinfectants on viruses. Recently, a comparative study of the efficacy of chlorine dioxide, chlorine, ozone and peracetic acid in the inactivation of viruses in a municipal sewage effluent was reported [67]. The viruses selected were bacteriophafe f_2, poliovirus 1, echovirus 1, (*Coxsackie* virus B5, simian rotavirus (SA11) and human rotavirus, this last being one of the most important enteric viral pathogens present in wastewater. The results shown in Table 4.6 indicate a wide range in the response of the viruses to chlorine dioxide. Of the three enteroviruses

Table 4.8. Protozoa which can be pathogenic to man and are transmitted by contaminated water (adapted from ref. [61])

Organisms	Disease	Principal side affected
Entamoeba histolytica[a]	Amoebiasis	Gastrointestinal tract
Giardia lamblia	Giardiasis	Gastrointestinal tract
Naegleria gruberi	Amoebic meningoencephalitis	Central nervous system
Acanthamoeba	Amoebic meningoencephalitis	Central nervous system

[a] More commonly occurring infections.

tested, *Coxsackie* virus B5 was the most resistant. In the case of the 2 rotaviruses, human rotavirus was more resistant than SA11. On the other hand, the other viruses tested responded differently to other disinfectants. The most resistant virus on nearly all occasions was the human rotavirus.

The pathogenic bacteria which are well characterized and most commonly present in sewage polluted water can include strains of *Salmonella, Shigella, Leptospira*, enteropathogenic *Escherichia coli, Francisella, Vibrio, Legionella* and *Mycobacterium* (see Table 4.7). A variety of cases of infections caused by these pathogens have been reviewed [61].

The most common pathogenic protozoa which can be transmitted by contaminated water belong to the genera *Entamoeba, Giardia, Naeglaria* and *Acanthamoeba.* The diseases caused by these protozoa and the principal sites which are affected are summarized in Table 4.8. Further data can be found in ref. [61].

4.2.8 Aquatic microorganisms and the cycle of matter

The totality of the regions of the planet Earth that contain living organisms is known as the biosphere; it includes the lower part of the atmosphere, the land surface of continents, and lakes, rivers and the oceans. The whole biosphere exists in a chemically dynamic state which depends on two main factors: the cyclic turnover of biogenic elements, particularly, carbon, nitrogen, sulphur, oxygen and phosphorus; and a steady input of energy from the Sun. Through the conversion of solar energy by photosynthesis many elements are withdrawn in the form of inorganic compounds from the environment and are accumulated in the organic constituents of the cells and tissues of living organisms. The major producers of organic matter are seed plants on land and unicellular algae in the oceans. These organic materials provide the energy sources for heterotrophic organisms.

The biologically important elements present in photosynthetic (and chemosynthetic) organisms remain in the organic state and serve as food sources for the primary consumers: animals and heterotrophic microorganisms. The primary consumers may serve as food sources for the other non-photosynthetic organisms so that these elements remain in the organic state. Before they again become available for autotrophic organisms, they must be converted once more to the inorganic forms in the process of mineralization. The principal agents of mineralization are non-photosynthetic bacteria and fungi. It has been estimated that at least 90 per cent of the carbon dioxide present in the biosphere arises through the metabolic activities of these two microbial groups.

Every organic compoud that occurs naturally is decomposed by some type of microorganisms. Highly specialized physiological groups of microorganisms play important roles in the mineralization of specific classes of organic compounds.

The turnover of all the elements that enter into the composition of living organisms constitutes the cycle of matter (see also Section 2.1.2).

Some biologically important elements undergo incorporation into living matter and their return to inorganic form is accompanied by cyclic changes in their state of oxidation (e.g., carbon, oxygen, nitrogen and sulphur). Others, such as phosphorus, do not change in valence.

Phosphorus is assimilated by living organisms in inorganic form as phosphate. In the cells, it is incorporated into organic compounds by the esterification of the phosphate ion. In mineralization, it is again liberated as inorganic phosphate. The cycles of other biogenic elements are considered below, and the participation of aquatic and other microorganisms in these cycles is characterized.

4.2.8.1 The carbon and oxygen cycles

The principal process in the cyclic turnover of biologically important elements is oxygen-evolving photosynthesis performed by plants, algae and cyanobacteria. In this type of photosynthesis the oxidized form of carbon (carbon dioxide, bicarbonate and carbonate) is reduced to carbon in organic compounds, and molecular oxygen is produced by the oxidation of water. Inorganic carbon is also converted to organic compounds by bacterial photosynthesis and chemosynthesis, processes in which molecular oxygen is not produced.

The oxidized forms of carbon available for photosynthesis are the carbon dioxide in the atmosphere and the soluble bicarbonate and carbonate in the waters of the earth's surface. On land, seed plants are the principal agents of photosynthesis accompanied by a minor contribution by the algae and cyanobacteria. In the oceans, the unicellular photosynthetic algae play the most important role in photosynthesis. It has been estimated that the total annual fixation of carbon in the oceans amounts to approximately 1.2×10^{10} tons, whereas that on the land is about 1.6×10^{10} tons [11].

The subsequent oxidation of the organic compounds produced in photosynthesis is coupled with the reduction of molecular oxygen back to water. The most direct means by which this is achieved are combustion and respiration in which organic carbon is converted back to carbon dioxide. Algae and plants, as well as the animals that feed on them, contribute to respiration.

The bacteria and fungi oxidize the bulk of organic matter. Three general routes of catabolism ("breaking down") of organic compounds are used by microorganisms:

(a) aerobic respiration in which molecular oxygen is used as the terminal receptor of electrons,

(b) anaerobic respiration in which bacteria use inorganic electron acceptors in the absence of oxygen; thus nitrate is reduced to molecular nitrogen or ammonia, sulphate is reduced to sulphide, and carbon dioxide is reduced to methane,

(c) fermentation in which no external electron acceptor is required and the organic compounds are degraded anaerobically by a series of reactions that release energy.

The biological (and non-biological) carbon cycle is shown in Fig. 4.15.

Anaerobic fermentation is an important process used in the wastewater treatment. The following stages of the process are recognized: (a) hydrolysis and fermentation, (b) acetogenesis and dehydrogenation, and (c) methane fermentation [69]. The process can be entered at any step, but the mixture or organics contained in most wastewaters is largely confined to components of the first stage. Complex organic substances include particulate material that must be hydrolysed into soluble components. Soluble materials are oxidized to low-molecular-mass organic acids, including acetic acid, the principal precursor of methane. Hydrogen gas is also produced, and this compound is extremely important in the system's ecology. The thermodynamic balance for the reactions converting alcohols and volatile acids to acetic acid is extremely sensitive to the hydrogen partial pressure. If the hydrogen partial pressure is maintained at a sufficiently low level,

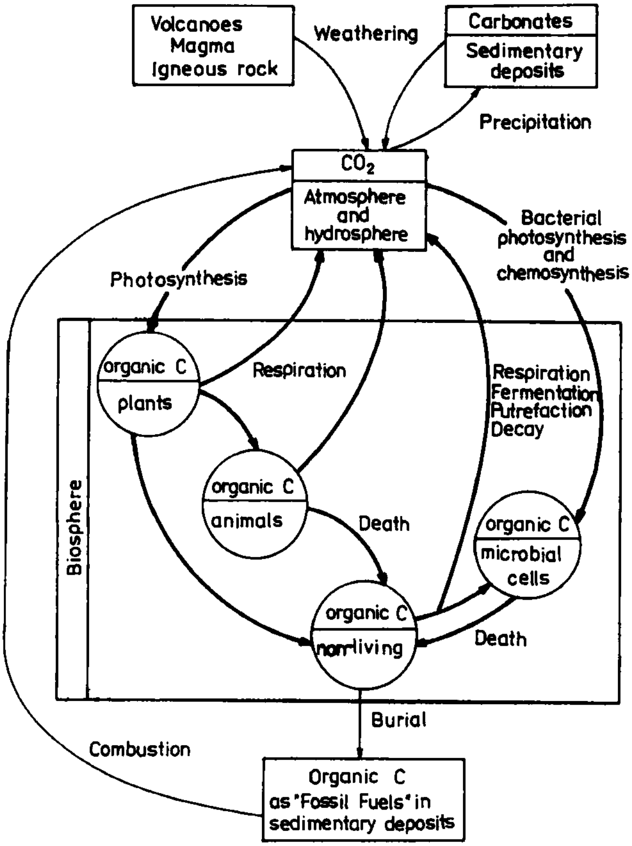

Fig. 4.15. The biological carbon cycle. Thick arrows — biological processes, thin arrows — non-biological processes (modified from ref. [68])

the free energy of conversion to acetic acid is negative, and the reactions proceed. Thus a symbiotic relationship exists between the bacteria using H_2 and CO_2 to produce CH_4 and those splitting acetic acid to CH_4 and CO_2.

In plant photosynthesis large quantities of insoluble polymers are produced which only microorganisms can degrade. These include cellulose and aromatic macromolecules — lignins and tannins. "Methods of aerobic degradation of aromatic compounds in the biosphere are well understood, but is only relatively recently that it has been shown how some bacteria can also degrade these substrates in the absence of molecular oxygen. This occurs by photometabolism (Athiorodaceae), nitrate respiration (*Pseudomonas* and *Moraxella* sp.) and methanogenic fermentation (a consortium) in which the benzene nucleus is first reduced and then cleaved by hydrolysis to yield aliphatic acids for cell growth. These methods may be used by microbial communities to catabolise man-made pollutants" [68].

The microbiology of accidental or routine oil discharges into aquatic environments has been reviewed by Bartha and Atlas [7]. Some of the observations quoted in their review deserve to be mentioned in relation to the environmental carbon cycle, as follows.

A large increase in numbers of hydrocarbon-degrading *Pseudomonas* sp. and of a non-hydrocarbon-utilizing *Staphylococcus* sp. occurred in Prudkoe Bay, Alaska, in the water column beneath experimental oil spills. The distribution of hydrocarbon-utilizing microorganisms in Chesapeake Bay was related to sources of oil pollutants; numbers of petroleum-degrading microorganisms were higher in natural environments exposed to oil. Populations of *Cladosporium resinae* and actinomycetes were predominant among the hydrocarbon-utilizing isolates. In the Indian Ocean and the Black Sea, populations of hydrocarbon-oxidizing microorganisms were found to be highest near shipping zones.

Most of the increases in microbial populations were associated with chronic inputs of petroleum hydrocarbons. Petroleum hydrocarbons can limit the growth of bacteria in sediment and water in non-oil contaminated estuarine ecosystems, and may also result in selective decreases in algal and protozoan populations. Not all microbial populations increase or decrease in response to the addition of petroleum hydrocarbons; some microorganisms show a neutral response to certain hydrocarbons, and, in these cases, population size of these organisms remains unchanged.

Petroleum and its hydrocarbon components have a low solubility in water and in the event of a spill form a separate liquid phase or "oil slick". Under metabolic attack by microorganisms, an oil slick undergoes characteristic changes known as emulsification, biodegradation and mineralization. Emulsification is defined as physical dispersion of the oil promoted and stabilized by surface active metabolic products, but without a reduction in biological oxygen demand (BOD). In contrast, biodegradation involves chemical changes in the parent hydrocarbons, usually accompanied by a reduction of BOD, but the products of biodegradation are not necessarily simple or harmless. "Mineralization" implies a complete recycling to harmless inorganic end products (CO_2 and H_2O for hydrocarbons) and a complete disappearance of the BOD. Typically, emulsification, biodegradation and mineralization processes affect an oil slick simultaneously, and form a logical sequence in the recycling of individual hydrocarbon molecules [70].

The genera of aquatic hydrocarbon degraders reported by various workers are listed in Table 4.9.

Table 4.9. Hydrocarbon-degrading microorganisms isolated from aquatic environments (adapted from ref. [70])

Bacteria	Fungi	Algae
Achromobacter	*Aspergillus*	*Prototheca*
Acinetobacter	*Aureobasidium*	
Actinomyces	*Candida*	
Aeromonas	*Cephalosporium*	
Alcaligenes	*Cladosporium*	
Arthrobacter	*Cunninghamella*	
Bacillus	*Hansenula*	
Bacterium	*Penicillium*	
Beneckea	*Rhodosporidium*	
Brevibacterium	*Rhodotorula*	
Corynebacterium	*Saccharomyces*	
Flavobacterium	*Sporobolomyces*	
Micrococcus	*Torulopsis*	
Micromonospora	*Trichosporon*	
Mycobacterium		
Nocardia		
Proactinomyces		
Pseudobacterium		
Pseudomonas		
Sarcina		
Spirillum		
Vibrio		

Polycyclic aromatic hydrocarbons of natural and anthropogenic origin are widely distributed in aquatic environments and soils. Their occurrence in aquatic and terrestrial ecosystems has received considerable attention since many of these compounds are recognized as mutagens and carcinogens. Bacteria, cyanobacteria, filamentous fungi, yeasts, diatoms and other algae have the enzymic capacity to oxidize polycyclic aromatic hydrocarbons. Some experimental results suggest that microbial degradation of these compounds may be important in their detoxification and elimination in the environment [71].

The significance of microorganisms in degradation of man-made chemicals (xenobiotics) including plastics, solvents, lubricants, detergents, pesticides and other pollutants in the environment has been reviewed by several authors (e.g., refs. [68, 71–74]).

4.2.8.2 The nitrogen cycle

The cyclic transformation of nitrogenous compounds is of great importance in the total turnover of this element in the biosphere. The main features of the biological nitrogen cycle are illustrated schematically in Fig. 4.16. Plants and algae assimilate nitrogen as either nitrate or ammonia to form

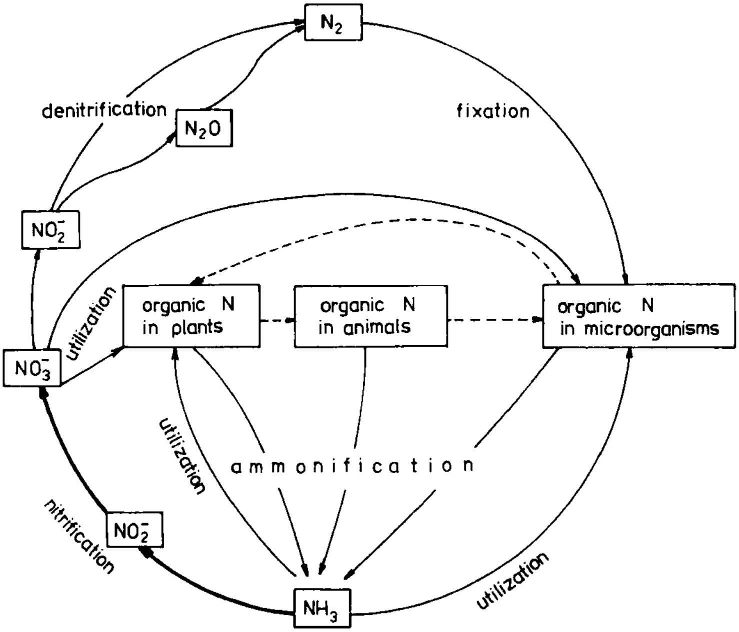

Fig. 4.16. The biological nitrogen cycle: the oxidations of the nitrogen atoms are shown as tick arrows, reductions as thin arrows, and reactions involving no valence change as broken thin arrows

organic nitrogenous compounds. These serve as the nitrogen source for the animals. During the assimilation of complex nitrogenous compounds by animals, significant quantities of nitrogenous compounds are excreted in the course of their metabolism. Depending on the animal groups, ammonia, uric acid or urea is excreted into the environment. Both uric acid and urea are decomposed with the liberation of ammonia. Part of the nitrogen is assimilated by the microorganisms themselves and converted into microbial cell constituents. These are ultimately converted to ammonia following the death of the microorganisms. The overall process of decomposition is called ammonification, with ammonia as the final product. Under anaerobic conditions (putrefaction), protein decomposition leads to amino acids which are converted to amines. In the presence of air, the amines are oxidized with the liberation of ammonia. Part of the ammonia can be again utilized by microorganisms.

Another process, the nitrification, is a conversion of ammonia to nitrate and it is brought about in nature by two groups of obligate aerobic bacteria. The first group, belonging to the genus *Nitrosomonas*, is capable of oxidizing ammonia into nitrite whereas the second group, *Nitrobacter*, oxidizes nitrite to nitrate. In the soil and water, nitrate is again assimilated by plants and algae.

Nitrification, followed by denitrification, is an important process in the removal of nitrogen from wastewaters. Removal of the nitrogenous constituents helps to minimize the toxicity of the water and to reduce its oxygen demand. The removal of nitrogenous material commences when the sewage is formed and almost all the urea is decomposed to ammonia and carbon dioxide. The toxic ammonia in a waste is first nitrified to nitrite and nitrate by aerobic biological processes and then denitrified anaerobically to molecular nitrogen.

Nitrification is achieved in the following steps:

$$3O_2 + 2NH_4^+ \xrightarrow[\text{species}]{\textit{Nitrosomonas}} 2NO_2^- + 4H^+ + 2H_2O$$

and

$$2NO_2^- + O_2 \xrightarrow[\text{species}]{\textit{Nitrobacter}} 2NO_3^-$$

The maximum rates of nitrification for *Nitrosomonas* and *Nitrobacter* occur in the pH range 7–9. The nitrifiers may be sensitive to temperature since the extent of nitrification is usually less in winter than in summer. Nitrification in the activated sludge process can be controlled by a long aeration period and by retention of the solids. Nitrification also takes place during the treatment of organic wastes by the biological filtration process.

If complete removal of nitrogen is required, then the most promising way is to use biological denitrification of the effluents which have been nitrified. Denitrification is a step in the biological nitrogen cycle in which nitrate and nitrite are reduced to molecular nitrogen. During the process nitrous oxide may be formed, but it does not appear to be a significant intermediate during denitrification in aqueous solutions.

The ability to carry out denitrification is known among a broad range of facultative anaerobic and anaerobic bacteria such as *Pseudomonas*. Denitrification requires a source of carbon, and methanol is often used for this purpose:

$$3NO_3^- + CH_3OH \rightarrow 3NO_2^- + CO_2 + 2H_2O$$
$$6NO_2^- + 3CH_3OH \rightarrow 3N_2 + 3CO_2 + 6OH^- + 3H_2O$$

If molecular nitrogen were completely inert biologically, the denitrifying bacteria would deplete the biosphere of all nitrogen available for growth, and life would cease on the planet. However, atmospheric nitrogen can be used by a few specialized microorganisms as a source of nitrogen for their growth. These nitrogen-fixing microorganisms compensate for the losses of combined nitrogen due to denitrification, and maintain its more or less constant amount in the biosphere. Nitrogen fixation is carried out by symbiotic and non-symbiotic nitrogen-fixing microorganisms.

Symbiotic nitrogen fixation results from a mutualistic partnership between bacteria belonging to the genus *Rhizobium* and leguminous plants such as peas, beans, alfalfa, clover and lupine.

The most important agents of non-symbiotic nitrogen fixation are cyanobacteria *Anabaena* and *Nostoc*, aerobic bacteria of the genera *Azotobacter* and *Beijerinckia*, and some other bacteria with a less important contribution to nitrogen fixation. Hence, nitrogen fixation, ammonification, nitrification and denitrification are the principal stages in the biological cycle of nitrogen in the biosphere.

4.2.8.3 The sulphur cycle

In many respects, the sulphur cycle (Fig. 4.17) is similar to the nitrogen cycle. Sulphur is abundant in the earth's crust. It is available to plants and microorganisms in the form of soluble sulphtates which must be reduced because sulphur occurs in living matter almost exclusively in the reduced form as –SH or –S–S– groups. The utilization of sulphate for the synthesis of sulphur-containing cell constituents and the subsequent decomposition of these substances results in an overall reduction of sulphate to H_2S, which is also formed more directly from sulphate through the activity of the sulphate-reducing bacteria (e.g., *Desulfovibrio*). These obligate anaerobes oxidize organic compounds and molecular hydrogen by using sulphate as an oxygen donor. Their role in the sulphur cycle is comparable to the role of the nitrate-reducing bacteria in the nitrogen cycle.

"The activity of sulphate-reducing bacteria is particularly apparent in the mud at the bottom of ponds and streams, in bogs, and along the seashore. Since sea water contains a relatively high concentration of sul-

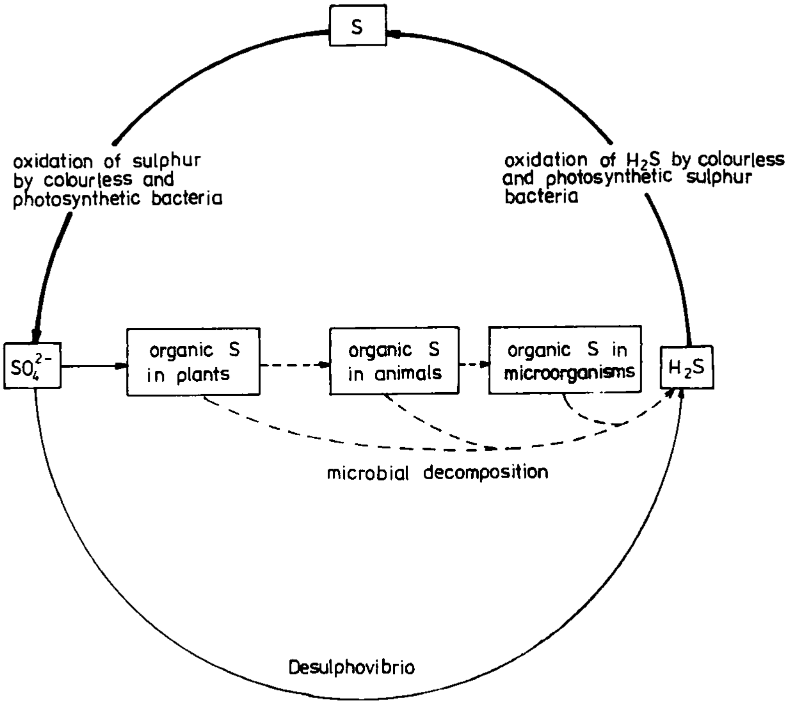

Fig. 4.17. The biological sulphur cycle: the oxidations of the sulphur atoms are shown as tick arrows, reductions as thin arrows, and reactions involving no valence change as broken thin arrows

phate, sulphate reduction is also an important factor in the mineralization of organic matter on the ocean floors. Signs of the process are the odour of H_2S and the pitch-black colour of the mud in which it occurs. The colour of black mud is caused by the accumulation of ferrous sulphide. Some coastal areas, where an accumulation of organic matter leads to a particularly massive reduction of sulphate, are practically uninhabitable because of the odour and the toxic effects of H_2S" [11].

A small part of H_2S in the biosphere remains in the form of insoluble sulphides or is spontaneously oxidized with oxygen to elementary sulphur. Photosynthetic and chemoautotrophic bacteria are capable of oxidizing H_2S and elementary sulphur to sulphate. This biological oxidation is affected either aerobically (colourless sulphur bacteria) or anaerobically (photosynthetic purple and green sulphur bacteria).

The aerobic sulphur bacteria *Thiobacillus thiooxidans* and *T. thioparus* are obligate chemoautotrophs. They occur in soils, muds, lakes and oceans and use the oxidation of sulphur and sulphur compounds as their energy sources for growth. *T. thiooxidans* is notable for its extreme tolerance of acidity, it will continue to grow until the pH has fallen to approximately 1.0.

The photosynthetic species, *Chlorobium* and *Chromatium*, develop under anaerobic conditions when light is available to provide the source of energy for growth. H_2S is used as a reductant in converting CO_2 to their cell material. During photosynthesis in muds and lake waters they may oxidize the sulphide and precipitate sulphur on such a scale that it can be ecomomically mined.

Many shallow coastal lagoons polluted by urban sewages have anaerobic layers (sediments or waters) in which activities of sulphate-reducing bacteria are important. They receive both continental fresh waters with organic material, and marine waters with salts and mineral nutrients. The high concentration of sulphate from sea water stimulates sulphate reduction in the anaerobic layers, which are highly involved in the mineralization of organic matter originating from in situ primary production [75].

4.2.8.4 The cycle of matter in anaerobic environments

In anaerobic environments, provided that light can penetrate, distinctive microorganisms are able to maintain an almost completely closed anaerobic cycle of matter (Fig. 4.18).

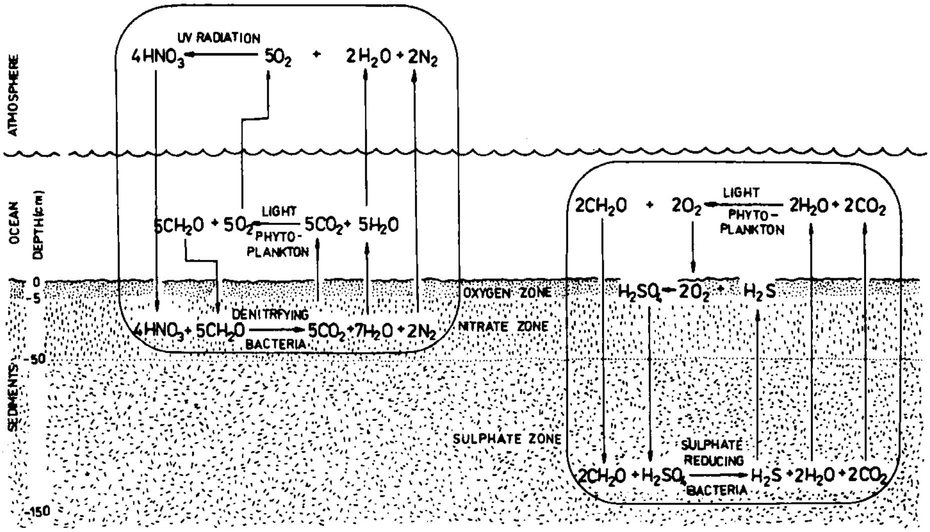

Fig. 4.18. Relationships of nitrogen, sulphur and carbon cycles in aerobic and anaerobic environments of the biosphere, i.e. atmosphere, ocean and sediments of the ocean ground (modified from Scientific American)

Under these conditions the primary synthesis of organic compounds is mediated by photosynthetic purple and green sulphur bacteria. They convert CO_2 to cell material and use H_2S as reductant. The purple non-sulphur bacteria assimilate acetate and other simple organic substances. The organic cell constituents of dead photosynthetic bacteria are decomposed by fermentative anaerobes which form CO_2, H_2, NH_3, organic acids and alcohols. Some of these products are anaerobically oxidized by sulphate-reducing and methane-producing bacteria. Under these conditions, H_2S and acetate are formed and both are utilized in turn by photosynthetic bacteria. The methane-producing bacteria convert CO_2 and the methyl group of acetic acid to methane. Much of this methane escapes to aerobic regions and is oxidized by *Methanomonas* and other bacteria. Part of the methane may be used by photosynthetic purple non-sulphur bacteria. The anaerobic sulphur cycle is completely closed, sulphate and H_2S being interconverted by sulphate-reducing and photosynthetic bacteria. The anaerobic nitrogen cycle is also closed, alternating between ammonia and the amino groups in nitrogenous cell materials [11].

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4.3 Macroorganisms in surface waters

Aquatic macroorganisms include mostly the higher forms of plants and animals living in water. However, it is useful to consider not only the taxonomic classification, but also the actual size of the organisms. Therefore, for example, aquatic plants also include some species of algae and mosses growing to large dimensions although they belong to microorganisms or lower forms of plants, according to the system classification.

As far as the quantity of produced mass is concerned, the aquatic plants follow the algae. In terms of the species, plants are quite distinct from algae: the majority of higher forms of aquatic plants belongs to families whose species are mostly terrestrial [1].

Some aquatic plants are fixed to the bottom by their roots and are thus called "rooting" plants. Others float on water with roots freely submersed in water without being fixed to the base, and are called "non-rooting".

Total biomass of fresh-water animals is formed mostly by molluscs, aquatic insects (larvae), bark beetles and fish. Less important from the aspect of weight, but often ecologically significant are the *Annelida*, whirligig beetles, and other worms [1, 2].

4.3.1 Plants and animals in stagnant waters

The arrangement of plants and animal communities in stagnant waters shows the general character of vertical zonation. As already mentioned, this is governed primarily by light and temperature conditions. For the primary production, the depth of the compensation point is decisive. For water aeration, formation and depth of the jump layer is important.

4.3.1.1 Littoral zone communities

(1) *Plants.* An important part of producers in the littoral zone consists of rooting plants, also called *benthic plants.* Their number and species are significantly influenced by the bottom quality and reservoir size. The bottom of large reservoirs with frequent surf is usually sandy or stony. Under such conditions plants can survive on the surface only with difficulty. Therefore, they grow in deeper layers with less intensive effect of the surf, or even none. In small protected reservoirs or backwaters the waves are negligible and the plants can grow up to the surface layer, or even above it, thus even further restricting surface motion. The residues of dead plants do not accumulate on the free surface, but remain on the spot and sediment to the bottom. The mud layer which provides very good conditions for the growth of the plants thus increases, and gradually water changes into a vegetated mud-flat which results in the backwater or reservoir filling with soil [3]. Sometimes, *Lemna* is intensively reproduced — a tiny (neustic) plant floating on the surface without being fixed to a solid base. If it covers the surface with a continuous layer it suppresses the development of other green plants. In the case of the littoral flora a distinct zonation depending on the depth of water can frequently be observed [1, 2, 4]. There are then

three zones inhabited with three groups of plants from the margin to the centre of the reservoir (Fig. 4.19).

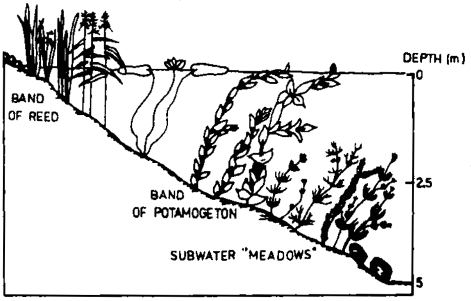

Fig. 4.19. Plant bands in the littoral zone

(a) *The zone of emerging vegetation.* These plants take root in the bottom, however, the majority of their photosynthetically active surface is above the water surface. Oxygen and CO_2 are taken from air, other necessary substances are taken via the roots from the mud, often also from anaerobic sediments so that they enrich upper water layers with nutrients deposited on the bottom. This zone is also called a *zone of emergent flora* or *solid growth.* It involves the regions from the water edge to a depth of about 2 m. The typical representatives of the emerged vegetation include *Typha, Phragmites, Sagittaria, Schoenoplectus, Scirpus, Sparganium* and *Glyceria.*

Some examples are shown in Fig. 4.20. Together with the plants growing on wet banks the emergent vegetation provides a natural transition between the aquatic and terrestrial environments.

(b) *The zone of rooting plants with leaves floating on the surface.* They take oxygen and CO_2 partially from water, from its best aerated layer. The floating leaves provide much more shade than the emerging plants, and they also provide suitable shelters for aquatic animals. This zone is usually at a depth of 0.1–2.5 m. Typical plants of this zone are *Nymphaea alba* or *N. candida, Nuphar luteum* and *Potamogeton natans* (Fig. 4.21). Water lilies *N. alba, N. candida* and *Nuphar luteum* are protected.

(c) *The zone of submerged vegetation.* This zone includes plants which are fixed to the bottom and which are more or less submerged. They often have narrow or even thread-like leaves by which they take nutrients from water. The roots of many submerged plants play the role of fixation rather than nutrition because they can take up nutrients by their whole body, particularly by the leaves. The zone of submerged plants covers a depth range of approximately 1–12 m. Sometimes, it is also called a *zone of soft growth.* One can find here the following species: *Myriophyllum*

Fig. 4.20. Some plants from the emerging-vegetation band. 1 — *Typha latifolia* (bulrush), 2 — *Phragmites communis* (reed), 3 — *Sagittaria sagittifolia*, 4 — *Sparganium erectum* (bur-weed)

spicatum which can be as much as 2 m long, with its flowers above the surface; *Ceralophyllum* sp.; *Anacharis canadensis* — also called elodea.

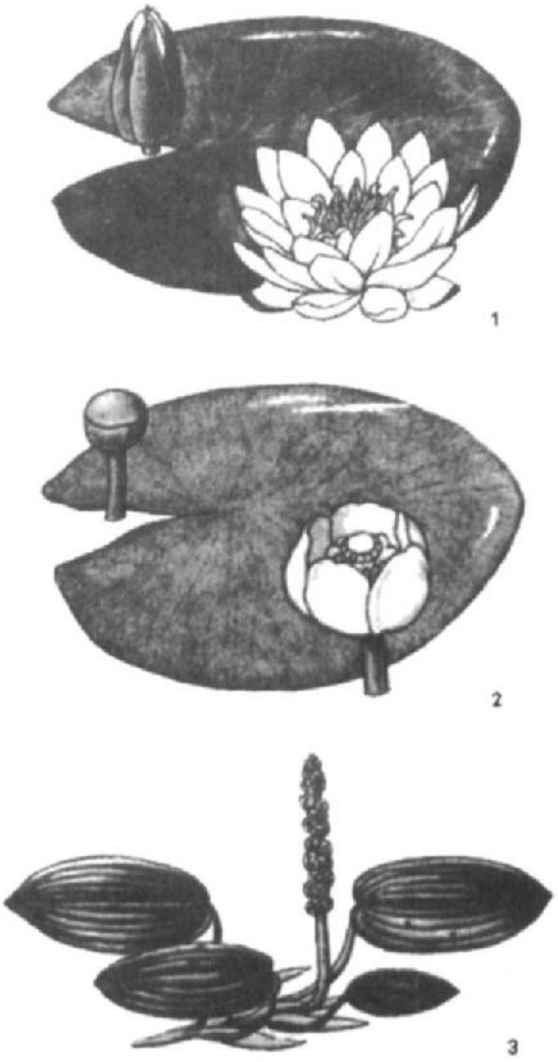

Fig. 4.21. Some representatives of the rooting water vegetation with floating leaves. 1 — *Nymphaea alba* (white water-lily), 2 — *Nuphar luteum* (yellow water-lily), 3 — *Potamogeton natans*

Sometimes, the lowest part of this zone is called *characetum* after chara (*Chara* sp.) which belongs to algae and often occurs in the deepest layers of the littoral zone, 8 to 12 m. The aquatic moss of the genus *Fontinalis* is sometimes also ranked among the submersed vegetation; with its long, divided branches and dense leaves it resembles higher plants. However,

Fig. 4.22. Representatives of the immersed vegetation band. 1 — *Myriophyllum spicatum*, 2 — *Anacharis canadensis* (elodea), 3 — *Fontinalis antipyretica*

it requires clean water. Some representatives of submersed vegetation are shown in Fig. 4.22.

Similarly to the land, it is vegetation which gives certain characteristic features to the aquatic environment. Vegetation in the littoral zone contributes to a special character for each reservoir and at the same time it reflects the sequential active cooperation of the plants during gradual formation or extinction of reservoirs. Depending on the circumstances, not all vegetation zones are always formed, or they need not to be in the given order. Also the boundaries between the individual zones can be fairly imprecise and overlapping, whereas in other places they are clearly separated with sharp intermediate boundaries [1–5].

The character of vegetation, i.e the producers, influences quite remarkably the character of the consumers' community, i.e. the animals.

(2) *Animals.* Animal communities of the littoral zone are noted for a greater variety when compared to other zones of stagnant waters. Also in the habitats of animals a certain zonation is evident, however, it is less distinct than that of the plants; a lot of species live in the whole of the littoral zone. Many animals live in a certain type of aquatic vegetation, and thus, also in the aquatic environment the animal community depends on the prevailing type of vegetation, in fact which is clearly observed on dry land. For example, in the zone of the emerging vegetation, the animal representation is poorer when considering both the quality and quantity

in comparison with the zone of the soft growth. Generally, four types of mutual relationships can be defined between the aquatic plants and animals [1, 4, 6, 7]:

(a) *Animals feed directly on plant tissues.* They do this by burrowing into the leaves or stems and eating them. They include some larvae from the Chironomidae family, for example, from the *Glyptotendipes* and *Endochironomus* genera, or young caterpillars of aquatic butterflies *Catachysta lemnata* L. Other animals nibble the plants, for example, older caterpillars of *C. lemnata* and some other caterpillars of aquatic butterflies, etc. In general, only a small amount of the plant mass is consumed by direct eating. A special group is that of herbivorous fishes. Some species, such as *Aristichthys nobilis, Hypophthalmichthys molitrix* and particularly *Clenopharyngodon idella* were imported into Czechoslovakia to eradicate the too-rich vegetation.

(b) *Animals eat the living growth on the plants (periphytone on the leaves and stems), or detritus sedimented on the leaves.* The majority of aquatic shellfish (*Gastropoda*) live in this way, and some, for example, *Limnaea stagnalis* eats also plants after having consumed the growth. Large quantities of the growth and detritus are consumed by tiny aquatic bark beetles, such as water fleas (*Cladocera* with the well-known daphnia) and *Copepoda*, or worms, particularly *Oligochaeta*. The growth and detritus on the plants sometimes serve as food for numerous tiny aquatic animals belonging to different systematic groups.

(c) *Animals employ the plants only as a basis to which they are fixed, but their food is the neighbouring sestons*, i.e. all bodies living and nonliving, floating or swimming on the water surface. These animals include many small predatory animals, such as larvae of, for example, *Phryganea*, or the *Cyrnus* and *Holocentropus* genera which prepare threads between the plants in order to catch their prey. Larvae of the *Ablabesmyia* and imagoes and nymphs of the *Ranatra linearis* L. heteropter and many others are in evidence, and *Hydra vulgaris* is abundant.

(d) *Animals living freely among the plants or fixed to them for a short time.* They include small predatory animals, such as aquatic heteropters of the *Plea, Notonecta, Naucoris* genera, or the only spider living in water *Argyroneta aquatica* L. which forms an air bell among the plants. They also include many leeches (*Hirudinea*), and *Hydracarina* parasiting on the aquatic instects, species such as the *Sitodes* or *Triaenodes* genera floating among the plants, and many others.

For the littoral zone, tadpoles, frogs, salamanders and other amphibians are also typical, and there may be some reptiles (snakes and tortoises).

These move freely among the plants which they sometimes use for a rest, many of them frequently appear on the adjacent parts of the land. They belong to the group of primary and higher consumers. If their stock density becomes too high, for example, in the case of tadpoles, then they play an important ecological role in the littoral zone.

Many animal species live in mud or on its surface. They are usually organisms which are satisfied with a minimum concentration of oxygen — a few tenths of mg l^{-1} — but they are also able to survive for a certain period of absolute oxygen deficiency. Typical inhabitants of mud are various aquatic worms, particularly *Oligochaeta*. *Lumbriculus variegatus* is sometimes even 10 cm long, however, the best known is *Tubifex tubifex* which is used as live food for fishes in aquaria. They are abundant and sometimes cover the whole muddy bottom. Their characteristic feature is that their head and the front part are in the mud, and their rear part which is used for breathing is permanently waving in the water. Another group of worms living in the muddy bottom of the littoral zone are *Dendroelum lacteum* Müll. and many species of the *Planaria* genus. There are also larvae of the *Chironomus* and *Tanytarsus* genera, dragon flies, and other insects. Sometimes, they are also used for characterization of the trophic level of water.

Tanytarsus lakes are oligotrophic, larvae of the *Tanytarsus* genus live on their bottom and require several mg of O_2 l^{-1}. Chironome lakes are autotrophic, water at the bottom is strongly oxygen-deficient and therefore they are inhabited by the larvae of the *Chironomus* genus requiring very low concentrations of oxygen, and even its complete deficiency for a short period.

Of the higher forms of animals, shellfish can be frequently found, particularly the well-known *Anodonta cygnea* L. and crayfish *Astacus leptodactylus.*

Rather different properties and communities are found in the sandy or stony littoral zone. Sand is permanently being moved and transferred due to the surf and therefore only some special species are able to live in it. They include, for example, larvae of the species of the *Molanna* genus which build shells of such shape that it is impossible to turn them over easily. Some larvae, e.g. of *Sialis flavilatera* or predatory larvae of dragon flies, are buried in sand. Because the conditions in the sandy littoral zone are similar to those in running waters, the species living in the torrentile sections of the stream can also appear here, for example, dung-beetles and crayfish. In the stony littoral zone small animals living on the surface of aquatic plants or employing another solid base can also survive quite well. They include, for example, the larvae of some *Chironomidae* and some leeches.

4.3.1.2 Profundal zone communities

The profundal zone is below the boundary of efficient light, therefore no photosynthesizing vegetation occurs there. They consume only food produced in the euphotic zone.

Another important characteristic of this zone is the near or complete deficiency of oxygen in the period of stagnation, and therefore the inhabitants of the profundal zone must be adapted to these conditions. Some of these consumers are saprophytes, i.e. they are mostly microorganisms some of which are anaerobic. There are also other animals whose common feature is that they require only very little oxygen. Generally, the animals of the pelagic zone are similar to those of the littoral zone, except that the variety of species and the quantity, are not so rich [2, 4, 8]. The most abundant of them are as follows:

(a) larvae of the *Chironomus* and *Ceratopogon* genera and *Oligochaeta*,

(b) small moluscs from the conchoid class, for example, *Sphaerium*, but also larger ones *Anodonta cygnea*, and

(c) an interesting group is that of the larvae of two-winged insects of the *Chaoborus* genus which move into the limnetic zone during the night.

4.3.1.3 Limnetic zone communities

Among the producers in the limnetic zone there are particularly algae and blue-green algae, which belong to microorganisms [2, 7]. Higher forms of plants are rare in free water, except in the case of shallow ponds, 2–3 m deep. They could become overgrown by macroflora typical of the littoral zone without any treatment. In deep waters only non-rooted plants can grow, floating on the surface, such as several species from the *Lemna* genus [1].

The number of animal species is higher, especially in small ponds. They can be divided into the species which are part of the net plankton, and nekton. In the plankton particularly small bark beetles such as *Calanoidea, Cyclopoidea* or *Cladocera*, are present. Among the most important species one should mention, for example, *Eudioptamus vulgaris*, or central-European largest water-flea *Daphnia magna*. Many of them perform so-called diurnal migration. They inhabit the surface water layers during the night, and deeper layers during the day. The height difference ranges from several cm

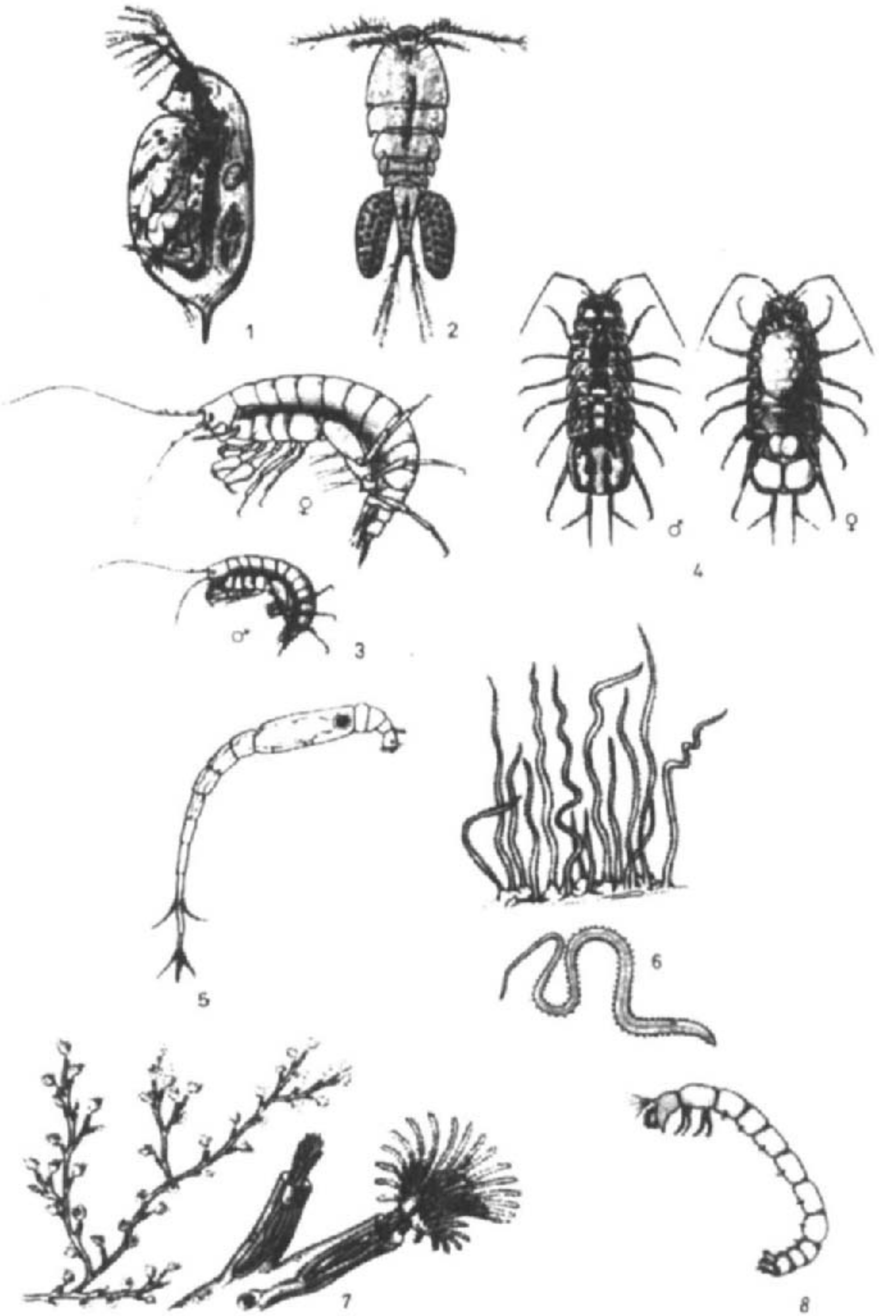

Fig. 4.23. a) Representatives of smaller water animals Crustacea: 1 — *Daphnia magna* (2–6 mm), 2 — *Diaptomus vulgaris* (2.5 mm), 3 — *Gammarus pulex* (12–15 mm), 4 — *Asellus aquaticus* (8–12 mm). Worms: 5 — *Rotaria neptunia* (0.5–0.9 mm), 6 — *Tubifex tubifex* (25–40 mm)

Fig. 4.23. b) Representatives of smaller water animals. Others: 7 — *Plumatella repens* (5 mm), 8 — Larva of *Chironomus thummi* (10–12 mm), 9 — *Phryganea grandis* (caddisfly): imago, larva without and with receptacle, and different receptacles (15–20 mm), 10 — water-spider *Argyroneta aquatica* (10–20 mm) with its air bell, 11 — shell of *Lymnaea stagnalis* (45–60 mm)

to tens of metres. They are stratified according to species and different stages of the same species. The larvae of the *Chaoborus* genus move during a day even in deep water right to the bottom, experiencing temperature differences from 4 to 25°C.

Organisms on the water surface membrane form neuston which can be further divided into *epineuston* and *hyponeuston.*

Epineuston is on the surface and includes *Gerris lacustris* L., many whirligig-beetles (*Rotatoria*) and spring-tails (*Colembola*).

Hyponeuston consists of organisms suspended from the bottom of the surface film, such as hydra (*Hydra* sp.), small bark-beetles, such as water flea *Scapholaberis* or *Notromas monacha* Müll. and different insect larvae. The limnetic nekton consists almost exclusively of fishes freely moving in the limnetic and littoral zones [2, 4, 6, 7]. They feed mostly on plankton and fauna of the bottom. Except for *Clenopharyngodon idella* and *Hypophthalmichthys molitrix* which were artificially acclimatized in the author's country (Czechoslovakia) they consume higher forms of vegetation only to a very small extent. From the agri-economics point of view the most important is carp (*Cyprinus carpio*), eating mostly plankton bark-beetles, and later also insect larvae. The food of tench (*Tinca tinca*) and of some other fish is similar. In many reservoirs eel (*Anguilla anguilla*) also flourishes; it is often artificially stocked. Some fish are predatory animals. They eat other fish and thus represent the final link of the food chain in the case of aquatic organisms. The pike (*Esox lucius*) is often stocked in ponds to control the trash fish. The largest predatory fish in such waters (in central Europe) is the sheat-fish (*Silurus glanis*) which can be as much as 2 m long and its weight can rise to 200 kg. Some typical representatives of aquatic animals are shown in Fig. 4.23.

4.3.1.4 Communities in special types of stagnant waters

In high-level bogs and peat bogs some plants and animals typical of the stagnant water environment are present [9–11]. In the peat bogs various aquatic plants and animals occur, some of which can also be found in the littoral zone of common stagnant waters, but some occur very rarely in other places than the peat bogs. The higher are the bogs, the more typical are the plant and animal communities, and this is particularly due to water quality, which becomes ever more acid and poorer in salts. The pH of the water of high bogs ranges from 4.5 to 5.5, and sometimes it can be as low as 3.5. Such water is practically free from electrolytes and is oxygen-deficient, which represents a very clearly delimited microclimate. The most typical components of peat vegetation are different species of peat-moos (*Sphagnum*). In the wet environment of high-level bogs and peat bogs *Eriophorum vaginatum* or *E. angustifolium* can be found together with other species. Here, also are present two interesting species of carnivorous plants: *Drosera rotundifolia* and *Pinguicula vulgaris.*

The animal communities are also rather poorly represented. In the peat bogs some whirligig-beetles, leeches, bark-beetles, other insects and higher forms of animals can be found. As typical representatives *Keratella serruhata* Ehrb. and *Elosa woralli* Lwd. of whirligig-beetles should be mentioned, and from the leeches, *Rotifer roeferi* and *Callidina reclusa*; significant insects are the dragon-fly *Leucorhinia dubia* Vanderl., *Neuronia reficrus* and the water scavenger beetle *Crenitis punctatostriata* Letzn. Frogs are represented by *Rana arvalis* which lives in muds and peat lands.

In the low-level bogs with a lower content of salts, communities similar to those of fresh waters are present, but with increasing salinity the number of species decreases rapidly.

In more salty waters no aquatic mosses can be found, but some fresh water fungi (*Ephydatia fluviatilis*) live here. Whereas no molluscs live in the peat bogs, in the low-level bogs with a salt content up to 6% often *Lymnaea stagnalis*, a well-known inhabitant of fresh water can be present.

In waters with a higher content of salts some worms live, such as *Stylaria lacustris* and *Nais elinguis.*

Typical inhabitants of strongly saline waters are, for example, the bark-beetle *Artemia salina* L., larvae of the fly *Ephydra reparia* Fall. and the beetle *Enochrus bicolor* F. It is interesting that in the low-level bogs no representatives of the sea forms are present. These organisms develop almost always from the fresh water types.

4.3.2 Plants and animals of running waters

Plants in running waters are almost the same as those in the stagnant waters, but their distribution, individual species and total number are different. The faster the flow of water, the greater the difference. However, many plants can live also in fast streams, often in considerable quantities nowadays. It seems that this is primarily due to the increasing content of nutrients in running waters and sediments. In the case of a more intensive overgrowth the flow-rate conditions can change markedly. Vegetation is able to change the direction of the main stream and the more dense growth can distinctly slow-down the flow-rate of water. The aquatic moss *Fontinalis* can remain attached in fast flows, providing a shelter and protection for animals which would not be otherwise able to live there. Higher plants, such as *Ranunculus* sp., *Callitricha verna, Veronica beccambunga, Myriophyllum*, and many others are fixed to the bottom with roots, and others flow down with the stream influencing thus significantly its speed, and finally they also change the river bed profile. Thus, vegetation can influence the properties of a stream without substantial changes of the plants in comparison to those living in stagnant waters.

Quite an opposite relationship is true between the running water and animals. While the aquatic animals usually have no significant effect on the properties of the stream, the problems caused by running water are resolved by several marked adaptations differentiating them from the fauna of stagnant waters [4, 12]. The most important methods of adaptation are as follows:

(1) *Permanent adhesion to a solid base.* Among the higher animals there are, for example, the larvae of *Plecoptera* or macroscopic *Ephydatia fluviatilis.* Stones, wood, tree branches, tufts of plants, etc. can serve as the substrate.

(2) *Suckers and hooks.* Suckers are used, for example, by *Planaria alpina*, larvae of ephemers of the *Rhitrogena* genus, *Prosopistoma*, *Origoneuriella* and others. The larvae of the mosquitos from the Blepharoceridas family have very well-developed suckers, e.g. *Blepharocera fasciata.* The suckers are the most efficient of the auxiliary organs, they also enable fixation onto a smooth surface. Hooks are used by the larvae of the *Hydropsyche* genus.

(3) *Fixing with filaments.* Some larvae of insects excrete secreta which solidify in water and form strong filaments by which they are fixed to a solid base. This is the case, for example, of larvae of some species of the *Rhyacophila* genus. Sometimes, the filaments are combined with suckers and hooks. The larvae of double-winged insects of the *Simulium* genus have suckers and also produce filaments. If they are removed from the base, they return to it using the filaments. Sometimes, the filaments are used not only for fixation, but also for catching food. *Hydropsyche* can use in addition to the hooks also a net made from the filaments, thus catching its food in a similar way as the larvae of the species of the *Philopotamus* genus.

(4) *Strong legs.* Most of the larvae of ephemers and flatworms living in flowing water have strong legs with spurs on their body sides. In contrast to the previous adaptation these enable quick motion in both directions. The larvae of some species of the *Hydropsyche* and *Rhyacophila* genera also have strong legs.

(5) *Sticky lower surface.* Many animals produce a sticky mucus which they use for fixation to a base. These include, for example, some molluscs (*Ancylus fluviatilis*) and the flatworms *Planaria.*

(6) *Fixed shelters and shells.* Many larves of *Chironomidae* make tunnels in the growths where they are protected against flowing water and thus they can also live in very fast flowing streams. Larvae of some *Brachycentrus* live in hiding places fixed with a filament, or they load them using bigger stones (*Goera, Silo, Lithax*). The larvae of the *Stemophylax* genus build whole shelters from bigger stones.

(7) *Streamlined body shape.* Most of the animals, from insect larvae through fishes have a streamlined body shape, i.e. they become narrower towards the tail end. Thus, they offer a smaller resistance to the water. For example, salmon-like fish living in quickly running waters, such as trout (*Salmo*) or grayling (*Thymallus*) have cylindrical bodies with a narrow muscular tail.

(8) *Flat body.* Flat body forms also reduce the water resistance. They enable the animal to find hiding places under the stones and in various gaps. The larvae of ephemers and others living in running water are clearly flatter than the larvae of similar species living in stagnant waters.

(9) *Positive rheotaxis.* Most of the animals living in running waters have a tendency to turn or move against the stream. This feature is hereditary and cannot be observed in the animals living in stagnant waters. If the latter come into flowing waters they are simply carried away without showing any attempt to orientate or move against the direction of flow. The fundamental factor conditioning rheotaxis is probably the flow of water itself. In the case of some animals, particularly flatworms, it is probably combined with the response to temperature changes or odours.

For the communities of running waters, the primary limiting factor is possibly the flow rate. However, the bottom quality was also found to have a significant effect. In fast (torrentile) sections the bottom is usually stony and offers a convenient surface to which both plants and animals can adhere. It is a good environment for the species which are able to fix to a solid base by suckers, hooks or filaments. In addition to these there are also various species of leeches (e.g. from the *Nephelis* and *Glossosiphonia*), and *Plecoptera. Plumatella repens* L. are fixed to the underside of stones. Many animals living mostly in stagnant waters can also be found here; they belong to various genera of worms (*Nematoda*), whirligig-beetles (*Bdelloidea*), mites or *Chironomidae.*

In slower flows (fluviatile) the bottom is often soft and unsteady, and consists mostly of gravel, sand or mud. The least suitable base is sand

and therefore such sections are the poorest in plants and macrofauna. Of the benthic animals, only those which burrow themselves live here. These include, for example, the larvae of damsel-flies of the *Gomphus* genus which protrude only the heads and the end of the tail out of the sand, and some bark-beetles of the *Gammarus* genus.

The animal communities on a gravel bed are also not rich in variety. Among the insects, some larvae of ephemers can be found here, as well as those of dragon-flies and others. In sections with larger stones and clean water it is sometimes possible to find — now rather rare — *Margaritana margaritifera* L.

A muddy bottom predominates on the slow sections of streams enabling sedimentation of fine particles. Communities in the mud with a high content of organic matter are more numerous as regards population, but on the other hand, in the muds poorer in organic matters more species occur [13]. The most typical inhabitants of a muddy bottom are *Oligochaeta* of the *Tubiflex, Ilyodrilus* and *Rhyacordilus* genera. The larvae of the *Chironomus* and *Glyptotendipes* genera are also present in higher amounts. Of the molluscs, the *Unio* genus especially *Unio pictorium* along with the *Anodonta* genus occur here. For example, also *Viviparus fasciatus* lives here, fixed to the stones carried down by torrent waters. Under the stones, leeches of the *Nephelis* genus often occur. The larvae of ephemers of the *Siphlonurus* genus and flatworms are not so frequent.

In running waters there are also organisms which are not fixed to the bottom. Many of them are on the river plankton, also known as potamoplankton. It can be said that the slower the stream, the richer the potamoplankton since the conditions for the reproduction and life of small organisms are better. In addition to various microorganisms there are particularly whirligig-beetles and water fleas; *Daphnia cucullata, Bosmina longirostris, Diaphanosoma brachyurum* are the main ones.

On the surface of slow streams small animals live, whose community forms the so-called pleuston. The most numerous are those from the *Gerris* genus (*G. paladum, G. odontogaster, G. lacustris*).

Fishes are also a natural component of the animal community in running waters. The specific requirements and characteristics of particular species are dealt with in the relevant literature. However, it is necessary to emphasize that although fish are not permanently resident at one place, there is a typical zoning along the stream, demonstrated in Table 4.7. This illustrates the dependence of the occurrence of fish in a mountain stream in Virginia (USA) on the flow rate (the highest being at the beginning of the stream), pH and the water temperature [14].

The occurrence of fishes in streams is considerably influenced by water pollution. A species which is very resistant against putrefactive pollution is *Leuciscus cephalus*, in contrast to the majority of salmon-like fish, for example, trout (*Salmo*), which need clean water. Eels (*Anguilla*), crucian carp (*Carasius*) and some others also tolerate a considerable degree of pollution.

4.4 Macroorganisms of groundwaters and springs

The habitat of groundwaters is naturally very different from that of surface waters. The dominating factor is light deficiency, so that producers are almost entirely absent. Therefore, inhabitants of dark places completely depend on other communities for their nutrition. Macroorganisms get necessary organic matter from leaves, pieces of wood or other organic matter transported by water from the surface, or they consume microorganisms. The latter live under the ground by their ability to degrade the same substrates or they consume organic substances already dissolved in water.

Since photosynthesis is not possible, the plants cannot grow in these underground spaces. Exceptions are some mosses and ferns on the walls of caves or wells where at least some light can enter [15, 16]. Here, the ferns *Cystopteris filix-fragilis, Aspelnium trichomanes, Phyllitis scolopendrium* and *Pellia fabronniana* are found. Animals live on mucus from chemoautotrophic sulphur and iron bacteria, or as carnivorous animals. Generally, in the case of the underground fauna a distinct relict character can be observed, its representatives often having systematically related forms only among extinct animals. It is probable that those evolutionary older animals which were unable to compete with younger and more capable forms entered the underground space. The life in groundwaters is manifested primarily by gradual degeneration of the organs of seeing, so it is not probable that they could again adapt to the life in running waters. The loss of the organ of sight did not proceed in the same way in all organisms and thus it is possible to encounter many forms of different stages of degeneration from eyes with normal pigmentation to completely reduced ones. The loss of pigments does not concern only the eyes but the whole body, and again all forms can be found. In place of sight the inhabitants of groundwaters have well-developed touch and olfactory senses, manifested in elongated feelers. Some also have long legs which render them faster and more nimble.

Since, together with the typical underground species, also species living on the surface occur also in groundwater, they are divided according to their relationship to the underground space as follows:

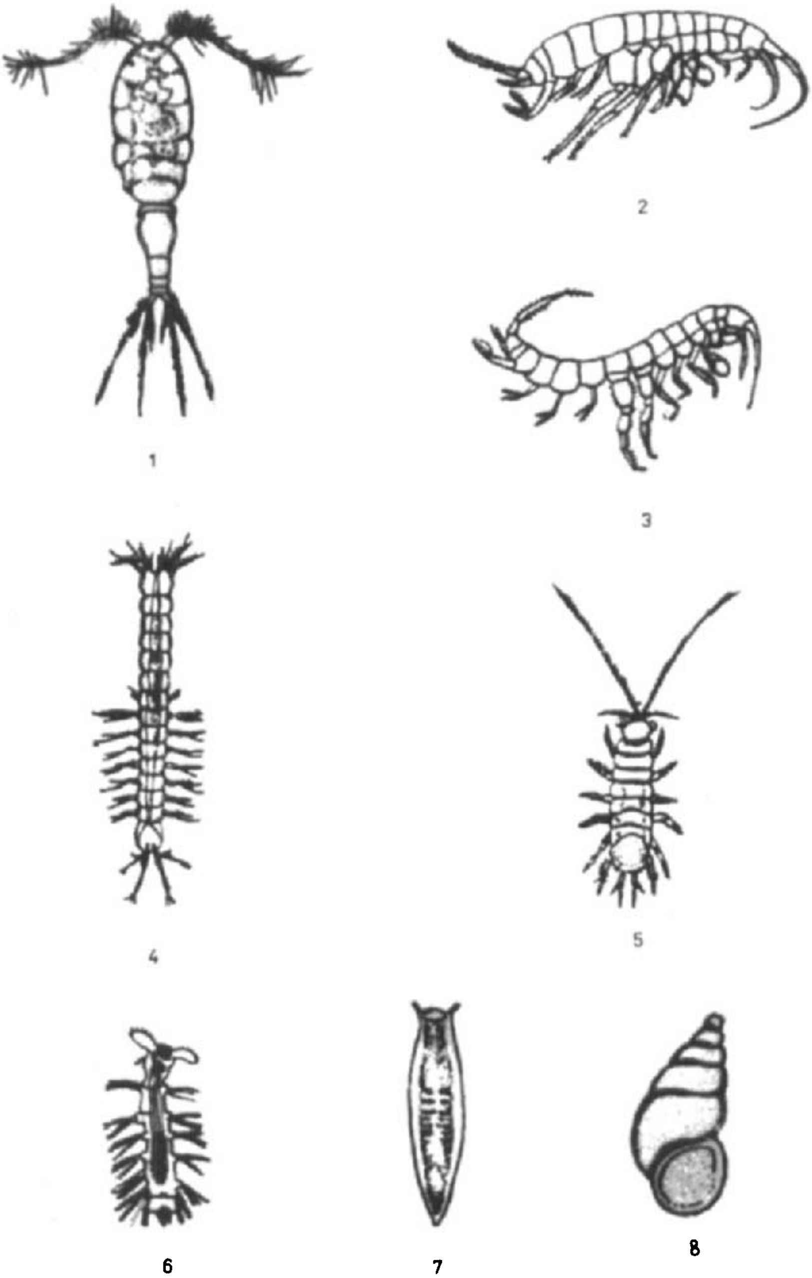

Fig. 4.24. Some animal inhabitants of caves. Crustacea: 1 — *Cyclops sensitivus*, 2 — *Niphargus puteanus*, 3 — *Niphargus aquilex*, 4 — *Bathynella natans*, 5 — *Asellus cavaticus*. Worms: 6 — *Trochlochaetus beranecki*, 7 — *Planaria alpina*, 8 — snail *Lartetia quenstedti*

— typical inhabitants of groundwaters living only under the ground are called *stygobionts*,

— species living in both ground- and surface waters are *stygophiles*,

— animals which occur in groundwaters only accidentally and rarely are *stygoxenes*.

Higher forms of animals, such as fish, amphibians and higher forms of bark-beetles can be found only in caves. However, they are very rare. Other typical inhabitants of caves are rather small animals (some of them are shown in Fig. 4.24).

For cave stygobionts the term troglobiont or filyxenes is sometimes used, involving also other animals, for example, *Asellus aquaticus*, various mites, worms, molluscs of the *Lartetia* genus, insects such as spring-tails belonging to the Sminthuridae and Onychiuridae families, and *Troglophilus cavicola.*

From among syglophiles the following should be mentioned: flatworms, some bark-beetles particularly of the *Cyclops* genus, and photophobic centipedes of the *Polydesmus* genus. Mosquitos often also occur in groundwaters (especially in mines) [17].

Typical inhabitants of wells are bark-beetles of the *Niphargus* and *Crangonyx* genera, and *Bathynella natans*, well known in Czechoslovakia and found in the wells of Prague [18]. This bark-beetle without the usual armour was also found in the Bratislava water main.

Inhabitants of groundwaters also appear in cold springs. Higher fauna in hot springs are poorly represented. In the hot springs of the Yellowston Park with a temperature of water 54°C, only two species of mites were found, two species of *Chironomidae* and few species of double-wing insects in addition to a few species of microorganisms [19, 20]; however, the larvae of this insect occur in the microbial coatings on the surface [4, 20]. Communities of springs reflect in general the transition between ground- and surface waters.

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4.5 Biological wastewater treatment

Any change of physical and chemical properties of water which results in the deterioration of its quality and utility value is considered to be pollution. In nature no water can be entirely clean and therefore when evaluating water pollution its expected use is always taken into consideration. Water can be polluted in a natural way, for example, by processes involving mechanical and chemical erosion, by biological processes taking in it, or by organic and inorganic substances from the neighbouring vicinity brought by wind and precipitation water. This natural pollution is easily managed with the crucial assistance of microorganisms. Much worse consequences follow from anthropogenic pollution caused by illegal or careless human activity.

According to its origin, water pollution can be

— *autochthonous*: where it is evoked by factors originating directly in the aquatic environment (for example, substances released in the course of degradation of dead aquatic organisms);

— *alochthonous*: this includes all types of pollution from foreign sources, both natural and artificial (for example, leaves and other residues of terrestrial organisms, but its main source are the products of various social and industrial processes).

Slight pollution, even alochthonous, need not be necessarily detrimental. Some communities in trophically poor waters, such as mountain streams, even depend on the supply of alochthonous substances. And in water sufficiently supplied with nutrients, slight pollution need not have harmful impacts because it is quickly eliminated by self-purifying processes. Adverse consequences occur when the degree of pollution is too great for the self-purifying capacity of water. This happens rarely in the case of natural pollution, but considerably more serious problems are caused by solid and liquid wastes of anthropogenic origin. These wastewaters represent a real danger. Usually, such pollution cannot be eliminated by natural self-purifying processes, and therefore it must be adequately treated before being discharged. Mechanical, chemical and biological methods are employed for wastewater treatment. The method of treatment depends to a high degree on the predominant type of pollution and particularly on which adverse effects are to be eliminated. In spite of the very wide variety of wastewaters, they can be categorized into several types (for details see Section 3.9).

4.5.1 Principles of biological treatment

For biological treatment the same principles are used as those applied involved in self-purifying processes, i.e. degradation of organic matter by microorganisms. The difference is that artificial conditions are created so that the degradation processes are as fast as possible. These conditions are modified by various technical procedures so that the degradation of organic matter can be either aerobic or anaerobic. An advantage of the aerobic treatment lies in quicker degradation and only slight odour, but the initial concentration of organic matter must be fairly low. Anaerobic methods can be applied to the treatment of concentrated wastewaters, but the temperature optimum is rather high and a lot of unpleasant smelling substances are produced.

Organic matter consists primarily of proteins, fats and saccharides which are degraded during biological treatment by microbial enzymes. Proteins are gradually hydrolysed by proteases to form amino acids, and by their further degradation final products are formed: ammonia and its compounds, hydrogen sulphide, sulphates, phosphates, carbon dioxide and water. During anaerobic degradation in alkaline media several off-odour intermediates are produced. Fats are degraded by lipases first into their basic components, i.e. glycerol and fatty acids, which are subsequently degraded to form carbon dioxide and water. The degradation of saccharides depends on the degree of polymerization. Simple saccharides are degraded very quickly to form the final products of carbon dioxide and water. The degradation of cellulose, pectins and some other polysaccharides is very slow. During anaerobic degradation, cellulose gives rise to hydrogen together with CO_2 in acid media, and methane in alkaline media.

In the course of biological treatment all types of organic matters are degraded simultaneously but at different rates. Since biological treatment is in fact biological oxidation the total progress in the treatment is given by the oxidation degree of degraded products per given time. The last oxidized compounds are those of nitrogen which occur originally in reduced forms such as ammonia or molecular nitrogen. Their higher oxidation states — nitrites and nitrates — appear rather late, only after organically-bound carbon and hydrogen have been oxidized. Thus, there are two stages of degradation:

(1) *Oxidation* — carbon is oxidized to CO_2, hydrogen to H_2O, other elements except nitrogen are oxidized to their oxides or oxy-salts.

(2) *Nitrification* — organic nitrogen is oxidized into nitrites and nitrates. The occurrence of nitrates in clean water is therefore evidence of the completion of degradation of most of the organic matters. However, the degree of nitrification is achieved rather late and usually it is not required during the treatment [1, 2].

4.5.2 Methods of biological treatment

Depending on the degree of wastewater pollution, hydrological, geological and climatic conditions, and depending also on economic considerations various methods of biological treatment exist. The degradation capabilities of microorganisms are applied in all of them, but generally the treatment efficiency is proportional to the technological requirements and available finance. It is therefore of great importance when choosing the treatment method, to correctly assess the effect of all factors, but it is also a very complex matter.

4.5.2.1 Irrigation with wastewater

Water for irrigation should be free from all toxic or other hygienically detrimental substances, and it must not have a high content of salts. Suitable water can be used for irrigation of all types of agricultural land including forests. The approximate volume required, per ha and per day, is 90 m^3 for meadow land and 30 m^3 for arable land. Irrigation can also be used for the final sedimentation of wastewater, in the so-called *third stage of treatment.* Disadvantages of irrigation are the increased requirements for loosening of soil, limited applicability after rains, freezing of soil, and odour [1, 3].

4.5.2.2 Treatment by soil filtration

Wastewater flows through a layer of sandy soil of granularity of 0.3–0.5 mm and a minimum thickness of 0.5 m. These soils are not used in agriculture, and groundwater must be at a sufficient depth. Wastewater is supplied at the most twice a day to a height of 5–20 cm, but percolating water should not dwell in the filtration layer longer than 4 h. The daily load is within the range from 300 to 1300 m^3 of wastewater per ha. This method is convenient, for example, for the final treatment of wastewaters from the food and drink industry, such as breweries, distilleries, yeast production plants, etc. [1, 3].

4.5.2.3 Treatment in stabilization reservoirs

This is one of the simplest methods. The term stabilization resevoir denotes all modifications of wastewater treatment in shallow ground-reservoirs in which both aerobic and anaerobic processes take place. The reservoirs can be either through-flow or accumulation ones [1, 3, 4].

In the accumulation reservoirs wastewater is retained until the stage of mesosaprobe is reached. Water can then be discharged without any risk, and the bottom is prepared for further use by sludge removal and liming. For a one-off operation, one reservoir is sufficient; in the case of continuous operations several reservoirs are required (one is fed, in the second one degradation takes place, while the third is discharged). First, anaerobic degradation takes place; in the case of wastewaters from sugar plants this lasts for the whole winter until April, and during this period the reservoir acquires an offensive smell. Either mainly bacteria or only bacteria participate in the degradation — *hypersaprobic stage*, then colourless flagellata are reproduced — *metasaprobic stage*, later infusoria occur — *isosaprobic stage*, green flagellata indicate the end of the anaerobic phase and water goes from the *polysaprobic* to the *alpha-mesosaprobic stage.* If the treatment is effective, the *beta-mesosaprobic stage* is achieved in autum. After the full aerobic phase has been reached fish can live in the reservoir. For anaerobic disposal of liquid wastes lagoons can also be used [3, 5]. These are deeper ground-reservoirs into which concentrated wastewaters and sludges are discharged. Anaerobic degradation takes place in them, the volume of water is reduced by evaporation and wastewater can be continuously fed into the lagoon. However, its use is limited especially because of percolation into groundwaters and its offensive smell.

Through-flow reservoirs, also called assimilation ponds, have a permanent supply of water. This is controlled so that the alpha-mesosaprobic stage is never exceeded. Thus, no anaerobic conditions with the accompanying offensive smell occur. In the case of too-high loading, aerobic conditions during the day and anaerobic ones during the night are permitted.

This is because the main supplier of oxygen is the photosynthetic algae, and diffusion from air at a quiet surface is very low. It is recommended that water be discharged away, from the banks or to several places so that no offensively-smelling anaerobic zones are formed at the banks. Rush and other higher plants must be removed. Occurrence of zooplankton, water-fleas and whirligig-beetles indicate good oxygen conditions, the occurrence of green-blue algae indicates a reduced nitrogen content. Degradation processes and photosynthesis take place also in winter, therefore, it is necessary to remove snow from ice or to water it so that it becomes transparent. The depths of the through-flow reservoirs range from 0.5 to 3 m.

Sometimes, biological treatment is combined with fish breeding, or original ponds are used for the treatment. It is important to keep the oxygen concentration higher than 3 mg l^{-1} and therefore wastewater must be adequately diluted and must not contain toxic substances. The water for dilution should not contain high quantities of humic acids and iron. In these ponds carp and sloths live, but their meat has rather unpleasant flavour and therefore they must be kept in clean water for a certain period of time before being consumed.

Stabilization reservoirs are a set of mutually connected reservoirs in which the process of treatment takes place gradually from the anaerobic stage in the first reservoir to the aerobic stage, for example involving fish breeding, in the last reservoir [1, 3, 5, 6].

4.5.2.4 Biological columns (sprinkling filters)

Biological columns are large-sized concrete or masonry structures, usually round with a gridded base. They are filled with filtration packing through which treated wastewater flows downstream (Fig. 4.25).

A column can be used only after a coat of microorganisms for degrading organic matter is formed on the surface of the filtration packing. The diameter of the packing particles is about 8 cm. Larger particles reduce the area of the active surface and thus also the treatment efficiency of the column; smaller granularity increases the active area, but the packing with its microbiological coating is easily clogged and the column becomes flooded. Material for the filtrafion packing should have a rough surface so that microorganisms are well attached, it must not be toxic and must be water-resistant. Until now, natural materials have normally been used, such as granite and slag; lava tuff which is light and durable was found to be the best. Recently, good results were obtained with plastic mouldings.

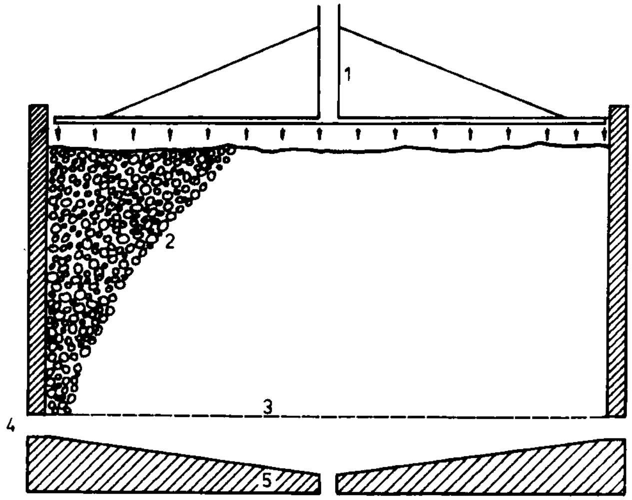

Fig. 4.25. The trickling filter (biofilter). 1 — rotating distributor, 2 — filling space, 3 — grate bottom, 4 — air holes, 5 — bottom with outlet

Degradation should be aerobic, therefore it is necessary to aerate the whole column sufficiently. If the oxygen conditions deteriorate the efficiency of treatment decreases. A worsened state is indicated by the formation of black sulphide sludge inside the column. Before coming into contact with the packing, wastewater should be evenly dispersed over the whole cross-section of the column. Therefore, it is applied on the filter surface by means of a Segner wheel or other sprinkling equipment. The biological filters operate most efficiently at temperatures from 8 to 20°C. When the temperature decreases below 8°C it is recommended that the columns be covered and at higher temperatures aeration should be intensified.

The most important technological parameters are as follows:

— hydraulic surface loading $q = \frac{Q}{F}$ (m^3 m^{-2} d^{-1}),

— volume loading $Z = \frac{S_0 Q}{Fh} = \frac{S_0}{h} q$ (g BOD$_5$ m^{-3} d^{-1}),

where Q is daily supply of wastewater on the filter (m^3 d^{-1}), F is filter area (m^2), h is height of the packing (m), S_0 is concentration of organic matter in wastewater expressed, for example, in the value of BOD$_5$ (BOD$_5$ g m^{-3}).

At a high volume loading the microorganisms can reproduce to such a degree that the flow-rate capacity of the column seriously decreases and the column becomes flooded. However, it should be noted that increased thickness of the microbial coat above the optimum limit does not result in increased efficiency of the column. At a high hydraulic surface loading the treated water can remove the microbial coat. This phenomenon, called the *circulation effect*, results in the fact that together with mineralized substances, floccules of the coat are also removed from the column. Therefore, a settling tank should be placed after the biological column. To obtain the optimum treatment effect of the column it is necessary to chose the correct ratio between the volume and hydraulic loadings.

The efficiency of a biological column is expressed in per cent of removed BOD_5:

$$E = \frac{S_0 - S_2}{S_0} 100 = \frac{\Delta S}{S_0} 100\%$$

where S_2 is concentration of organic matter in the treated water and ΔS is concentration of organic matter degraded in the biological column.

An efficiency of 95% has been achieved experimentally, but an efficiency of 85% BOD is considered to be good.

Biological columns are classified according to the degree of loading, the construction, operation, etc. The most frequently used types can be categorized as follows:

(1) *Low loading* (slow) — are characterized by low hydraulic and volume loading. Water flows for 20–60 min, and flushing is not much used. The efficiency is very good, BOD_5 decreases by 80–90%, 70–90% of suspended solids is retained, and the amount of organisms in the wastewater is reduced by 90–95%. Volume loading is about 175 g O_2 m^{-3} d^{-1}. Usually, no settlement tank is required.

(2) *Heavy loading* (fast) — with a high hydraulic and volume loading. Water flows for 10–40 min, and flushing is used. BOD_5 decreases by 60–65%, 65–90% of suspended solids is retained, and settling is necessary. The sludge is watery, its processing is more difficult and its quantity is about 50% higher in comparison with the first type. Volume loading is about 700–850 g O_2 m^{-3} d^{-1}.

(3) *Tower biological columns* (tower biofilters) — their volume loading is as much as 3000 g O_2 m^{-3} d^{-1}. They have several superimposed filtration blocks with ventilation openings (Fig. 4.26). Since the ratio of the diameter to height is 1:8 the area is smaller but the costs for pumping the water to the higher level increase. Some tanks are as much as 20 m high. Other modifications are, for example, *grate columns* (multizonal) in which grates with a 10 cm thickness of filtration packing alternate with a 10 cm free gap which results in better aeration. So-called "aerofilters" are similar to the slow types, but their capacity is increased by artificial blowing-in of air

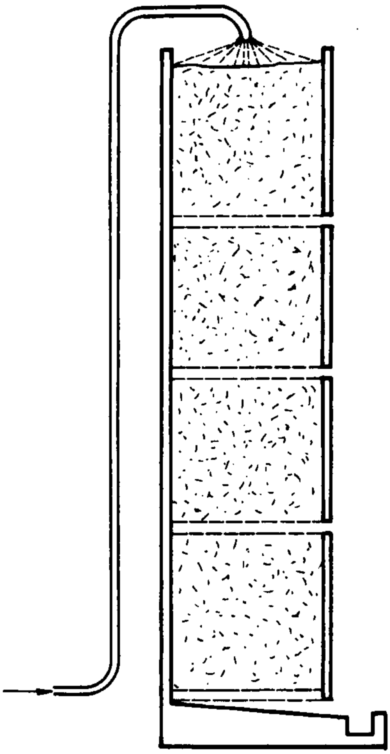

Fig. 4.26. A tower trickeling filter

or sucking of air into the packing from the bottom. Other types have also been tested.

In a new column the required microbial coating is formed within 5–10 days; in the case of a change of wastewater the column must be allowed to adapt for a certain time interval. Quite good results were recorded with wastewaters with a lower content of difficultly-degradable or toxic organic matter. However, the column must be first adapted, for example, missing nutrients must be supplied artificially and total loading must be reduced. Recently, the use of biological columns is being replaced by activation [1, 3, 7].

4.5.2.5 Activation tanks

At present, the most frequently used method of biological treatment is *activation of wastewaters* [1, 3, 6, 7]. In the activation tank, water is mixed with *activated sludge*. Whereas in the biological columns water flows through immobile microbial growth, in this case the activated component of the treatment, i.e. microorganisms, are dispersed in water in the form of activated sludge, which is a mixed culture of various microorganisms, particularly bacteria, fungi and protozoa. However, higher forms of organisms are also present here, such as whirligig-beetles, nematodes, land and freshwater worms *Oligochaeta* and others. The sludge composition depends largerly on the composition of the degraded substrate and technological parameters of activation [8]. It is important, however, that the activated sludge is flocculated so that it can be easily separated from the liquid phase by sedimentation. The activation process does not consist only of biochemical degradation, but also adsorption of colloidal and some soluble substances on the sludge floccules is important. Complete activation takes place in three stages:

(1) *Sorption stage.* First, colloids coagulate and their agglomerates are adsorbed on the floccules of active sludge. This stage is very fast and takes only few minutes.

(2) *Carbonization phase.* During this phase degradation and oxidation of organic matter to form CO_2 and H_2O take place. Particularly saccharides are mineralized; the degradation of nitrogen substances does not go beyond the stage of ammonification. In this phase all biological factors are applied, especially the activity of microbial enzymes.

(3) *Nitrification phase.* This involves degradation and oxidation of nitrogen substances into nitrites and nitrates, and is performed by nitrification bacteria. This stage takes quite a long time (4–5 h) even with intensive aeration; and because of economic reasons it is not usually carried out; the wastewater is discharged earlier and nitrification takes place in the recipient.

The activation process takes place in long, aerated activation tanks. At one end mechanically pretreated wastewater is supplied. Aeration is ensured by blowing compressed air by mechanical systems, such as paddle wheels, revolving cylinders, etc., or several methods can be combined. The concentration of oxygen in the tank should not drop below 2 mg l^{-1}, therefore, it must be well stirred during aeration. Wastewater is discharged from the other end into a settlement tank where the surplus sludge sediments. Part of this sludge is recycled from the sedimentation tank to the beginning of the activation reservoir. Because this recycled sludge is a live microbial culture it activates the treatment process in the reservoir.

The fundamental requirements for good treatment efficiency are as follows:

(1) *A sufficient amount of oxygen.* This is critical for the whole process of activation, which is in fact biooxidation. Only in the case of slow- and low-loaded activation is the content of oxygen permitted to decrease below

2 mg l^{-1}. The requisite level of oxygen is ensured by proper aeration of the activation reservoir. The air consumption depends on the concentration of organic matter in wastewater as well as on the required treatment effect. It is always necessary to supply a higher amount of air than that corresponding to theoretical calculations because it is necessary to provide aerobic conditions not only in the activation but also in the sedimentation tank. Usually, the air demand during activation ranges from 4 to 10 m^3 of air per 1 m^3 of wastewater, or between 25–40 m^3 of air per 1 kg of BOD_5.

(2) *A sufficient amount of microorganisms.* This is related to the required quantity of activated sludge in the activation tank. It depends particularly on the concentration of degraded substances, requirements for the rate of the treatment processes, and on the bioactivity of the microorganisms. These relationships are rather complex and their proper harmonization is necessary. Even if no microorganisms were directly supplied into the activation tank, microorganisms from air and wastewater would decompose organic matter. However, this process would take a long time. Therefore, it is clearly necessary to prepare properly each new activation reservoir. In the environment rich in nutrients, that is, in wastewater the degrading microflora reproduces itself — similarly to that in the biological columns. However, several weeks could elapse before it would reach the required density. This period can be shortened by recycling of all sludge from the settlement tank until activation sludge in the activation tank reaches approximately 15% of treated water volume. Even more convenient is to supply sludge from the nearest biological wastewater treatment plant. Into a properly prepared activation tank only such a proportion of sedimented sludge is added which is necessary for the required treatment efficiency. One might expect that up to a certain limit the more is sludge returned, the higher the treatment effect, or the higher quantity of organic matters that can be loaded. However, if the optimum amount of microorganisms with respect to the concentration of organic nutrients is exceeded, further degradation will not increase with increasing amounts of recycled sludge since the amount of newly formed microbial mass in the activation tank is reduced. This influences both its biological and physical properties. Increasing content of organic matter and biological activity of sludge also increases the requirements for aeration.

(3) *The requisite temperature.* Activated sludge has good treatment effects within a surprisingly wide temperature interval. Temperatures ranging from 7 to 17°C are considered to be optimum, but satisfactory treatment capacity is achieved at temperatures from 3 to over 30°C, due to the adaptability of the microbial heteroculture [9].

(4) *pH value.* Optimum effects of treatment are at pH 6.8–7.5.

The most important technological parameters of activation treatment are as follows:

Dwell time (t) is the ratio between the tank volume V (m^3) and the supply of wastewater Q_p ($m^3\ h^{-1}$):

$$t = \frac{V}{Q_p} \qquad \text{(h)}$$

Volume loading Z_0 is that quantity of substrate which is supplied into 1 m^3 of tank per day:

$$Z_0 = \frac{24 Q_p S_0}{V} \qquad (\mathrm{kg\ m^{-3}\ d^{-1}})$$

where S_0 is the concentration of substrate in wastewater, usually expressed by BOD_5 ($kg\ m^{-3}$).

Sludge loading (Z_s) is the quantity supplied per kg of dry residue of sludge per day:

$$Z_s = \frac{Z_0}{X} \qquad (\mathrm{kg\ kg^{-1}\ d^{-1}})$$

where X is the concentration of sludge dry residue in $g\ l^{-1}$ ($kg\ m^3$).

Sludge age (A) is the ratio between the weight of sludge dry residue in the activation tank (G) and weight of sludge dry residue per day (G_m) as surplus sludge:

$$A = \frac{G}{G_m} = \frac{XV}{X_m Q_m - X_2(Q_p - Q_m)} \qquad \text{(d)}$$

where X_m is the concentration of dry residue of surplus sludge in $g\ l^{-1}$ ($kg\ m^{-3}$), Q_m the volume of surplus sludge ($m^3\ d^{-1}$), and X_2 the concentration of sludge in the discharge from the settlement tank in $g\ l^{-1}$ ($kg\ m^{-3}$).

In the case of conventional low-loaded activation the age of sludge is 3–4 days; for heavily loaded activation it is several hours, maximum 24 h.

Currently, several technological modifications of activation treatment are used:

(1) *Low-loaded activation* — classical: mechanically pretreated water is fed into the activation tank together with recycled sludge, water to be treated flows into the settlement tank at the other end (Fig. 4.27). Here,

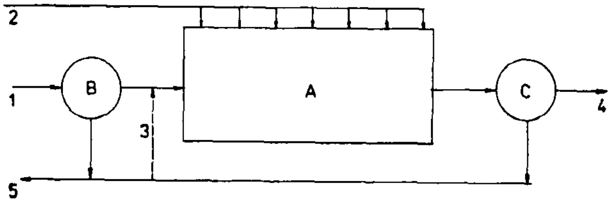

Fig. 4.27. Schematic diagram of conventional activated sludge process. 1 — wastewater, 2 — air supply, 3 — sludge return, 4 — clarified effluent, 5 — waste sludge, A — aeration basin, B — primary sedimentation tank, C — secondary sedimentation (thickening) tank

treated water is separated from sludge. Part of the sludge from the settlement tank is returned into activation tank, surplus sludge is removed and processed. Volume loading is only 0.5–1 kg BOD_5 m^{-3} d^{-1} and sludge loading is 0.2–0.6 kg BOD_5 kg^{-1} d^{-1}. The advantages of this method are its efficiency, which is as much as 90%, good balancing of short-term changes in the composition of wastewater and the fact that it does not require permanent attendance.

(2) *Highly loaded activation* — this employs the fact that the smaller the sludge particles the better dispersion of microorganisms and the better their degradation capability. The volume loading can be increased up to 3.8 kg BOD_5 m^{-3} d^{-1}, but the finely dispersed sludge does not settle well.

(3) *Activation with graded aeration*: because during classical activation the rate of oxygen demand decreases towards the run-off, this method uses more aerating units at the beginning of the activation tank.

(4) *Gradually loaded activation* — wastewater is fed at several places into the activation tank. Thus, loading of the tank and the rate of oxygen demand are balanced. All returned sludge is fed in at the beginning and thus it is sufficiently recovered if aeration is good. This method can be used for both low- and high-loaded activation and loading can be increased by 40% without reducing the treatment effect.

(5) *Activation with separate sludge recovery* (contact, combined) — employs the fact that during activation the sorption stage takes place first. Dwell time is short, 0.5 to 1 h, sludge from the settlement tank is fed into the recovery tank. Here, the oxidation phase takes place within 2–4 h provided that there is intensive aeration. Sludge is then returned into the activation tank. Volume loading is 1–1.2 kg BOD_5 m^{-3} d^{-1}, sludge loading is 0.4–0.6 kg BOD_5 kg^{-1} d^{-1}, purification effect is 85–90% BOD_5.

(6) *Shortened activation*: this is similar to the classical treatment, except that the dwell time is shortened to 1–2.5 h, but sludge loading is increased up to 0.6–2.0 kg BOD_5 kg^{-1} d^{-1}. The efficiency is 65–90% BOD_5.

(7) *Fast activation*: the lay-out is identical with that of shortened activation, but the dwell time is short, loading is above 1 kg BOD_5 kg^{-1} d^{-1}. Sludge is quickly exchanged, it consists almost exclusively of bacteria but recovery of this is impossible. The efficiency is 60–70% BOD_5.

Oxidation ditches represent a simplified modification of activation treatment. They are oval ditches about 1 m deep and water is moved by rotary cylinders. The flow rate is at least 0.3 m s^{-1}. At the same time, the water is aerated. Continuous operation requires only occasional attendance. The ditches operate at low loading, they are simple and cheap, the efficiency of treatment is usually higher than 90%, and also nitrification partly takes place.

4.5.2.6 Anaerobic wastewater treatment

Anaerobic treatment is used especially for disposal of excess sludge, of sludges from the primary settlement tanks and also as the first stage of biological wastewater treatment in cases of a high content of organic matters. In this case aerobic treatment follows as the second stage [1, 3, 6, 9, 10].

Anaerobic treatment is in fact fermentation taking place in the absence of atmospheric oxygen. Organic matter is degraded by enzymes, but its mineralization is not complete. Final products of the degradation are organic acids, alcohols, ketones and other substances which do not undergo anaerobic degradation. At the same time large amounts of gases are generated: methane 65–95%, carbon dioxide 5–35% and small amounts of nitrogen, hydrogen and hydrogen sulphide.

Anaerobic digestion is perfomed by bacteria only, and it takes place in two stages:

(1) *Acid fermentation* is caused by a mixed culture of facultatively anaerobic bacteria which produce lower organic acids and alcohols, H_2 and CO_2.

(2) *Methane fermentation* is caused by strictly anaerobic methane bacteria, the final products being CH_4 and CO_2.

The pH value should be within the range from 6.5 to 8.0. Methane fermentation stops at pH lower than 6, and at higher values large amounts of ammonia are produced.

Methane bacteria have a wide temperature tolerance: they are active at temperatures as low as 4–6°C, the optimum temperature is about 30°C. In technological practice three ranges of temperature are important: *cryophile* — digestion up to 20°C, *mesophile* — up to 37°C and *thermophile* — up to 60°C. In the cryophile region digestion takes 1.5–3 months, in the mesophile region only 20–30 days, and in the thermophile region only 15 days.

In the course of anaerobic digestion of excess activated sludge approximately half of the organic dry residue is decomposed and the remaining digested sludge can be more easily dehydrated and processed.

Two modes of digestion are used:

— normal (low loading),

— fast (high loading).

Digestion takes place in digestion tanks of different types: they should be heated in the case of mesophile and thermophile digestion. Fast digestion takes place only with sufficiently concentrated sludge or wastewater. The high heating value of the sludge gases produced allows them to be used for energy purposes, for example, for heating of digestion tanks. Aerobic treatment can also be applied for the treatment of concentrated organic wastes from animal husbandry, foodstuff plants, or for municipal waste processing.

4.5.2.7 The third stage of wastewater treatment

Biologically treated water contains considerable quantities of mineral nutrients which, because of ever increasing eutrophization will have to be disposed in the future as well. At present, the third stage is not much applied (particularly because the costs increases by 50%), but from the experimental viewpoint it has already been quite well elaborated. From industrial waters, first of all phosphorus has to be eliminated, and then, to a lesser extent, the nitrogenous compounds [1–3]. Physico-chemical methods of treatment have been successfully developed, for example, by adsorption, precipitation or the use of ion exchangers; studies involving the biological elimination of nutrients are so far rather scarce.

Phosphates are eliminated primarily by precipitation with the salts of iron or aluminium, calcium or magnesium chloride. For biological removal of phosphorus, intensive growth of algae in assimilation ponds can be used. The effect is as much as 80%, but because intensive photosynthesis is required, it depends considerable on the temperature and amount of sunlight. The efficiency of elimination of the biogenous elements is rather poor in cold, cloudy or rainy weather.

Algae must be removed from water so as to avoid the return of nutrients into the cycle. One of the possible solutions might consist in the utilization of biologically treated water for growing the algae which could be used, for example, as fodder.

Nitrogenous substances could be removed by microbial denitrification into gaseous nitrogen or its oxides following the nitrification of ammonia nitrogen. Currently, these methods are mostly at the experimental stage. Nitrogen and other nutrients in wastewater can be adequately reduced in assimilation ponds, oxidation ditches and irrigation types of treatment.

4.5.2.8 Final processing of sludge from biological treatment

Even after anaerobic digestion the voluminous sludge contains a lot of water. It is thus necessary to decrease the amount of water in it and hence also its volume so that its transport and eventual further processing would become more economical. For this purpose various methods can be used, especially thickening, dehydration and drying, or eventually incineration (for details see Section 3.11).

Dried and concentrated sludge contains many nutrients and therefore it can be well used as a fertilizer for either direct fertilization or for composting. Since it has a high content of nitrogen in comparison to phosphorus and potassium, it is recommended to add the lacking nutrients [3–6].

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5 Chemistry of air

5.1 Composition and structure of air

The gaseous envelope of the Earth, called the atmosphere, is a mixture of gases containing nitrogen, oxygen, water, argon and carbon dioxide as the main components. Neon, helium, methane, krypton, carbon monoxide, sulphur dioxide, ammonia, hydrogen, nitrogen oxides, formaldehyde, xenon, ozone, hydrogen sulphide, iodine and further components are present in negligible amounts. Water can be found as liquid as well as solid phases. Besides the gaseous components, the atmosphere also contains liquid and solid substances represented by dust particles, droplets and small crystals of salts. Upper layers of the atmosphere also contain positively and negatively charged ions.

Physical phenomena and processes occurring in the atmosphere, the chemical transformation and propagation of polluting components affect the chemical composition and characteristics of the atmosphere.

The atmosphere structure may be considered from different standpoints. A classification frequently accepted is that connected with change in the vertical direction: i.e. the vertical arrangement of the atmosphere in layers dependent on temperature, changes of the air composition at different altitudes, etc.

5.1.1 Composition of the atmosphere and its development

The earth's atmosphere, as in the case of the whole planet, has been formed in the course of a long and complex development process. The evolution of the earth's gaseous envelope remains still unclear. This, however, implies neither refuting the many unambiguously demonstrated conclusions in this field of interest nor the impossibility of successful future investigations of the huge body of complex chemical, physical, biological and other processes occurring in the atmosphere.

On the basis of results of absolute geochronology (based on determining certain isotopes of lead, uranium, thorium, potassium and argon in the oldest rocks), we can assume that the Earth was formed about 4.6 milliard years ago [1] from a protoplanetary gas-dust cloud. Hydrogen and helium were the essential gaseous components of its cloud (in accordance with current knowledge about the composition of the Universe).

Dust particles of a size of several micrometers probably contained metals and condensates of water, ammonia, methane and admixtures of formaldehyde, acetonitrile, methylacetylene and other substances occurring in interstellar space.

Due to the gradual gravitational contraction of the gas-dust cloud, as well as by action of the radioactive decay of numerous radionuclides, gravitational action of the simultaneously formed Moon and other processes, the cloud became heated, which resulted in its partial melting. As a direct consequence of the temperature increase, large amounts of gases and vapours were released and a certain portion, due to high kinetic energy, was scattered into cosmic space. Thus, a dense atmosphere formed about the planet some 4 milliard years ago, containing hydrogen, water, carbon oxides, methane and some sulphur compounds as its main components [2].

At the same time, a massive condensation of water vapours occurred with the gradual formation of the hydrosphere, which necessarily affected the evolution of the atmosphere, e.g. by dissolving a portion of carbon dioxide in liquid water with a subsequent formation of the oldest sedimentary rocks. Hydrogen and helium gradually left the region in space affected by the earth's gravitation on account of their low molar masses, and the atmosphere became relatively enriched in nitrogen.

At this stage, the atmosphere was characterized by the absence of free oxygen (which is also absent in gases erupting from current volcanoes). Small amounts of oxygen, possibly formed by water photodissociation, did not become concentrated in the atmosphere to a larger extent because of the presence of considerable amounts of reducing gases (SO_2, H_2S, H_2, CH_4). In addition to this, rocks, which were in contact with the atmosphere, also exerted reduction effects. Thus, this stage of the atmosphere's evolution was typically anaerobic (reducing) and the development of organisms producing oxygen by the photosynthesis was the only reason for a gradual change to an aerobic (oxidizing) atmosphere.

The first living organisms in ocean water became the most important factor in the development of the current atmosphere. Due to their existence, free oxygen accumulated in the atmosphere. It is still impossible to find a precise answer to the problem of the time required to convert the reducing atmosphere to an oxidizing one. In Precambrian sediments (age about 600 million years) many species of recently-formed multicellular organisms may be found. Thus, in this period, the oxygen concentration was necessarily at least of 20% of the current value.

Certain ferric formations ("redbed"), formed by the oxidation of rocks containing iron by action of the atmosphere and surface waters on dry land may serve as an important source of data. The age of the oldest formations is two milliard years, which suggests that the transition to the oxidizing atmosphere was not accomplished earlier than two milliard years ago [3].

In the course of milliards of years the primary atmosphere underwent change with respect to the relative abundance of inert gases, and particularly with respect to isotopes of those gases, which were not products of nuclear conversions occurring in nature and thus they were not supplied steadily into the atmosphere. In this respect we can consider argon as a typical example. It is present in an amount of 0.93 vol.% (related to dry air) at the present time. In nature, argon is represented by its three isotopes, the current relative abundances of which are as follows: ^{36}Ar 0.34%, ^{38}Ar 0.06% and ^{40}Ar 99.6% [4]. It is clear that with respect to the primary atmosphere, a remarkable decrease has occurred of the abundances of ^{36}Ar and ^{38}Ar with an increase of the relative abundance of ^{40}Ar. The reason for this is that ^{36}Ar and ^{38}Ar are not continually being supplied in nature, whereas ^{40}Ar is produced by the radioactive decay of ^{40}K. This involves an electron capture with a half-life of 1.27×10^9 years. Out of the many hypotheses explaining the evolution of the molecular nitrogen, forming about 4/5 of the today's atmosphere (78.08% by volume as related to dry air), the long-term release of the gas during the formation of primary rocks is the most probable. Important characteristics of nitrogen, resulting in its high relative representation in the atmosphere are its very low chemical reactivity and fairly high molar mass, hindering its escape from the region of the earth's gravitation.

Thus, the evolution of the gaseous envelope of the Earth was an extraordinarily compact dynamic process, which has taken several milliard years and which is still continuing. The dynamic character of this process is also supported by the fact that particular components do not occur permanently in the atmosphere — they only pass through it. The development was very slow (the composition of the earth's atmosphere has remained essentially unaltered from the beginning of the Tertiary period) and thus, it is reasonable to assume that the earth's gaseous envelope is in the state of dynamic equilibrium.

For the quantization of the rate of the passage of particular components through the atmosphere, we may consider the mean time of residence (τ), which is defined on the basis of the following consideration.

Let us assume that in the atmosphere, or possibly in a certain bounded region of the atmosphere, there are M mass units of the components of interest. If F is the rate of its formation, i.e. supply into the atmosphere (or into the bounded region) and R the rate of its conversion or release from the given region of the atmosphere, then for a dynamic equilibrium state it holds that $F = R$ and the mean time of the residence $\tau = M/F = M/R$. Thus, from the physical standpoint τ is the time after which the given component could completely disappear from the atmosphere in the absence of its source. The data in the literature concerning the mean times of the residence are not uniform and values for particular components of the atmosphere are very variable (from several hours to several years). In Table 5.1 the most probable values of τ are summarized for certain atmospheric components.

Table 5.1. Approximate mean time of the residence of certain components in the atmosphere

Components of the atmosphere	Aproximate mean time of the residence
He	10^7 years
N_2	10^6 years
O_2	5×10^3 years
CO_2	15 years
N_2O	8.0 years
H_2	6.5 years
CH_4	4.0 years
O_3	2.0 years
H_2O	10 days
NH_3	7 days
NO_2	6 days
SO_2	4 days
H_2S	2 days

Besides natural processes, interventions from the human activity, mostly negative, affect ever increasingly the chemical composition of current earth's atmosphere [5]. At the present time, the air contains eighteen permanent components besides water, as reported in Table 5.2.

Table 5.2. The chemical composition of dry atmospheric air

Gas	Vol. %	Gas	Vol. %
N_2	78.084 ± 0.004	N_2O	$(2-3) \times 10^{-5}$
O_2	20.946 ± 0.002	Xe	8.7×10^{-6}
Ar	0.934 ± 0.001	CO	$(1-20) \times 10^{-6}$
CO_2	0.034 ± 0.001	NH_3	$(0-2) \times 10^{-6}$
Ne	1.8×10^{-3}	O_3	$(0-5) \times 10^{-6}$
He	5.2×10^{-4}	NO_2	$(0-1) \times 10^{-6}$
CH_4	2.0×10^{-4}	NO	$(0-1) \times 10^{-6}$
Kr	1.1×10^{-4}	SO_2	$(0-2) \times 10^{-7}$
H_2	5.0×10^{-5}	H_2S	$(0-2) \times 10^{-7}$

5.1.2 Physical characteristics of the atmosphere

The physical state of the air is determined by its basic state quantities, temperature, pressure and density.

5.1.2.1 The equation of state of an ideal gas

The relationship between the pressure, temperature and density of ideal gases is given by the equation of state, which may be expressed as follows:

$$pV = R_i T \tag{5.1}$$

where p and T are the pressure and temperature of the gas, respectively, V is the specific volume (volume of 1 g of gas) and R_i is the specific gas constant of the relevant gas. Since $1/V = \rho$, equation (5.1) may be rewritten in the form

$$p = \rho R_i T \tag{5.2}$$

where ρ is the gas density.

Expressing the gas volume via its molar volume, then

$$pV_i = M_i R_i T \tag{5.3}$$

where M_i is the molar mass of the gas.

According to Avogadro's law, the molar volumes of all gases are the same for a given pressure and temperature. Thus, for k gases $V_l = \cdots = V_i \cdots = V_k$ and it hence follows that

$$M_l R_l = M_i R_i = M_k R_k = R$$

The product of the specific gas constant and molar mass is therefore the same for all gases and it is termed the universal gas constant.

Hence the state equation of ideal gas may be written

$$pV = \frac{1}{M_i} RT \tag{5.4}$$

For air, which is a mixture of gases, the apparent molar mass M_d is defined. It is the ratio of the total mass of gases contained in 1 kg and total amount of k mols in the mixture.

$$M_d = \frac{\sum_i m_i}{\sum_i \frac{m_i}{M_i}} \tag{5.5}$$

where m_i and M_i are the mass and molar mass, respectively, of the i-th component in the mixture.

The state equation of ideal gas for air is thus

$$pV = \frac{R}{M_d} T \tag{5.6}$$

5.1.2.2 The air temperature

The air temperature at the earth's surface varies over a rather wide range. Extreme values are achieved at the equator and at poles (60 and −90°C, respectively). Changes of the air temperature in the lowest layers of the atmosphere are mainly governed by changes of the earth's surface temperature, which leads to an important local variability of the temperature.

The distribution of the atmospheric temperature, together with its continuous changes, describe the temperature regime of the atmosphere. It is the result of the exchange of heat between the earth's surface and atmosphere, atmosphere and cosmic space and mutual exchange of heat between particular air masses.

5.1.2.3 The atmospheric pressure

The pressure of a gas is the force per unit area in any direction. The mean atmospheric pressure is the force acting per unit area of the earth's surface due to the earth's gravitational field. It may be deduced from the expression $m_A g_0 / 4R_e$, where m_A is the total mass of the atmosphere, g_0 is the mean gravitational acceleration and R_e is the mean earth's radius. Assuming the atmosphere mass to be uniformly distributed around the Earth, then the pressure at the sea level will be 101.3 kPa.

The air pressure is a variable quantity, varying in space and time. Periodic as well as non-periodic fluctuations occur in the changes with the time.

Non-periodic fluctuations are connected with the general air circulation and result from changes of the air density, i.e. from heating and cooling the air mass.

We now consider the equation of the hydrostatic equilibrium in the atmosphere.

The equilibrium between forces originating as a result of the thermal motion of the air and gravitational force is expressed by the basic equation of the atmosphere statics, also referred to as the hydrostatic equation of the atmosphere. The following consideration may be used for deriving the equation. Let us consider an infinitely thin layer $\mathrm{d}z$ in a vertical air column of a unit cross-section. The air mass in the layer $\mathrm{d}z$ is $\rho \mathrm{d}z$, where ρ is the air density at the height z and the weight of the air column of unit horizontal cross-section and weight $\mathrm{d}z$ is $\rho g \mathrm{d}z$, where g is the gravitational acceleration at the height z. The layer $\mathrm{d}z$ is bounded by planes situated at heights of z and $z + \mathrm{d}z$. The pressure on the area at the height z is p and that at the height $z + \mathrm{d}z$ it is $p + \mathrm{d}p$. The difference between the two pressures, $-\mathrm{d}p$, equals the weight of this part of the air column, so that

$$-\mathrm{d}p = \rho g \mathrm{d}z \tag{5.7}$$

$\mathrm{d}p$ is negative since the pressure decreases with increasing height and simultaneously, the vertical force affecting the pressure as a result of the vertical pressure gradient acts in the upward direction and it has a positive value.

Equation (5.7) may also be rewritten as follows

$$\frac{\mathrm{d}p}{\mathrm{d}z} = -g\rho \tag{5.8}$$

or

$$-\frac{1}{\rho}\frac{\mathrm{d}p}{\mathrm{d}z} - g = 0$$

The expression $\mathrm{d}p/\mathrm{d}z$ is termed the vertical baric gradient. It expresses the pressure drop corresponding to an increase of the height by unit length. Considering now the change of the pressure in the vertical direction; by integrating equation (5.8) from the level z with a pressure $p(z)$ to $z = \infty$, where $p(\infty) = 0$, we obtain

$$p(z) = \int_{z}^{\infty} g\rho \, \mathrm{d}z \tag{5.9}$$

This means that the pressure at the height z equals the weight of the vertical column of the air with a horizontal unit area above this height.

In the lowest atmosphere layers, the logarithm of the pressure decreases essentially linearly with the weight up to a height of 100 km, so that

$$\log\,[p(z)] = \log\,[p(0)] - kz \tag{5.10}$$

where $p(0)$ is the pressure at sea level and k is a constant.

The vertical change of the pressure is much larger than its horizontal or time variability. Thus, it is convenient to define a standard atmosphere [7], which represents the atmospheric structure averaged with respect to time and to the horizontal direction and varying only with height changes.

5.1.2.4 The air density

The air density is determined by the temperature, pressure and air humidity. Moist air may be considered as a mixture of dry air and water vapour. The air humidity is expressed by the tension of water vapour e. Of the total pressure p, the partial pressure of the dry air is $p - e$. The value of the density of dry air ρ_{D} may be determined from the equation of state of an ideal gas

$$\rho_{\mathrm{D}} = M_{\mathrm{D}} \frac{p - e}{RT} \tag{5.11}$$

where the subscript D stands for values valid for dry air.

This equation for an ideal gas, may be applied to any component of the air, and for water vapour equation (5.11) is in the form

$$\rho_{\mathrm{w}} = M_{\mathrm{w}} \frac{e}{RT} \tag{5.12}$$

where M_{w} is the molar mass of water and ρ_{w} is the water vapour density. Thus the total density of the moist air equals the sum of densities of the dry air ρ_{D} and water vapour ρ_{w}

$$\rho = \rho_{\mathrm{D}} + \rho_{\mathrm{w}} \tag{5.13}$$

so that after substituing from (5.11) and (5.12) into (5.13) and rearranging, we obtain

$$\rho = \frac{1}{RT}\,[M_{\mathrm{D}}(p-e)+M_{\mathrm{w}}e] \tag{5.14}$$

Since

$$R = R_{\mathrm{D}}M_{\mathrm{D}}$$

after a substitution from (5.14), with using numerical values of M_{D} and M_{w} we obtain

$$\rho = \frac{1}{R_{\mathrm{D}}T}\left[1-0.377\frac{e}{p}\right] \tag{5.15}$$

This equation may be written in the form

$$\rho = \frac{p}{R_{\mathrm{D}}T} \tag{5.16}$$

where

$$T_{\mathrm{v}} = \frac{T}{\left(1-0.377\frac{e}{p}\right)} \tag{5.17}$$

T_{v} represents the virtual temperature.

Equation (5.16) gives the physical meaning of the virtual temperature. This is a temperature, which could be attributed to the air heated at the same pressure and temperature by a latent heat, which is released during the condensation of all the water vapours contained in it. The virtual temperature T_{v} is always greater than T. Thus, the moist air density is always lower than that of the dry air.

The vertical profile of the air density. Similarly as for the pressure, the logarithmic dependence for the change of the density with height above sea level is approximately linear, so that it is possible to write

$$\log\,[\rho(z)] = \log\,[\rho(0)] - kz \tag{5.18}$$

where $\rho(z)$ is the air density at a height of z, $\rho(0)$ is the density at the sea level, k is the slope of the straight line, having for air almost the same value as that for the pressure dependence described by equation (5.10) [6, 7].

5.1.2.5 The diffusion processes in the atmosphere

In the atmosphere, two types of physical processes may be observed as follows:

— *molecular diffusion*, where a molecule in the gas moves with its individual velocity, and

— *turbulent diffusion* resulting from masses of air moving on a large scale.

In the lower layers of the atmosphere, up to about 90 km above sea level, turbulent mixing is prevalent; above this level, the molecular diffusion starts to prevail, so that above an altitude of 120 km it is already the governing process. Simultaneously, a gravitational separation starts to occur. Depending on this, the atmosphere structure is also varied.

At levels with prevalent gas convection, the ratio of gaseous components in the atmosphere is constant and the molar mass of the air is 28.966. In contrast to this, the random motion of molecules during the molecular diffusion leads to the formation of an atmospheric structure with a mean molar mass of the mixture of gases depending on the height, up to a level where only the lightest gases are present. (The density of each gas decreases exponentially with the altitude, the value of k in (5.18) being, however, different for different gases, so that the density of lighter gases decreases much more moderately as compared to that of heavier gases.) The molecular diffusion increases proportionally to the square root of the mean square velocity of the random motion of molecules and mean free path of molecules. The mean free path of molecules is most dependent on the height. In lower atmosphere layers, it is very short, so that the time necessary for the separation of lighter and heavier components of air is several orders of magnitudes greater than that necessary for the homogenization obtained by the air motion.

5.1.2.6 Changes of the air composition

Considerable changes of the air composition may be observed depending on the height. The ratios between particular gaseous components in the atmosphere at different altitudes are governed by diffusion processes, temperature and pressure.

The atmosphere layer which is characterized by the change from the turbulent mixing to the molecular diffusion is termed the *turbopause*; below the turbopause and above it there are the *homosphere* and *heterosphere*, respectively (Fig. 5.1).

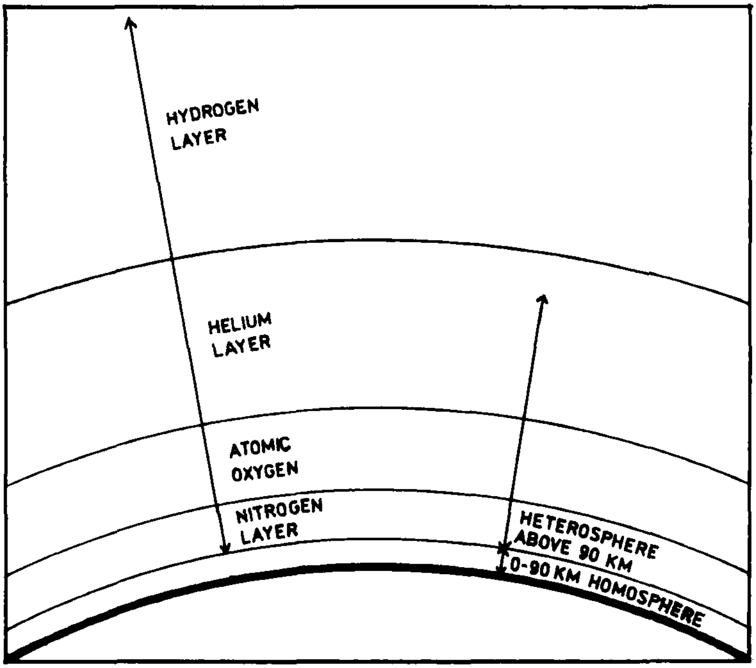

Fig. 5.1. Atmospheric layers

The maximal altitude of the *homosphere* is 90 km. Except for the content of water vapour, whose content varies over a wide range, and for certain trace elements and ozone, its composition remains fairly constant.

In the *heterosphere*, a stratification of gases depending on molar masses, occurring by action of diffusion and gravitation, may be observed. It is possible to recognize 4 layers [10–20] as follows:

1st layer — contains prevalently molecular nitrogen. The change of its composition is affected mainly by the photodissociation of molecular oxygen (biatomic), which is present mostly in its atomic form at a height altitude of 120 km. As a result of molecular diffusion, the nitrogen content gradually decreases.

2nd layer — contains prevalently atomic oxygen. This extends to an altitude of 1100 km. From this layer we consider the so-called exosphere, characterized by electrically neutral atoms which overcome the earth's gravitation and escape into cosmic space.

3rd layer — this is enriched in helium, it reaches a height of 3200 km above earth's surface.

4th layer — named the hydrogen layer or earth's corona extends beyond the 3rd layer.

At an altitude of 700 km, the mean molar mass of the air decreases to 16, which corresponds to the mass of atomic oxygen. In the third and fourth layers it decreases to 4 and 1, respectively (which corresponds to the atomic masses of helium and hydrogen, respectively) [7]. In the far outer reaches of atmosphere, light gases escape from the atmosphere into cosmic space. All species of molecules have a certain escape velocity v_0, at which the kinetic energy of molecules equals the potential energy which needs to be supplied for the particle to leave the earth's gravitational field. The escape velocity is a function only of the height above sea level. The most probable velocity of any molecule is given by the relationship

$$v_0 = \sqrt{\frac{2kT}{Mm_{\mathrm{H}}}} \tag{5.19}$$

where k is the Boltzman constant, T is the absolute temperature, M is the molar mass, m_{H} is the hydrogen atomic mass. It follows from (5.19) that the mean escape velocity of light molecules is higher than that of the heavier ones. In the region of the atmosphere, characterized by the escape of molecules or atoms, the temperatures are approximately 600 K. After inserting this value into (5.19), for hydrogen atoms we obtain an escape velocity of $v_0 \simeq 3$ km s^{-1} and for oxygen atoms 0.8 km s^{-1}.

Water and ozone exert a remarkable time and space concentration variability in the atmosphere, in contrast to the other gaseous components. They are extraordinarily important for the atmospheric energy equation and for the absorption of the radiation passing through the atmosphere. Water occurs prevalently in the lowest layers. With increasing altitude, its content decreases rapidly down to a negligible value at an altitude of 10 km. It is transported into the atmosphere particularly by the evaporation from water areas, moist soil and from plant transpiration. Molecules of the water vapour reside in the atmosphere for an average of about one week. Their content may vary over a wide range of 0.02–6 vol.% depending on the geographic situation, surrounding air temperature, directions of the wind and distances from water areas.

Ozone is produced during photochemical reactions at altitudes of 20–60 km. Lower amounts are formed in the course of chemical reactions in the polluted atmosphere. Its concentration increases gradually in the direction from the earth's surface, and at altitudes of 10–17 km its sea level value is increased by a factor of five [13]. At these altitudes, ozone resides for several months. In polluted atmosphere, near the earth's surface, ozone is fairly rapidly decomposed by reactions with plants and with components of the polluted atmosphere, or it is dissolved in water. At altitudes below 10 km, there is only 10% out of the total ozone amount present in the earth's atmosphere [13]. At different geographic latitudes, there is a remarkable variability of the ozone concentration up to an altitude of 36 km, maximal differences being observed at altitudes of 16 km [13, 14]. Up to altitudes of 50 km, the concentration profile of ozone remains unaltered during a diurnal cycle; above this altitude, diurnal changes of concentrations can occur.

At the higher geographic latitudes, it is possible to observe seasonal changes; maximum and minimum concentrations are observed in the spring and autumn, respectively [9].

5.1.2.7 Charged particles in the atmosphere

Charged particles represent a negligible fraction of the total mass of the atmosphere, however, in spite of this, they are of major importance in geophysical processes. Different types of radiation contribute to their origin, such as ultraviolet radiation, X-rays, and high-energy cosmic rays, emitted from the sun and from sources beyond the solar system. In the close vicinity of the earth's surface, the radioactive decay of the earth's crust components also contributes to the production of charged particles.

In the ionization of the atmosphere, positively and negatively charged ions and free electrons are produced. In lower layers of the atmosphere, the ionization occurs particularly by action of the cosmic radiation. Thus, the amounts of charged particles show no diurnal variation, however, the amounts increase with increasing geographic latitude. In higher layers of the atmosphere, the ionization occurs by action of high-energy ultraviolet radiation. Since this radiation is absorbed very rapidly during its penetration into lower layers, the major portion of charged particles is located at altitudes above 60 km. Their amount depends on the solar radiation intensity and thus, it exhibits diurnal variations. The free electron density depends on the mean free path of the particles: the longer the mean free path, the longer is the electron life-time. The electron density at altitudes above 60 km increases up to 100 km, where it is stabilized and it is maintained constant up to 160 km. Above this altitude it starts to increase, again, up to a maximum value at about 220 to 250 km [6, 9, 10].

The region with altitudes exceeding 60 km is named the *ionosphere*, and it may be divided into D, E, F_1, F_2 layers [12]:

— the *D-layer* is formed at altitudes of 60 to 90 km. Here, a strong photoionization of NO occurs;

- the *E-layer* is situated between 90 to 120 km and it is characterized by the prevalent photoionization of O_2;
- the *F_1-layer* reaches an altitude of 160 km. In this layer, O_2, N_2, O are essentially ionized. Here, chemical processes are prevalent;
- the *F_2-layer* is at altitudes exceeding 160 km. Physical processes are prevalent in this layer.

In the *D-layer*, the concentration of free electrons is lower than that of positive ions. This means that the layer also contains negative ions, with NO_3^- and CO_3^- being the most important ones. Among the positive ions, NO^+ and H^+ are prevalent.

In the *E*- and *F-layers*, the negative ions are absent; thus, in order to achieve charge neutrality, the sum of concentrations of positive ions must equal the electron concentration. During the photoionization of components present in these layers, the ions N_2^+, O_2^+, O^+ are formed.

5.1.2.8 The vertical temperature structure of the atmosphere

In the vertical direction, the atmosphere may be divided into four layers given by its temperature profile [10, 20] as follows:

- troposphere,
- stratosphere,
- mesosphere, and
- thermosphere.

The borders between the layers are named the *tropopause, stratopause, mesopause* and *thermopause*, respectively. The vertical temperature profile changes with the geographic latitude.

For example, at intermediate geographic latitudes, the temperature gradually decreases with increasing altitude, reaching a minimum value of approximately 210 K at an altitude of about 15 km; at the equator, the minimum temperature of 190 K is observed at an altitude of 17 km; and at poles a minimum temperature of 200 K is observed at an altitude of 8 km [9]. The vertical temperature structure of the standard atmosphere is shown in Fig. 5.2, which represents a typical distribution for intermediate geographic latitudes [6, 8].

In the *troposphere*, there is considerable vertical mixing of the air with a strong local variability of the temperature. The layer is characterized by a rapid decrease of the temperature with increasing altitude. Up to a height of 10 km, there is a mean temperature decrease of 0.7 K per 100 m, the maximum decrease being 1 K per 100 m. The troposphere is the densest layer of the atmosphere, it contains over 80% of the atmosphere mass,

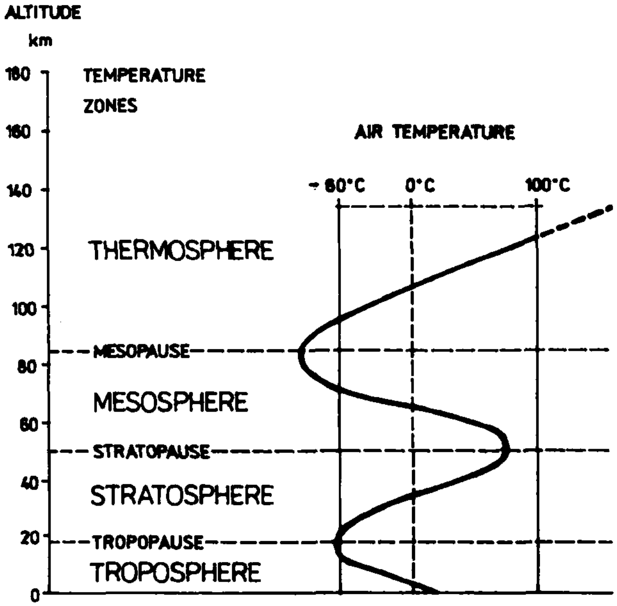

Fig. 5.2. Vertical temperature structure for standard atmosphere

and almost the whole content of water vapour and condensation products (clouds, precipitations).

In the troposphere, from the standpoint of the microclime and bioclime, it is possible to identify a limit layer or a friction layer, where the friction of the flowing air with the earth's surface is manifested, and which may extend up to 1 to 2 km depending on conditions. Inside the limit layer, a layer adjacent to the earth's surface of several tens of metres may be considered. It is characterized by vertical currents of the momentum, heat and water vapour independent of the height and by diurnal as well as seasonal variations of the temperature.

The troposphere is delimited by the *tropopause*, where the lowest temperature is reached, and which is more or less constant. At intermediate geographic latitudes, the tropopause is at altitudes of 10 to 12 km with temperatures of 220 to 210 K.

The *stratosphere* lies above the troposphere. The temperature increases with the altitude, the formation of the vertical temperature gradient being affected by the formation of a stratified structure of the stratosphere. The increase of the temperature with altitude may be explained by the absorption of the solar radiation by ozone. The air flow is negligible, which results in a considerable vertical concentration gradient. Thus, the time of the residence of particles in this layer is relatively long. Its major portion remains in the atmosphere for a whole year or even longer (e.g. for sulphate particles this time is assumed to be two years) [6, 15, 17]. In connection with the long time of the particle residence, complications are frequently emphasized, which may be caused by flights of supersonic aircraft throught the stratosphere. The emissions produced during these flights could form slowly diffusing zones with high concentrations of CO_2 and water vapour at these altitudes. Thus, the stratosphere acts as a reservoir of polluting components [15, 18].

At intermediate and lower geographic latitudes, the temperature remains essentially constant up to an altitude of 35 km and then it increases. The maximal temperature is reached at altitudes of 50 to 60 km being 273 K above the equator and at intermediate geographic latitudes [9, 16]. This region is referred to as the *stratopause* and, similarly to the tropopause, it is thermally stabilized. A portion of the stratosphere in the range of 15 to 35 km altitude is named the ozonosphere.

In the *mesosphere*, the temperature decreases with the altitude. Thus, the vertical motion is not completely obstructed and a week layer of clouds is formed. Under normal conditions, the concentration of components in this layer is, however, very low, so that the clouds cannot be observed from the Earth.

At the *mesopause*, there is again an extreme temperature (a minimum) at a height of 85 km. The temperature above the equator ranges between 190 and 200 K, at intermediate geographic latitudes it is 170 to 210 K and at higher latitudes, 130 to 230 K (the higher and lower values correspond to the summer and winter, respectively) [9, 16]. The layer is thermally stabilized.

The *thermosphere*, situated above the mesopause, achieves altitudes of several hundreds km and in this layer, the temperature increases (5 K km^{-1} at an altitude of 150 km). In the case of a quiescent condition of the Sun, the temperature change with altitude is much smaller as compared to the situation characterized by an enhanced solar activity.

At altitudes of above 500 km, collisions between particles occur very rarely, so that it is hard to define the temperature. At these heights, the motions of neutral and charged particles are more or less independent and thus, the temperature need not be uniform.

It needs to be emphasized that the vertical temperature profile varies depending on the geographic latitude and solar activity. For example, the tropopause is essentially higher and it has lower temperatures above tropical areas as compared to those above the polar regions. In the lowest layers of the stratosphere, the temperature profile depends on the geographic situation and on the season of the year. In the summer, cold and hot areas may be observed at the equator and at poles, respectively, whereas in the winter, maximal temperatures are encountered above intermediate geographic latitudes.

It is of interest to mention that the Earth is not the only planet having a vertical temperature profile of its gaseous envelope. Mars and Venus are also characterized by a well defined troposphere and thermosphere, separated from each other by the relevant layers (pauses) [6].

The relationship between the temperature profile and chemical composition of the atmosphere is important. In the upper layers of the atmosphere, the solar radiation of the ultraviolet region of the spectrum (< 200 nm) is absorbed by atoms and molecules of oxygen and nitrogen. The energy absorbed is conversed into heat, which results in a temperature increase. Due to this absorption, the intensity of the ultraviolet radiation is reduced in lower layers and the temperature decreases with decreasing height. At an altitude of 85 km, ozone is again of importance. Its concentration increases, the maximum being achieved at altitudes of about 25 to 35 km. Ozone absorbs solar radiation at wavelengths between 200 and 300 nm (this radiation was not absorbed in higher layers). The absorption leads to a temperature decrease, again, in the given case in the mesosphere, where the temperature increases with a decreasing altitude.

The increase of the temperature from the tropopause down to the earth's surface is due on the one hand to the absorption of the ultraviolet (> 300 nm) and visible radiation on the surface and, on the other by, the back emission from the surface.

5.1.3 Reactions in the atmosphere

Chemical and photochemical reactions occurring in the atmosphere are affected by a number of factors, governing the formation of intermediate products as well as the final products.

The reactions of polluting components released into the atmosphere are affected by meteorological factors, which determine their propagation and dilution. The solar radiation plays an important role in the chemical reactions, since it supplies the energy for the splitting of bonds in the reacting molecules. In spite of the variability of conditions and complex character of the whole system, the study of atmospheric reactions is necessary for the identification and elucidation of the mechanism of processes occurring in the air. The data obtained about the intermediate products and final products formed, together with the determination of the reaction kinetics, can help to explain many phenomena. They can explain, for instance, disagreements between experimentally established values of concentrations of oxidation products of hydrocarbons and data calculated on the basis of values obtained at the point of the output from the source.

In the atmosphere it is possible to observe essentially all the common types of chemical reactions: protolytic, oxidizing-reducing, precipitating and under certain conditions even complexation reactions. Photochemical reactions, induced by the light absorption are, however, the main focus of interest. Thus, the problems of photochemical processes are discussed in more detail below.

5.1.3.1 Photochemical reactions

The following two photochemical rules hold for these reactions:

(1) The molecule participating in the reaction has to absorb light radiation to be activated.

(2) A molecule of the reacting component is activated by one light quantum.

According to the quantum theory, the light absorption occurs only in integer energy quanta. The light quantum is the lowest possible amount of the energy Q_v emitted from the light flux of an arbitrary material system. For the energy Q_v it is possible to write $Q_v = h\nu$, where h is the Planck constant (6.6256×10^{-34} J s) and ν is the radiation frequency.

The energy supplied by the radiation absorbed in the molecule splits it into corresponding radicals. The larger the energy quantum (or the shorter the light wavelength), the larger is the resulting effect. For example, the energy of the light quantum of long wavelength radiation is usually very low as compared to the energy necessary for breaking chemical bonds and it affects only the vibration and rotation of the molecule. In certain cases, the molecule or atom is brought to an excited state during the light absorption and in this state it is able to participate in chemical or photochemical reactions.

By way of illustration, let us consider the reactions of oxygen, which are extraordinarily important in atmospheric chemistry.

The basic state of molecular oxygen is considered on the basis of a combination of two oxygen atoms having a common electron distribution adjusted with respect to suitable molecular orbitals [21, 22] as follows:

$$\mathrm{O}[(1\mathrm{s})^2, (2\mathrm{s})^2, (2\mathrm{p})^4] + \mathrm{O}[(1\mathrm{s})^2, (2\mathrm{s})^2, (2\mathrm{p})^4] \rightarrow$$
$$\rightarrow \mathrm{O}_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2],$$

where KK stands for $(\sigma 1\mathrm{s})^2$ $(\sigma 1\mathrm{s})^2$.

These configurations of molecular orbitals can lead to three states: $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$, formed depending on which electrons occupy the highest molecular orbitals. For the energy diagram of molecular orbitals in an O_2 molecule in its basic state, see Fig. 5.3. Table 5.3 [23] shows the effect on the basic state of occupying π molecular orbitals of the oxygen molecule.

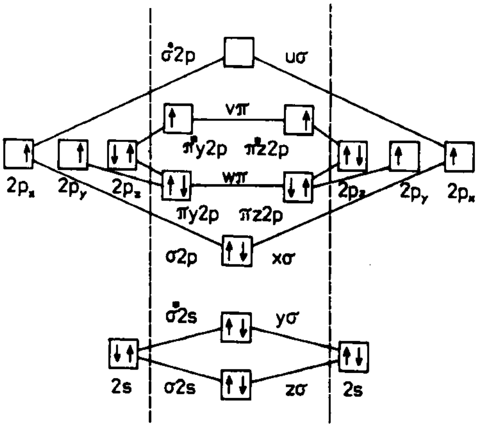

Fig. 5.3. Energy level diagram of oxygen

Table 5.3. The effect of occupying the π molecular orbital of oxygen with electrons [23]

Electron state of oxygen molecule	Occupation of the highest orbitals		Energy above the basic state (kJ mol^{-1})
Second excited state ($^1\Sigma_g^+$)	(↑)	(↓)	157
First excited state ($^1\Sigma_g$)	(↑↓)	○	94
Basic state ($^3\Sigma_g^-$)	(↑)	(↑)	

In the course of the photodissociation of O_2 and O_3 molecules, different products may be formed depending on the wavelength of the light

Table 5.4. Photodissociation reactions of molecular oxygen and ozone [22, 24]

Wavelength (nm)	Reactions
$\lambda < 175$	$O_2(^3\Sigma_g^-) + h\nu \rightarrow O(^1D) + O(^3P)$
$200 < \lambda < 242$	$O_2(^3\Sigma_g^-) + h\nu \rightarrow O(^3P) + O(^3P)$
$\lambda < 1140$	$O_3 + h\nu \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$
$\lambda < 308$	$O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D)$
$\lambda < 266$	$O_3 + h\nu \rightarrow O_2(^1\Sigma_g^+) + O(^1D)$

strinking the molecules. They may be given on the one hand by molecular oxygen in one of the three above-mentioned states and, on the other hand, atomic oxygen $O(^3P)$ or metastable $O(^1D)$ (which has a higher energy as compared to $O(^3P)$). Table 5.4 summarizes the possible photodissociation reactions [22, 24].

The presence of ozone in higher atmospheric layers is a results of the photodissociation reactions of molecular oxygen.

After the absorption of ultraviolet radiation by an oxygen molecule, it is split as follows:

$$O_2 + h\nu \rightarrow O(^3P) + O(^3P), \qquad \lambda < 242\ \text{nm}$$

In the presence of the third particle M, molecular and anatomic oxygen combine, producing ozone

$$O_2 + O(^3P) + M \rightarrow O_3 + M, \qquad \Delta H^0 = -100\ \text{kJ}$$

The solar radiation of appropriate wavelength also leads to decomposition of the ozone:

$$O_3 + h\nu \rightarrow O_2 + O(^3P), \qquad \lambda < 1140\ \text{nm}$$
$$O(^3P) + O_3 \rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-), \qquad \Delta H^0 = -390\ \text{kJ}$$

The amount of ozone produced at any time depends on the solar radiation intensity and the altitude. The maximal concentration may be observed at altitudes of 25 to 35 km [25]. The first and last of the three reactions above are exothermic and thus, heat is released, which results in an increase of the temperature with increasing height in the stratosphere.

The photodissociation is also connected with the origination of chain reactions, which are of a great importance, particularly in the polluted atmosphere of large urban areas. During the absorption of the light by a molecule, non-polar splitting of a certain covalent bond may occur, and radicals may be formed, which have one or more unpaired valence electrons, and are thus very reactive. The radicals may be either free atoms or atomic groups and they can enter into further reactions, without the further participation of the light. During these reactions, the chain mechanism is frequently encountered.

In photochemistry, a number of chain reactions in the gaseous phase are known, continuing even for a million steps [26]. This long chain usually includes a sequence of repeating short reactions, which begin and end by particularly active radicals. The reactions of this type may be expressed in general terms as follows (the dot represents a free radical) [26]:

$$\begin{aligned} A + R^{\cdot} &\rightarrow RA^{\cdot} \\ RA^{\cdot} + B &\rightarrow BA + R^{\cdot} \end{aligned}$$

A conversion of molecules A and B to the additive product BA is result of the two reactions. On the termination of the process the re-formed radical $R^{\cdot}$ enters into a further cycle. After a sufficient number of cycles, the amount of the product formed may be much larger than the amount of different species of radicals present in the system. The rapid conversion of nitrogen monoxide to nitrogen dioxide, and accumulation of ozone in photooxidation smog are examples.

Besides these types of reactions, the radicals may enter into reactions with a branched chain, where the number of radicals formed is higher than that of radicals entering into the reaction. In the reaction

$$R^{\cdot} + AB^{*} \rightarrow R^{\cdot} + A^{\cdot} + B^{\cdot}$$

two new radicals are formed. AB^{*} is a molecule in its excited state.

It is obvious that if the chain-branching reactions are more frequent than the reactions terminating the chain, radicals are very rapidly accumulated in the system. The production of a long or short chain is governed by the relative balance between the chain-starting, branching, and termination processes. In a polluted atmosphere, the chain may be terminated, for example, by the reactions

$$\begin{aligned} ROO^{\cdot} + NO_2 &\rightarrow ROONO_2 \\ ROO^{\cdot} + RO &\rightarrow ROR + O_2 \\ RO^{\cdot} + NO_2 &\rightarrow RONO_2 \end{aligned}$$

The chain can also be terminated by the adsorption of the radical on the surface of solid particles present in a polluted atmosphere.

5.1.3.2 The kinetics of atmospheric reactions

Components of the atmosphere and emissions released into the atmosphere may react with each other with the possible production of further, so-called secondarily polluting components. A knowledge of the rate of these reactions, together with the associated chemical thermodynamics, make it possible to determine the probability of their course, which may help to explain the mechanism of atmospheric processes.

The reaction rate depends on the concentration of the reacting substances, temperature, and the presence of other species (which may catalyse the process), and in photochemical reactions the rate depends also on the intensity and spectrum of the solar radiation.

High dilution of polluting components in the atmosphere causes that only very rapid reactions will occur to a sufficient extent. For example, when the rate of a bimolecular reaction for a content of 10 vol.% of reacting components leads to a 50% conversion being achieved in 3.6×10^{-3} s, then in the case of a content decreased by a factor of 10^6, the resulting decrease of the reaction rate will give rise to the same 50% conversion only after 1 hour. This means that the rate of relevant reactions should be very high indeed [26] in order to be able to observe these reactions.

There is a different situation in the case of reactions involving oxygen, carbon dioxide and water vapour. These stable components of the atmosphere are present in much higher concentrations. The oxygen content is frequently higher by a factor of 10^6 as compared to the content of polluting components, the concentration of carbon dioxide is higher by a factor of 10^2 to 10^3. Thus, it is safe to assume that the rate of oxidation reactions will be essentially higher than the rate of reactions of very diluted imissions, and similarly, though to a smaller extent, in the case of the reactions of carbon dioxide and water.

The kinetics of photochemical processes depend to a great extent on the solar radiation intensity. This also affects the production of photochemically produced secondary polluting components, which varies according to the rhythm of the diurnal cycle of the solar intensity.

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5.2 Polluted air

By the term "polluted air" we mean a condition of the atmosphere, where the pollutants are present in amounts leading to adverse effects on the environment.

According to the Convention on the Long-Distance Pollution of the Atmosphere passing over borderlines of countries (accepted by the ECE during a meeting in Geneva in 1979) the air pollution means either direct or indirect introduction of substances into the atmosphere as a result of human activity, which damage human health, living sources, ecosystems and material property and disturb the proper use of the natural and human environment.

The atmosphere is polluted either in the release of different substances into the air or during processes occurring directly in the air (e.g. chemical reactions). *The substances polluting the air* may be divided into *primary* and *secondary* ones, depending on the site of their production. In contrast to primary pollutants, which enter the atmosphere from natural sources or by the action of human activity, the secondary components are formed directly in the air during atmospheric reactions. These reactions occur as a result of mutual interactions between elements and compounds or by the action of different types of the energy.

By a "source of atmospheric pollution" we mean an object releasing polluting substances into the air.

5.2.1 Primary pollutants

The substances released into the air may be classified in different ways. According to the state of matter they may be divided into gaseous, liquid and solid ones, depending on chemical characteristics, they may be classed into groups mentioned in Section 5.2.4 and with respect to the effects on the human health we can consider allergens, mutagens and carcinogens, odiferous substances being considered as a specific group with respect to their detection by the sense of smell.

Special attention is paid to substances which may threaten or damage human health. They are considered as harmful substances. The most important of them, listed in the hygiene regulations of countries include hundreds of substances, presenting the maximum permissible concentrations, or recommended values of the concentrations. These concentrations, for the most frequently considered hazardous substances are summarized

Table 5.5. Occupational exposure limits for hazardous air pollutants. A compilation of values from selected countries

Substance	Maximal imission concentration ($\mu g\ m^{-3}$)					
	Czechoslovakia		FRG (east part)		USSR	
	C_{max}	C_D	C_{max}	C_D	C_{max}	C_D
Carbon monoxide	6000	1000	3000	1000	3000	1000
Sulphur dioxide	500	150	500	150	500	50
Dust	500	150	500	150	500	150
Ammonia	200	200	300	100	200	200
Oxides of nitrogen (as NO_2)	100	100	100	40	85	85
HCl (as H^+)	6	—	50^{a}	15^{a}	6	6
Chlorine	100	30	100	30	100	30
Formaldehyde	50	35	35	12	35	12
Carbon disulphide	30	10	30	3	30	5
Fluorine and its compounds F_2, HF, SiF_4	20	—	20	0.5	20	0.5
NaF, Na_2SiF_6	—	5	30	10	30	10
Phenol	10	10	30	10	10	1
Hydrogen sulphide	8	8	15	8	8	8
H_2SO_4 (as H^+)	6	—	50^{b}	20^{b}	6	2
Arsenic (inorganic compounds without AsH_3)	—	3	—	3	—	3
Lead (without tetraethyllead)	—	0.7	—	0.7	—	0.7

^{a}HCl, $^{b}H_2SO_4$.

C_{max} — maximum imission concentration, short-term (30 min).

C_D — maximum average concentration, diurnal (24 h).

in Table 5.5 (based on regulations in selected countries). Within the scope of the UNO program the pollutants are followed globally by the Global Environment Monitoring System, controlling the content of pollutants not only in the air, but also in the water, soil, foodstuffs and living organisms. Particularly significant substances are nitrogen oxides, carbon oxides, sulphur dioxide, sulphate, ozone, reactive hydrocarbons and photochemical oxidants, asbestos and non-sedimenting dusts.

Apart from hygiene aspects, the harmfulness of pollutants is also considered from the global standpoint, particularly with respect to a possible impact on climatic conditions and the overall life on our planet. In connection with changes of the earth's climate, a frequent subject of discussion is the amount of exhalations of solid and liquid particles and also of carbon dioxide and other components, that may affect the ozone layer in the stratosphere [1].

Among the various particles, the smallest non-sedimenting fractions are most important (of sizes comparable with wavelengths of visible light), which are accumulated in the upper layers of the atmosphere and which cannot be removed from there. The clouds they produce reflect a portion of the solar radiation, which is manifested in changes of mean temperatures in atmospheric layers adjacent to the surface of the Earth. Forecasts made in the past were based on assumptions considering only the reflection of the solar radiation, without taking into account the role of particles in the thermal balance of the Earth. Such simplified considerations resulted in the conclusion that the increase of the particle content in the atmosphere could be a reason for an abnormal decrease of the temperature. Currently used models, considering the two functions of the particles, offer solutions, where the particles may cause not only cooling but also actual increases of the temperature. The resulting effect depends on the surface albedo (the earth's albedo is defined as that fraction out of the total solar radiation striking the atmosphere, which is reflected back into space without absorption). Snow reflects a larger proportion of the solar radiation (albedo 0.6) as compared to the sand (0.3) or water (0.07). When the surface albedo is small, then the particles shield the Earth, which is manifested by a decrease of the temperature in the atmosphere adjacent to the earth's surface. In the opposite case, clouds formed from the particles retain a portion of the reflected radiation from the Earth in a layer formed between the earth's

Table 5.6. The increase of the surface temperature of the Earth induced by increasing concentration of certain trace components of the atmosphere [2, 3]

Component	Increase in the concentration in comparison with the current situation by a factor of n	Increase of the mean temperature of the earth's surface (K)
CH_4	2	0.20–0.28
C_2H_4	2	0.01
CF_2Cl_2	20	0.36–0.54
$CFCl_3$	20	0.36–0.54
CCl_4	2	0.01–0.02
CH_3Cl	2	0.01–0.02
N_2O	2	0.44–0.68
CO_2	1.25	0.53–0.79
SO_2	2	0.02–0.53
NH_3	2	0.09–0.12

surface and the clouds, which leads to an increase of the temperature of this layer.

Besides the dust clouds, changes of contents of carbon dioxide and certain other components in the air can also affect the mean temperature of the atmosphere close to the earth's surface. The assumed increase of the surface temperature induced by increasing concentration of certain trace components of the atmosphere is shown in Table 5.6. The problem of effects of increasing CO_2 emissions is discussed in more detail in Section 5.2.4.3, where possible effects of CF_2Cl_2 and $CFCl_3$ on the thickness of the ozone layer in the stratosphere are also considered.

5.2.2 Global sources of atmospheric pollution

Natural and anthropogenic sources of the air pollution both need to be considered. Each group includes a wide range of very different sources, and it is not always possible to find precisely the dividing line between them. For example, certain natural sources occur as a result of a preceding human activity (forest fires, dust nuisance, etc.).

It is estimated that approximately 90% of all the substances polluting the air come from natural sources, such as soil and rock erosion, volcanic activity, natural fires, sea water, spray, biological processes, etc. The contribution of anthropogenic sources is thus about 10% [4, 5]. Their amounts are, however, continually increasing and this ratio is thus rising. Its change adversely affects the equilibrium formed between the natural sources and the processes of the removal of pollutants from the atmosphere. Besides this, as a consequence of the human activity, much more highly aggressive substances frequently enter the atmosphere, which may threaten many biological processes on the Earth. Last, but not least, a particular danger of the emissions from human activity is the fact that the pollutants are concentrated in the atmosphere above and around industrial regions and urban areas.

Such sources caused by human activity include industry, energy production, transport, residential heating and waste incineration. These sources give rise to different contributions to the total emissions resulting from human activity, depending on the structure of the economy. Table 5.7 presents the relative percentage contributions to the pollution from the human activity.

Table 5.7. Relative contributions to the pollution from the human activity

Pollution source	Relative contribution, as a percentage of the total
Transport (all kinds)	50–60
Energy production	10–15
Industrial technologies and industrial boilers	15–20
Residential heating units	10
Waste incineration	5

5.2.3 The emissions from the main groups of anthropogenic sources

Estimates of annual amounts of emissions released into the earth's atmosphere are remarkably different from each other, depending on the choice of balance models [5–24]. For the anthropogenic sources, the following substances may be listed in decreasing order of importance: carbon dioxide, carbon monoxide, sulphur oxides, hydrocarbons, nitrogen oxides and liquid and solid particles. A summary of relative contributions of these substances to total emissions of main types of anthropogenic sources is given in Table 5.8.

Table 5.8. Estimates of relative contributions of pollutants arising from human activity to the total annual emissions [4]

Source type	Contribution to total annual emissions				
	CO	SO_x	NO_x	C_xH_y	Particles
Transport total out of:	75.2	0.4	8.5	14.6	1.3
motor vehicles	76.5	0.3	8.0	14.4	0.8
remaining transport	59.1	1.5	15.1	16.7	7.6
Fuel combustion total out of:	5.0	57.8	19.7	1.8	15.7
power stations	0.5	70.4	17.6		11.5
industry	2.5	45.8	25.9	0.8	25.0
domestic sources	28.3	39.1	10.9	13.0	8.7
remaining sources	12.5	43.8	25.0		18.7
Production (especially chemical)	31.7	29.3	0.8	14.2	24.0
Treatment and disposal of wastes	57.0	1.3	8.8	17.7	15.2
Contribution from particular pollutants to the total amount of emissions	50.4	17.6	9.7	13.7	8.6

Carbon dioxide is not included in the table, since it is not considered as a harmful substance and thus, the main carbon contribution to the total emissions is given by carbon monoxide.

The structure of emissions from industrial production itself (including industrial technology as well as industrial boilers) shows remarkable differences. Emissions of SO_x are prevalent (sulphur dioxide and sulphur trioxide) represented by a portion of 34.7%, after these there are particles with a portion of 24.3%, and CO with about the same portion (22.1%). The last positions with almost the same representations are occupied by C_xH_y (9.8%) and NO_x (9.1%).

Data concerning relative contributions of main industrial branches to the total annual emissions from industrial technologies in advanced countries are summarized in Table 5.9.

Table 5.9. Contributions to air pollution from main industrial branches

Pollution source with respect to particular industrial branches	Main pollutants	Relative portion out of total annual emissions (%)
Petroleum refineries	CO, SO_x, hydrocarbons particles	16.8
Non-ferrous metallurgy (production of aluminium, copper, lead, zinc)	SO_x, particles	16.8
Foundries	CO, particles	14.6
Paper mills	CO, SO_x, particles	17.7
Coal treatment plants	CO, SO_x, particles	9.3
Coke batteries (steel industry)	CO, SO_x, particles	8.9
Iron and steel mills	CO, particles	7.1
Cement production	Particles	3.5
Production of fertilizers	Particles, compounds of fluorine	0.9
Milling and treatment of cereals	Particles	4.4

In the advanced countries, the annual mass of substances released into the atmosphere per inhabitant is approximately 600 kg [4]. Table 5.8 makes it possible interpret the data about main types of emissions in this light. For example, the values for SO_x and CO are of about 100 and 300 kg per person per year, respectively.

5.2.4 Substances polluting the air

An air pollutant is a component which is able, either directly, or after relevant conversions occurring in the atmosphere, to damage or threaten living organisms and to affect adversely the environment. Depending on chemical and physical characteristics, we can divide substances polluting the air into several groups:

(a) sulphur compounds,
(b) nitrogen compounds,
(c) carbon compounds,
(d) halogen compounds,
(e) radioactive substances, and
(f) particles (frequently divided into two subgroups depending on the radius of isometric particles).

The behaviour of these particles in the air is determined by their chemical and physical characteristics and by their total amount released into the air. Besides these factors, the external atmospheric conditions, particularly the temperature, pressure, humidity, velocity and direction of wind and content of the remaining pollutants are also of importance.

5.2.4.1 Sulphur compounds

The pollutants containing sulphur are as follows: sulphur dioxide, sulphur trioxide, sulphuric acid, hydrogen sulphide, carbon disulphide and various organic compounds of sulphur.

An essential portion of sulphur in the atmosphere comes from hydrogen sulphide. It makes up 46.1%, whereas the proportions of sulphur corresponding to sulphur dioxide and to sulphites together with sulphates are 33.2 and 20.7%, respectively.

The global emissions of sulphur compounds estimated by Robinson and Robbins for the Northern and Southern Hemispheres are presented in Table 5.10.

The major proportion of sulphur compounds from human activity comes into the atmosphere from the Northern Hemisphere; of the total amount of sulphur compounds it is 69% and when considering sulphur dioxide emissions, then this portion is as high as 93% [6].

The most important source of SO_2 emissions is the combustion of coal, responsible for a contribution up to 71% [6]. As in the case of SO_2, the H_2S emissions are also much larger from the Northern Hemisphere. There is an inverse proportion only in the case of hydrogen sulphide produced by

Table 5.10. Global emissions of sulphur compounds (t 10^6 yr^{-1}) [25]

Compounds	Source	Northern Hemisphere	Southern Hemisphere	Total
SO_2	Coal	88.9	3.6	92.5
	Refining and treatment of petroleum	24.6	1.2	25.8
	Copper smelting	7.8	3.9	11.7
	Lead smelting	1.1	0.3	1.4
	Zinc smelting	1.1	0.1	1.2
	Total	123.5	9.1	132.6
H_2S	Biological (dry land)	47.2	18.1	65.3
	Biological (ocean)[a]	12.7	16.3	29.0
	Emission sources			
	SO_2^+	2.7	0	2.7
	Paper mills	0.05	0	0.05
	Total	62.65	34.4	97.05
Sulphites, sulphates	Sea spray	17.2[a]	22.7[a]	39.9[a]

[a] Expressed in t of sulphur.

the biological decomposition in oceans. This is not surprising, since in the Southern Hemisphere the relative area of seas is larger as compared to the Northern Hemisphere.

More recent estimates of the emissions of sulphur compounds [13, 21–24] consider primary and secondary sources; balanced amounts of H_2S roughly correspond to these estimates, different values are obtained for SO_2 with respect to large contributions from secondary sources (H_2S oxidation) in amounts ranging from 40 to 100 × 10^6 tons of sulphur annually.

Sulphur dioxide is the most typical and most frequently occurring component of emissions. It comes into the atmosphere from different sources. The major sources arise from the combustion of fossil fuels (Table 5.10). The sulphur content in coal varies according its origin in a range of 0.3 to 6.0%, and similarly in heating oils this content is also variable depending on the oil's origin. Natural sources introduce a smaller portion of the SO_2 emissions (from volcanic activity). The global estimates of amounts of SO_2 from anthropogenic sources amount to 132.6 × 10^6 tons annually according to data by Robinson and Robbins (more recent data indicate 101 × 10^6 ton of sulphur annually [13]). The long-term course of the increase of the sulphur dioxide emissions is given in Table 5.11. Between 1860 and 1965,

Table 5.11. Estimates of the increase of SO_2 emissions between 1860 and 1965 (t 10^6 yr^{-1}) [25]

Year	Source					
	Coal	Petroleum	Copper smelting	Lead smelting	Zinc smelting	Total
1860	4.50	0	0.20	0	0	4.70
1870	7.10	0.01	0.22	0	0	7.33
1880	11.10	0.06	0.23	0	0	11.39
1890	17.00	0.15	0.61	0	0	17.76
1900	25.50	0.30	1.45	0.42	0.14	27.81
1910	38.20	0.63	2.58	0.55	0.23	42.19
1920	44.90	1.62	2.96	0.49	0.20	50.17
1930	46.54	2.83	3.19	0.84	0.42	53.82
1940	55.34	4.19	4.95	0.88	0.48	65.84
1950	59.88	7.53	5.37	0.78	0.54	74.10
1960	86.83	18.05	9.07	1.16	0.90	116.01
1965	92.53	25.86	11.70	1.36	1.18	132.63

the amount of the SO_2 released increased by a factor of 28. Between 1860 and 1910, the amount doubled each 16 years, then the exponential increase was moderated and the last doubling of the amount may be considered to cover the period 1940 to 1965 [26].

Particular countries bring different contributions to global emissions, depending on the character of their economy. Particular sources also give rise to different contributions to the emissions, depending on conditions in the region considered. The situation as regards annual amounts of SO_2 emissions in Europe is presented in Table 5.12.

The SO_2 concentration in clean atmosphere does not exceed 0.25 $\mu g\ m^{-3}$ [6, 8, 28]. During pollution of the atmosphere, the data range between 500 and 2600 $\mu g\ m^{-3}$ [7, 10]. The mean residence time of the SO_2 in clean atmosphere is 2 to 6 days. In this time span, SO_2 may be transported even to a distance of 1000 km, however, the major portion starts to react with other components present immediately after its release into the atmosphere. The study of the effect of atmospheric reactions of SO_2 on the general condition and pollution of the atmosphere is extraordinarily complex and it remains still incomplete. Basic reactions of sulphur dioxide in the atmosphere, and the kinetics and effects of certain other pollutants on rate changes have been studied. The atmospheric reactions of SO_2 may be divided into several groups [8, 9, 29] as follows: homogeneous reactions in the gas phase, photochemical oxidation, reactions of free radicals with

Table 5.12. Present state and forecasts of SO_2 emission in Europe [27, 44]

State	Present state				Forecast		
	1972[a]	1980[b]	1982[a]	1990[b]	1992[a]	2000[b]	2002[a]
	(kt yr^{-1})						
Austria	700	430	430	—	570	200–300	720
Belgium	1140	760	810	—	840	—	870
Bulgaria	680	1000	770	400	1180	—	1600
Czechoslovakia	2910	3000	3370	3400	3780	2500	4180
Denmark	620	456	450	400–700	510	—	580
Finland	550	540	570	700–800	600	—	630
France	3220	3600	2890	2300	2240	—	1580
FRG (east part)	4000	4000	4000	—	4200	—	4400
Greece	200	704	340	—	540	—	740
Great Britain	5610	5120	4250	4800–5700	4750	4800–6400	5260
Holland	780	480	490	800–3600	500	700–6200	630
Hungary	1500	1500	1720	2100	1940	1900	2170
Ireland	330	174	260	—	450	—	640
Italy	3170	4400	3070	5000	3210	6900	3350
Yugoslavia	650	2950	830	—	1370	—	1910
Norway	180	150	140	100	140	100	180
Poland	3000	4300	2500	6700	2780	—	3070
Portugal	110	168	140	—	200	—	260
Roumania	850	2000	2090	—	2670	—	3350
Spain	1300	200	2090	—	2910	—	3730
Sweden	830	550	510	—	330	300–400	360
Switzerland	150	116	120	—	140	—	180
USSR(within the region)	23500	16200	25500	—	30050	—	34600
FRG (west part)	3910	3630	3510	4100	3720	—	3930

[a] By Highton N. H. and Chadwick M. J., 1982.

[b] By Barnes R. A. et al., 1978 and EMEP.

SO_2, oxidation with molecules, heterogeneous reactions in the gas phase, catalysed and non-catalysed reactions in liquid phase, and reactions on the surface of particles. These processes will now be discussed in turn.

The photolysis of SO_2. In the presence of oxygen SO_2 photolysis leads to the SO_3 production. In the case of the simultaneous presence of water vapour, a sulphuric acid aerosol is formed immediately [8, 29, 32]. The following course of events is assumed most frequently:

$$\begin{aligned} SO_2(\tilde{X}^1A_1) + h\nu(340\text{–}400\ \text{nm}) &\rightarrow SO_2(^3B_1) \\ SO_2(^3B_1) + O_2(^3\Sigma_g^-) &\rightarrow SO(\tilde{X}^1A_1 + O_2(^1\Sigma_g^+) \\ SO_2(^3B_1) + O_2(^3\Sigma_g^-) &\rightarrow SO_2(\tilde{X}^1A_1) + O_2(^1\Delta_g) \end{aligned}$$

$$\begin{aligned} SO_2(^3B_1) + O_2(^3\Sigma_g^-) &\rightarrow SO_4(\text{cyclic}) \\ SO_4(\text{cyclic}) + O_2 &\rightarrow SO_3 + O_3 \\ SO_3(^3B_1) + O_2(^3\Sigma_g^-) &\rightarrow SO_3O(^3P) \\ SO_3 + H_2O &\rightarrow H_2SO_4 \end{aligned}$$

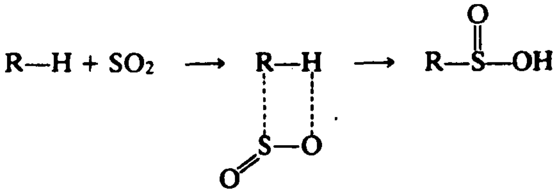
Besides the SO_2 photooxidation the reverse reaction can also occur according to the following scheme [8, 30]:

$$SO_3 + h\nu \rightarrow SO_2 + O(^3P)$$

the rate of which may be comparable to the SO_2 photooxidation rate.

The SO_2 photolysis in the presence of light paraffins and olefins, in the absence of O_2 leads to an aerosol formation, containing sulphinic acids.

Thus, the simplest mechanism of the production may be described by the following scheme [8]:

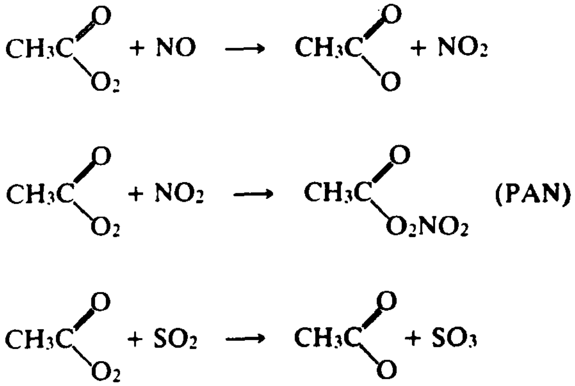


Reactions with the free radicals. The reaction of SO_2 with the OH radical can be of an importance in practice during the formation of the H_2SO_4 aerosol. H_2SO_3 is simultaneously formed as an intermediate product, which yields H_2SO_4 with a further OH according to the reactions

$$\begin{aligned} OH^\bullet + SO_2(+M) &\rightarrow H_2SO_3(+M) \\ H_2SO_3 + OH^\bullet &\rightarrow H_2SO_4 \end{aligned}$$

In this case, $OH^\bullet$ serves as a promotor during the formation of the H_2SO_4 aerosol. Theoretically, the reactions could also be of an importance for the removal of the radical OH from the atmosphere. However, if NO_2 is also present, the reaction of NO_2 with OH (producing HNO_3) has a higher rate and it thus takes precedence in the $OH^\bullet$ removal.

The reactions of SO_2 with the radicals RO and RO_2 may affect the oxidation of NO, which does not occur simultaneously with SO_2 in the polluted atmosphere. The mechanism of the process runs first through the reaction of NO with a relevant radical to form NO_2, which yields, together with a further radical molecule, an alkyl nitrate or peroxyacyl nitrate (PAN). A further reaction with SO_2, producing SO_3, may occur. For example [8]:



The last reactions reduces the rate of the conversion of NO to NO_2 and thus also PAN formation. Experiments performed during the study of reactions of mixture of olefins with NO_x in polluted air also unambiguously supported this finding. In the presence of SO_2, the oxidizing ability of the system is reduced and thus, the amount of peroxyacyl nitrate decreases. The aerosol production simultaneously increases.

SO_2 oxidation in the liquid phase. SO_2 is dissolved to form an aqueous solution, whence it can be oxidized to SO_3 or H_2SO_4. The mechanism of the process according to Miller and de Pena [31] is as follows:

$$\begin{aligned}
SO_2 + H_2O &\rightleftharpoons H_2SO_3 \\
H_2SO_3 &\rightleftharpoons HSO_3^- + H^+ \\
H_2SO_3 + HO^- &\rightleftharpoons HSO_3^- + H_2O \\
HSO_3^- &\rightleftharpoons SO_3^{2-} + H^+ \\
SO_3^{2-} + 1/2O_2 &\rightarrow SO_4^{2-}
\end{aligned}$$

There is a permanent state of equilibrium between SO_2 and H_2SO_3 and between HSO_3^- and SO_3^{2-} and thus, the rate of the process is determined by the remaining three reactions. The rate of the HSO_3^- and SO_3^{2-} oxidation to SO_4^{2-} increases in the presence of ions of metallic catalysts. For example, the conversion in the presence of Mn^{2+} ions may occur according to the following scheme:

$$\begin{aligned}SO_2 + Mn^{2+} &\rightleftharpoons Mn \cdot SO_2^{2+}\\ 2Mn \cdot SO_2^{2+} + O_2 &\rightleftharpoons 2Mn \cdot SO_3^{2+}\\ Mn \cdot SO_3^{2+} + H_2O &\rightleftharpoons Mn^{2+} + H_2SO_4\end{aligned}$$

The conversion of SO_2 to SO_3 or absorption of the SO_3 (or H_2SO_4) in rain drops results, together with HNO_3, in an increased acidity of the atmospheric precipitations.

The catalytic oxidation of SO_2. The process of catalytic oxidation can occur on the one hand on the surface of solid particles and, on the other, as mentioned above, in the liquid phase. One example is a process occurring in hot smoke produced from combustion products emitted from metallurgical works or during the combustion of fossil fuels in power plants. The SO_2 conversion to SO_3 can be catalysed by metallic components of fly ash suspended in smoke. The reaction occurs at a sufficient rate in the presence of ferric oxide according to the scheme:

$$SO_2 + 1/2O_2 \xrightarrow{Fe_2O_3} SO_3$$

The basic mechanism of the removal of SO_2 from the atmosphere is its oxidation to SO_3. In the day-time, at a low relative humidity, the SO_2 oxidation is prevalent in the presence of nitrogen oxides or possibly of intermediate products of the photooxidation of hydrocarbons. In the night and under conditions of high humidity, SO_2 is absorbed in water drops and the oxidation occurs in the liquid phase. SO_3, produced during the oxidation in the gas phase reacts with the atmospheric water vapour, producing an aerosol of H_2SO_4. The aerosol particles in the atmosphere gradually increase in size and after several days they are as large as 0.1 to 1.0 μm. Particles with diameters below 0.5 μm are the main source of the white smoke during the SO_2 emissions. In the final stage, they are washed out from the atmosphere by rain or snow precipitations.

Sulphur trioxide. This is formed together with sulphur dioxide during the combustion of fossil fuels. Its content is, however, essentially lower — 1/80 to 1/40 of the SO_2 content.

Low amounts enter into the atmosphere during sulphuric acid production, during the production of phosphate fertilizers, and during electroplating, etc.

In the atmosphere, SO_3 reacts immediately with H_2O, forming H_2SO_4. The H_2SO_4 in the atmosphere may be correlated with the content of SO_2.

Available studies indicate that the sulphuric acid content increases with increasing SO_2 concentration up to a certain critical value, beyond which it starts to drop with a further increase of the SO_2 content. The value of the critical SO_2 concentration is variable, depending on the locality.

Hydrogen sulphide. Natural processes are the main global source of hydrogen sulphide emissions — volcanic activity, biological decomposition processes, etc. Human activity brings a contribution of only a few per cent to these sources: H_2S is produced during the treatment of petroleum, coal, cellulose and in paper production. In view of its high toxicity, H_2S may be dangerous particularly in the case of larger local releases. The estimated total annual emissions amount to 103 million tons [5]. The mean tropospheric concentration expressed as the amount of sulphur from H_2S ranges between 0.14 and 0.25 $\mu g\ m^{-3}$ [6, 28].

In the atmosphere, hydrogen sulphide is converted stepwise to H_2SO_4 via the oxidizing action of atmospheric oxygen with participation of solar radiation and due to hydrolytic reactions with the atmospheric humidity. The mechanisms of the H_2S conversion to H_2SO_4 in the atmosphere may be as follows:

$$\begin{aligned} 2H_2S + 3O_2 &\rightarrow 2H_2O + 2SO_2 \\ 2SO_2 + O_2 &\rightarrow 2SO_3 \\ SO_3 + H_2O &\rightarrow H_2SO_4 \end{aligned}$$

The second reaction, which is very slow under normal conditions, can be catalysed by the solar energy of relevant wavelengths or metallic oxides in the atmosphere.

When further harmful substances enter the atmosphere together with hydrogen sulphide, then the number of possible reactions is extended by combinations with primary and secondary pollutants. For example, there are the emissions from plants for the production of viscose fibres, where particularly H_2S and CS_2 are released into the atmosphere. The following reactions probably occur in the atmosphere:

$$\begin{aligned} 2H_2S + 3O_2 &\rightarrow 2H_2O + 2SO_2 \\ CS_2 + 3O_2 &\rightarrow CO_2 + 2SO_2 \\ 2SO_2 + O_2 &\xrightarrow{\text{catalyst}} 2SO_3 \\ SO_3 + H_2O &\rightarrow H_2SO_4 \end{aligned}$$

$$\begin{array}{lcl}
CS_2 + 2H_2O & \rightarrow & CO_2 + 2H_2S \\
SO_2 + 2H_2S & \rightarrow & 3/e\ S_e + 2H_2O \\
1/e\ S_e + O_2 & \rightarrow & SO_2 \\
3SO_3 + CS_2 & \rightarrow & COS + 4SO_2
\end{array}$$

e — the numbers of the atoms in molecule.

Effects of sulphur compounds. The presence of oxides of sulphur in the atmosphere increases the rate of the corrosion of metallic materials, resulting in damage to structures of buildings and works of art.

The effect of the SO_2 concentration in the atmosphere on the rate of the corrosion of steel at different temperatures is shown in Fig. 5.4 [33].

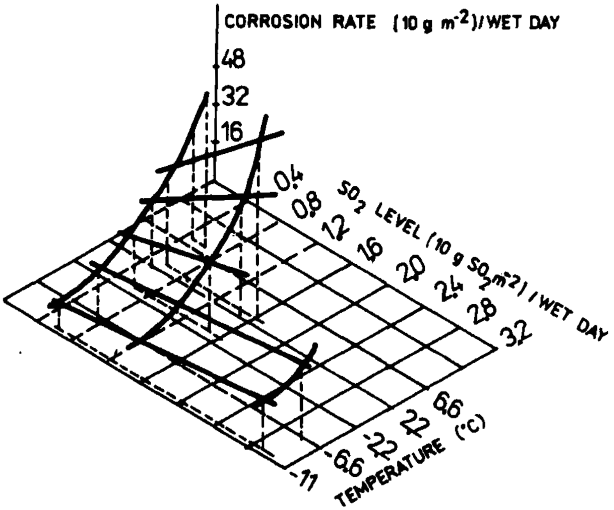


Fig. 5.4. Rate of steel corrosion increases with temperature and concentration of SO_2

The sulphur cycle. Sulphur, in common with all the basic biogenic elements, has an enclosed cycle in the system made up by the hydrosphere, lithosphere, atmosphere and biosphere. Besides flows of particular elements in the system, the cycles provide data on sources, conversions and disappearance in particular spheres. They represent dynamic systems, which are mutually connected and which may be considerably affected by the human activity. The global flow can be even doubled in certain cases. As a result, there can be an increase of the biological production on the Earth. The excess increase may, however, have opposite consequences. After reaching a certain limit value, biological activity may be suppressed.

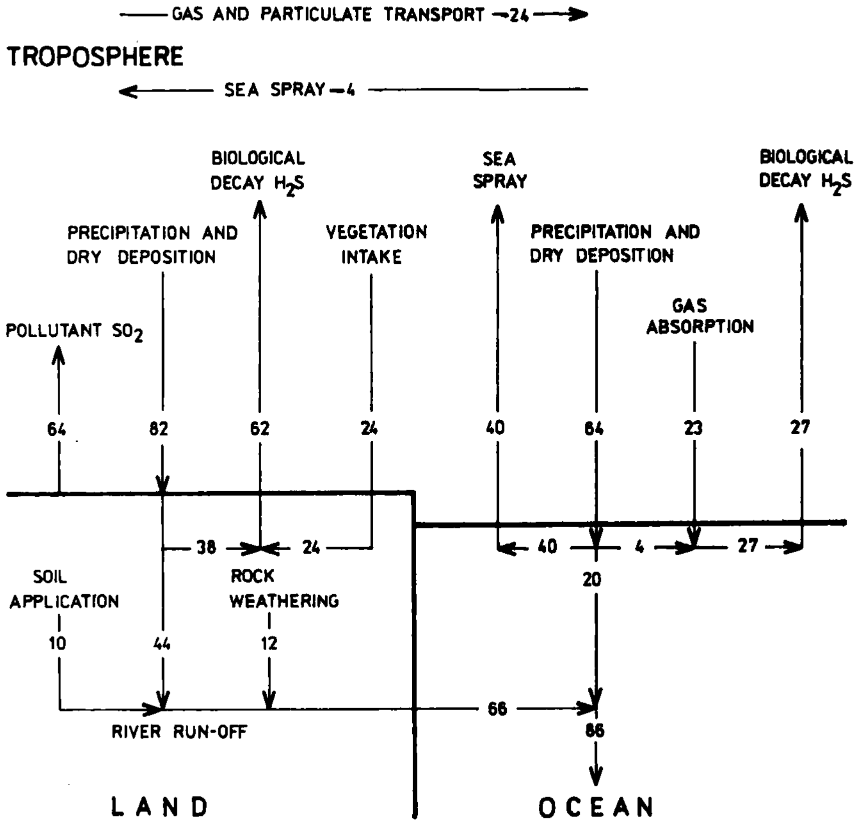


Fig. 5.5. The sulphur cycle in the biosphere (kg $\times 10^9$ yr^{-1})

The sulphur cycle is shown in Fig. 5.5 [6, 26]. Sulphur is recycled from seas and oceans through the atmosphere back to the Earth. It comes into the atmosphere from the following three main sources:

(1) The biological decomposition of sulphates occurring on the one hand on the earth's surface and, on the other hand, in the mouths of rivers and shoals of seas and oceans. In the course of this process, some microorganisms release H_2S, which enters into the atmosphere. In the air, H_2S is oxidized very rapidly to SO_3, and H_2SO_4 is produced in the presence of the air humidity. Sulphuric acid further reacts with components of the polluted atmosphere, producing sulphates. Last, solid sulphate particles fall back to the earth's surface by the action of gravity or atmospheric precipitations.

(2) The aerosol produced in sea water spray. In the atmosphere, in the course of water evaporation from fine droplets, sulphate particles are formed, which fall to the Earth and back into the oceans.

(3) Anthropogenic source. In this case, particularly sulphur dioxide enters the atmosphere. It falls back to the earth's surface, predominantly in the form of sulphates or H_2SO_4. It is estimated that about 1/3 of sulphates falling onto the earth's surface comes from human activity.

Besides the above-mentioned sources, sulphur comes to the earth's surface due to vegetation, which captures a portion of the atmospheric sulphur. Essentially the whole amount of sulphur is returned into the atmosphere after the biological decomposition, connected with the release of H_2S.

Sulphates are transported into the seas and oceans directly from the atmosphere and from surface waters. One third of sulphates in surface waters comes from the soil and rocks, two thirds from the atmosphere. As compared to the amount in surface water, sulphur is present in sea water in concentrations higher by a factor of 240. In coastal waters, which are characterized by a remarkable input of sulphur, the biological reduction occurs with a simultaneous H_2S release. This gas escapes into the atmosphere, when a mud layer is exposed in the course of the tidal variation. Since the process also occurs in the depths of seas, hydrogen sulphide reacts with the iron compounds present, producing sulphides, which are deposited continuously in sea sediments.

5.2.4.2 Nitrogen compounds

Of the various emissions of nitrogen compounds which enter into the atmosphere, the oxides N_2O, NO, NO_2, and NH_3, NH_4^+, NO_3^- are the most important species. Natural sources considerably exceed the sources from anthropogenic activity. Global emissions from natural sources are summarized in Table 5.13 [26]; amounts originating during the combustion processes may be found in Table 5.14 [26]. For an estimate of emissions from central European countries, Yugoslavia, Roumania and USSR in 1980 see Table 5.15.

Table 5.13. Natural global emissions of nitrogen compounds (originating during biological processes) [26]

Compounds	Emissions (t 10^6 yr^{-1})	Emissions in terms of nitrogen (t 10^6 yr^{-1})
NO	455	212
N_2O	537	342
NH_3	1053	867

Table 5.14. Global emissions of nitrogen compounds, produced during combustion, expressed as NO_2 ($t\ 10^6\ yr^{-1}$)

Compounds	Source	Emissions
NO_2	Coal combustion	24.4
	Petroleum refining	0.6
	Petrol combustion	6.8
	Oil combustion	12.8
	Natural gas combustion	1.9
	Combustion of other fuels	1.4

Table 5.15. The estimate of NO_x emissions from central European countries, Yugoslavia, Roumania and USSR on the basis of the fuel consumption or consumption of energy in thousands t NO_x in 1980 according to [45] and [46]

Country	Semb and Amble [46]	Eliassen et al. [45]
Czechoslovakia	500	600
Yugoslavia	190	210
Hungary	180	220
FRG (east part)	570	680
FRG (west part)	2200	3350
Poland	840	1000
Austria	150	275
Roumania	390	460
USSR(the whole territory)	6800	5000

Nitrous oxide. N_2O is one of the stable atmospheric components. Natural processes are the only source of this substance, which is formed as a waste product of the biological activity occurring on the earth's surface. It is not produced in the atmosphere itself. Nitrous oxide represents 97% of all the nitrogen components present in the atmosphere [6].

In the troposphere, its concentration is constant (0.9 mg m^{-3}), it increases rapidly with increasing above sea altitude, and in the mesosphere it is essentially negligible. The residence time of N_2O in the atmosphere is estimated to be 4 years. Most of it is returned to the earth's surface; only of about 6% diffuses into the stratosphere, where it is degraded by photodissociation with a partial contribution of the chemical reaction

$$\begin{aligned} O(^1D) + N_2O &\rightarrow N_2 + O_2 \\ &\rightarrow 2NO \end{aligned}$$

The losses during this reaction make up only 4% out of the decrease estimated for the photodissociation. The destruction by the photodissociation is initiated by radiation with wavelengths below 250 nm. In the course of the reaction, N_2 and $O(^1D)$ are formed as follows:

$$N_2O + h\nu \rightarrow N_2 + O(^1D)$$

Out of the total amount of the N_2O destroyed by the reactions in the atmosphere, 98 and 2% are converted to N_2O and NO, respectively.

Nitric oxide. The major portion of this gas comes from natural sources, from which 455×10^6 t enters the atmosphere annually [26]. As regards human activity, mainly combustion processes contribute to the NO emissions (emissions from power stations, residential heating units and transport). The residence time in the atmosphere is considered to be 4 days.

Nitric oxide is formed during combustion processes at sufficiently high temperatures. In the first stage of the process, atomic oxygen is formed on the one hand by the dissociation of O_2:

$$O_2 \rightarrow 2O$$

and, on the other, by the reaction CO and OH

$$CO + OH \rightarrow CO_2 + H$$

with a subsequent reaction of the atomic hydrogen with an O_2 molecule

$$H + O_2 \rightarrow OH + O$$

The atomic oxygen generated in this way in the system initiates the chain reaction which produces NO:

$$\begin{aligned} O + N_2 &\rightarrow NO + N \\ N + O_2 &\rightarrow NO + O \end{aligned}$$

A side reaction can occur simultaneously:

$$\begin{aligned} N + NO &\rightarrow N_2 + O \\ O + NO &\rightarrow N + O_2 \end{aligned}$$

The reactions involved in NO production occur particularly in a mixture rich in air, since atomic oxygen reacts more easily with N_2 as compared, e.g., with reactions with hydrocarbons, which may be present during combustion processes of this type.

Under equilibrium conditions, in the presence of oxygen, most NO is oxidized to NO_2. Even at a concentration of 0.1 vol.% the colourless nitric oxide is converted in several seconds to coloured nitrogen dioxide. In the air, where its concentration is essentially lower, the oxidation rate rapidly decreases. For example, at a concentration of 10^{-4} vol.%, a period of 100 hours is necessary for achieving a 50% conversion of NO to NO_2, and in the case of a decrease to a concentration of 10^{-5} vol.%, this time is as long as 1000 hours [34].

A different situation is encountered in the case of the oxidation by ozone

$$NO + O_3 \quad \rightarrow \quad NO_2 + O_2$$

The rate of such oxidation is governed by the O_3 and NO concentrations in the atmosphere.

Nitrogen oxide is also produced as a secondary pollutant in the air during the NO_2 photodissociation

$$NO_2 + h\nu \quad \rightarrow \quad NO + O(^3P), \qquad \lambda \leq 397.9 \text{ nm},$$

or in the course of the reaction

$$N_2O + O(^1D) \quad \rightarrow \quad NO + NO$$

The last reaction may be the cause of the presence of NO in the stratosphere.

In the mesosphere and thermosphere the photodissociation of nitrogen oxide occurs according to the reaction

$$NO + h\nu \quad \rightarrow \quad N + O(^3P)$$

which provides an explanation for the disappearance of NO at higher altitudes of the atmosphere.

The photochemical conversion of NO to NO_2 may play an important role in the atmosphere pollution in city agglomerations. The OH radical has a key role in this process [35, 36]. In the presence of hydrocarbons (e.g. alkanes) the reaction of OH radicals with alkanes occurs primarily, e.g. in the case of C_4H_{10}, the sequence of the reactions is as follows:

$$\begin{aligned} C_4H_{10} + OH &\rightarrow C_4H_9 + H_2O \\ C_4H_9 + O_2 &\rightarrow C_4H_9O_2 \\ C_4H_9O_2 + NO &\rightarrow C_4H_9O + NO_2 \\ C_4H_9O + O_2 &\rightarrow C_3H_7CHO + HO_2 \\ HO_2 + NO &\rightarrow OH + NO_2 \end{aligned}$$

In the case of the last reaction, the OH radical is regenerated, so that the chain can recommence.

Nitrogen dioxide. A major portion of nitrogen dioxide is formed directly by the oxidation of NO in a polluted atmosphere. An essentially lower amount enters the atmosphere from anthropogenic sources, where the sum of $NO + NO_2$, referred to as NO_x is considered. Estimates of the amounts of NO_x emissions ranging from 21.4 to 50.4×10^6 yr^{-1} are reported in [13–16] (related to N), 48×10^6 t yr^{-1} in [5] (related to NO_2).

The NO_x content in combustion products from heating is estimated as 1.5 to 2.0×10^{-3} vol.%, in smokes from industrial processes as 0.05 vol.% and in exhaust gases from motor vehicles as 0.005 to 0.3 vol.%. The local NO_x concentration can vary considerably. For example early morning values in very large urban complexes may be higher by factors of 25 to 500 as compared to those in country areas.

The removal of NO_2 from the atmosphere occurs via its oxidation and hydration to form nitric acid. In the course of the oxidizing process, NO_3 may be formed by the reaction with ozone:

$$O_3 + NO_2 \rightarrow NO_3 + O_2$$

or it may be formed during the interaction with atomic oxygen:

$$O(^3P) + NO_2 + M \rightarrow NO_3 + M$$

The NO_3 formed reacts with NO_2, producing N_2O_5:

$$NO_3 + NO_2 \rightarrow N_2O_5$$

In the presence of the air humidity, nitric acid is obtained:

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

The nitric acid can further react in the polluted atmosphere, forming nitrates, which are washed out from the atmosphere as the final stage.

The nitrogen dioxide is very active photochemically. It absorbs solar radiation over the whole of the visible and ultraviolet range. In a spectral range of 600 to 380 nm, excited molecules are formed, and below 43 nm its photodissociation occurs. From the standpoint of air pollution, the NO_2 photolysis is most important; this may initiate photochemical smog production. The whole cycle of the formation of photochemical smog consists of 4 photolytic processes, including the NO_2 and O_3 dissociation, photolysis of aldehydes and ketones, HNO_2 photolysis and photolysis of nitrites and peroxides [8]. The cycle may be described by the following reactions:

$$\begin{array}{llll} (1) & NO_2 + h\nu & \rightarrow & NO + O(^3P), \quad \lambda \leq 397.9\ \mathrm{nm} \\ & O(^3P) + O_2 & \rightarrow & O_3 + M \end{array}$$

(2) During the photolysis of aldehydes and ketones, the photodissociation of CH_2O and CH_3CHO is of major importance:

$$\begin{array}{lll} CH_2O + h\nu & \rightarrow & H_2 + CO \\ & \rightarrow & H + HCO \end{array}$$

and for CH_3CHO:

$$\begin{array}{lll} CH_3CHO + h\nu & \rightarrow & CH_4 + CO \\ & \rightarrow & CH_3 + HCO \\ & \rightarrow & CH_3CO + H \end{array}$$

(3) In the course of the HONO photolysis, the OH radical is produced. Its importance for the production of the photochemical smog was mentioned earlier (during the NO oxidation reactions). The photolysis of HONO may thus be considered as the governing factor for the formation of the whole cycle:

$$HONO + h\nu \rightarrow OH + NO$$

(4) The photodissociation of nitrites, nitrates and peroxides is connected with the formation of free radicals:

$$\begin{aligned}
\mathrm{RONO} + h\nu &\rightarrow \mathrm{RO} + \mathrm{NO}\\
\mathrm{RONO_2} + h\nu &\rightarrow \mathrm{RO} + \mathrm{NO_2}\\
\mathrm{RO_2NO_2} + h\nu &\rightarrow \mathrm{RO_2} + \mathrm{NO_2}\\
\mathrm{ROOR} + h\nu &\rightarrow \mathrm{2RO}\\
\mathrm{ROOH} + h\nu &\rightarrow \mathrm{RO} + \mathrm{OH}
\end{aligned}$$

The cycle of the photochemical smog formation may be terminated by several reactions, as follows:

$$\begin{aligned}
\mathrm{OH} + \mathrm{HO_2} &\rightarrow \mathrm{H_2O} + \mathrm{O_2}\\
\mathrm{2HO_2} &\rightarrow \mathrm{H_2O_2} + \mathrm{O_2}\\
\mathrm{HO_2} + \mathrm{NO_2} &\rightarrow \mathrm{HONO} + \mathrm{O_2}\\
\mathrm{OH} + \mathrm{NO(+M)} &\rightarrow \mathrm{HONO(+M)}\\
\mathrm{OH} + \mathrm{NO_2(+M)} &\rightarrow \mathrm{HONO_2(+M)}\\
\mathrm{RO} + \mathrm{NO_2} &\rightarrow \mathrm{RONO_2}\ \text{(alkyl nitrate)}\\
\mathrm{RCO_2} + \mathrm{NO_2} &\rightarrow \mathrm{RCO_2NO_2}\ \text{(acyl nitrate)}\\
\mathrm{RCO_3} + \mathrm{NO_2} &\rightarrow \mathrm{RCO_3NO_2}\ \text{(peroxyacyl nitrate)}\\
\mathrm{OH} + \mathrm{HONO} &\rightarrow \mathrm{H_2O} + \mathrm{NO_2}\\
\mathrm{O(^3P)} + \mathrm{HONO} &\rightarrow \mathrm{OH} + \mathrm{NO_2}
\end{aligned}$$

The formation and residence time of the photochemical smog depends on the chemical composition and extent of pollution of the atmosphere, and on the intensity and spectrum of solar radiation. It is frequently formed on hot sunny days, at the time of intense and slow moving. Discussions of the problems of photochemical smog are generally concerned with its undesirable effects. These are particularly a deterioration of visibility and the toxic or harmful effects of components produced. Ozone especially acts as a strong oxidizing agent during these processes. It initiates a number of further reactions with organic substances thus affecting, e.g., the ageing of elastomers. Peroxyacyl nitrate (PAN), which is a product of this process has toxic effects on the human organism.

Ammonia. The greatest amounts of ammonia enter into the atmosphere during the biological decomposition of organic matter and in the reduction of nitrites and/or nitrates. The anthropogenic sources are lower by several orders of magnitude and they include particularly the chemical industry, chiefly the production of fertilizers and urea. Industrial wastes represent a further source. The total anthropogenic emissions are considered to supply 3.5 to 5.5×10^6 tons of ammonia annually [37, 38].

The ammonia concentration in the clean atmosphere is 7 μg m^{-3} [7], for a polluted atmosphere the data differ and they range between 1.4–14 μg m^{-3} [39].

Gaseous ammonia reacts with sulphuric and nitric acids in the atmosphere, producing sulphates and nitrates, respectively. In the final stage, self-purification processes occurring in the atmosphere (sedimentation, washing out with rain precipitation) help to remove the salts produced from the air. The stratospheric ammonia is probably removed by the reactions

$$\begin{aligned} NH_3 + OH &\rightarrow H_2O + NH_2 \\ NH_3 + h\nu &\rightarrow NH_2 + H \\ NH_2 + NO &\rightarrow N_2 + OH \end{aligned}$$

The residence time of ammonia in the atmosphere may be about 7 days.

The mean concentration of the NH_4^+ aerosols in the atmosphere is about 0.1 μg m^{-3}, whereas the value for NO_3^- aerosols is 0.3 μg m^{-3}. A greater portion, which returns to the Earth during rain precipitations, falls onto the Northern Hemisphere between 30 and 55° north geographic latitude.

The sedimentation of large amounts of atmospheric NH_4^+ and NO_3^- on the earth's surface and in the hydrosphere presents a potential danger to the biosphere (due to their subsequent conversion to nitrites and nitrosamines).

The nitrogen cycle. The nitrogen cycle, which shows the distribution and exchange of nitrogen compounds in particular spheres, is presented in Fig. 5.6 [26]. This indicates clearly that the atmosphere is the most important source of nitrogen. The atmospheric nitrogen is fixed in different biochemical ways. "Fixation" is the binding in different chemical compounds, which may be utilized by plants or animals. Nitrogen is fixed by different soil and sea microorganisms and further by plants in the assimilation process to form eventually proteins. In the opposite process — ammonification — which occurs during the biological decomposition of decayed plants and animals, the fixed nitrogen is released in the form of ammonia. The NH_4^+ ions formed are oxidized by certain microorganisms to nitrites or nitrates. This process, called *nitrification*, occurs in nature on a large scale. The nitrates obtained, retained in the soil, are eventually washed into underground waters. A certain portion of nitrates may be assimilated by plants

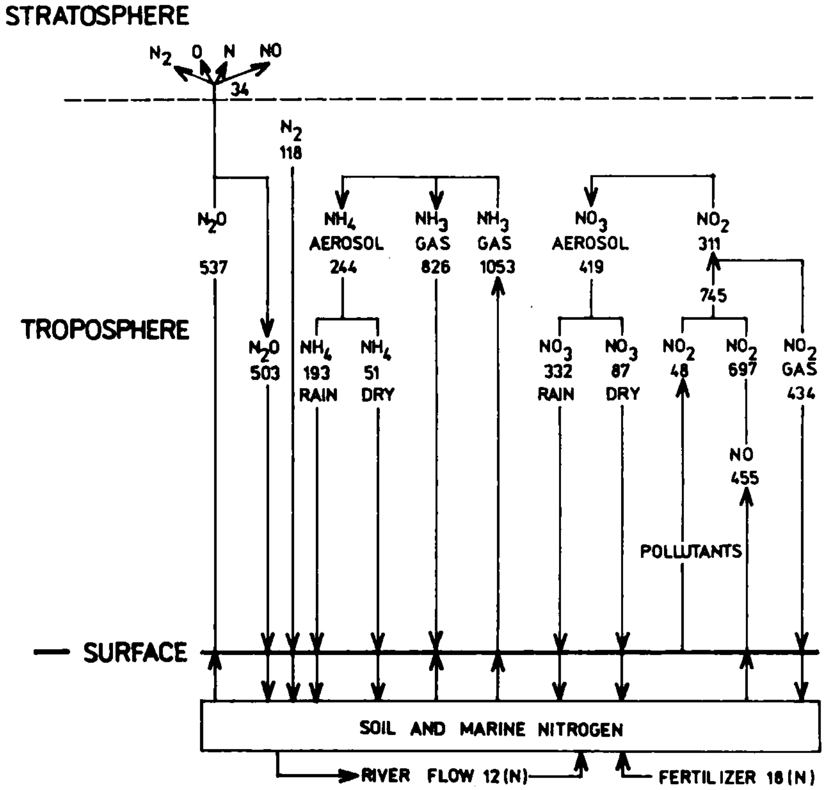


Fig. 5.6. The nitrogen cycle in the biosphere (kg $\times 10^9$ yr^{-1})

and a portion undergoes the denitrification process, forming nitrogen or nitrogen monoxide. There is hence a closed nitrogen cycle.

The global nitrogen cycle is actually based on three independent cycles including the N_2O, NH_3 and NO_x [6] cycle.

The nitrogen monoxide cycle is essentially independent of the rest of the system, not taking into account its production by means of soil bacteria. Approximately 6% of tropospheric N_2O diffuses into the stratosphere, where it is converted to NO, oxygen and nitrogen. The main portion returns to the earth's surface. The bacterial fixation in the soil represents approximately 118×10^6 tons annually.

Essentially all the ammonia is formed either on the earth's surface or near to it. In the atmosphere there is, according to estimates, about 33×10^6 tons of NH_3. Because of its very high solubility, the time of its residence in the atmosphere is fairly short. It is returned to the earth's surface in the form of NH_3 or ammonium salts.

The source of nitrogen, forming the third cycle is due mainly to processes occurring in nature. Among the nitrogen oxides, particularly NO is released into the atmosphere, where it is oxidized to NO_2 or nitrates. Aerosol containing nitrates is returned to the Earth together with rain precipitations or it is sedimented on the surface by the action of gravitational forces. The dry deposition represents approximately 1/4 of the amount removed from the atmosphere by rain.

The complete nitrogen cycle includes amounts supplied into the soil in the form of fertilizers (18×10^6 tons annually, related to nitrogen) and the annual transport of compounds (predominantly nitrates) from the soil to rivers and seas is about 12×10^6 t of nitrogen annually. For completeness' sake we should mention amounts originating from the atmospheric fixation of nitrogen in the course of ionization. At the present time this source is small in comparison with remaining sources, but it was of great importance for the nitrogen cycle in the early developing stages of the Earth.

5.2.4.3 Carbon compounds

The major portion of gaseous carbon compounds comes into the atmosphere from natural sources as a result of biological processes and forest fires, etc. A certain portion is produced directly in the atmosphere during the reactions of primary pollutants. Industry and transport are responsible for very considerable contributions to anthropogenic sources of emissions of carbon compounds, which are particularly concentrated in the atmosphere above and around city agglomerations.

Carbon monoxide. The annual tropospheric production of carbon monoxide is considered to be 5×10^9 tons annually [14, 17–20, 40, 41]. The main portion of CO is produced in the atmosphere during methane oxidation, during the decomposition of chlorophyll and during the photooxidation of terpenes. On the earth's surface, the natural sources contributing to the content of carbon monoxide in the atmosphere are volcanic activity, forest fires and bacterial activity in the oceans. Human activity brings an annual contribution to the total emissions of about 6.4×10^8 tons [13, 14, 17–20], the main source being the combustion of fossil fuels. Carbon monoxide is contained in exhaust gases of motor vehicles, steam ships and aircraft, and it is formed during the combustion of wastes and in various industrial processes. The amount of CO which enters into the atmosphere in this way is increasing. Transport, whose density is directly correlated with the CO concentration in large urban areas, is largely responsible for increase. It should be noted that estimates presented by different authors differ considerably from each other. They depend on the degree of sophistication of balance models and the choice of input data. In principle it is possible to agree with an opinion that the amounts of CO formed at the earth's surface are negligible in comparison with its total atmospheric balance.

The mean global CO concentration in the atmosphere, determined on the basis of data obtained over the Pacific, is approximately 0.125 mg m^{-3} [42]. The estimates of the residence time in the atmosphere again differ from each other. The actual residence time can be considered to range between 0.1 and 0.3 years [40, 41]; it depends on the rate of removal of carbon monoxide from the atmosphere. The process probably occurs through the oxidation of CO by certain components present in the atmosphere, e.g. OH radicals:

$$CO + OH \rightarrow CO_2 + H$$

The OH radicals play an important role not only in the removal but also in the formation of CO, so that their content in the troposphere may affect the total amount of the atmospheric carbon monoxide. They react with methane and with organic radicals, forming CO:

$$\begin{aligned} CH_4 + OH &\rightarrow CH_3 + H_2O \\ CH_2O + OH &\rightarrow CHO + H_2O \\ CHO + OH &\rightarrow CO + H_2O \end{aligned}$$

This sequence of the reactions describes the formation of a secondary pollutant originating during the interaction of primary pollutants directly in the atmosphere. This production represents the main source of the atmospheric carbon monoxide.

Carbon dioxide is the basic component of the animal and plant cycle. Its exchange between the biosphere and atmosphere is continuous. CO_2 respired by animals and plants enters the atmosphere, from which it is recycled back to the biosphere in the course of photosynthetic processes. Of the stable components of the atmosphere, CO_2 is the fourth component in order of proportion, present to the extent of 0.03 vol.%. The diurnal CO_2 concentration in the atmosphere varies, achieving a maximal value in the night. It also exhibits annual variations involving the participation of factors such as the vegetation period, decomposition of organic substances in the soil affected by the season of the year, etc. The mean residence time of CO_2 in the atmosphere is, according to the estimates, 2 to 4 years. The anthropogenic sources, including particularly combustion processes, contribute approximately 1.28×10^{10} tons to the global annual emission [5].

The total CO_2 content in the atmosphere is increasing. The increase results from an ever-growing consumption of fossil fuels (Table 5.16) [43]. Due to this, the atmospheric concentration of CO_2 has been enhanced by about 10% over the last 100 years.

Table 5.16. The increase of CO_2 emissions (t 10^9 yr^{-1}) [43]

Source	Emissions			
	1965	1970	1980	1990
Coal	6.65	6.71	6.85	6.99
Petroleum	3.66	4.79	7.77	12.61
Natural gas	1.08	1.47	2.53	4.35
Waste incinerations	0.42	0.46	0.56	0.66
Wood as fuel	0.62	0.62	0.62	0.62
Forest fires	0.35	0.35	0.35	0.35
Total	12.78	14.40	18.68	25.58
Relative increase	—	13%	46%	100%

It predicted that the anthropogenic emission will have doubled over the period 1965 to 1990 [5].

The increase of the CO_2 content in the atmosphere will most probably lead to an increase in the mean troposphere temperature near the earth's surface, which could affect climatic conditions on the Earth. The phenomenon is explained by the so-called "greenhouse effect". The solar radiation penetrates the atmosphere and it is absorbed by the surface of the Earth, which emits the energy back into space. The radiation from the Earth has, however, a different (longer) wavelength. The carbon dioxide in the atmosphere absorbs this radiation and thus, it contributes to heating the atmosphere.

Experimental data obtained during the measurement of the CO_2 concentration at Mauna Loa in Hawaii demonstrate that between 1958 and 1978 the concentration increased by 5%, which corresponds to an annual increase of 0.25%.

Certain authors also demonstrate a further possible reason for the increase of CO_2 in the atmosphere, resulting from extensive deforestation, particularly in tropical areas. The CO_2 consumption by photosynthesis is thus reduced, which leads to a reduction of the overall removal of carbon dioxide from the troposphere.

These two causes of CO_2 increase result from ever more intense exploitation of natural sources, with an impact on the environment and intervention in the global ecological equilibrium. This distrurbance of the CO_2 equilibrium could lead to very serious and much discussed consequences.

Hydrocarbons. The estimate of annual global hydrocarbon emissions is 1.69×10^9 tons [5]. The greatest portion is due to methane from natural sources. Together with anthropogenic sources, the annual CH_4 production is greater than 1.45×10^9 tons. Estimates of the residence time of CH_4 in the atmosphere differ from each other and range from 0.9 to 4 years [5, 8]. The second in importance to CH_4 are terpenes, for which the estimates of annual emissions from natural sources are 1.45×10^8 tons [5]. The estimate of hydrocarbon emissions (except methane) in Europe in 1980 are summarized in Table 5.17 [45].

Slightly less than 5% comes from the human activity; of this, petrol combustion produces 38.5%, waste incineration 28.3%, evaporation of solvents 11.3%, evaporation of crude oil and losses during transport 8.8%, wastes from refineries 7.1% [28]. The remaining portion is due to various other minor sources.

The highest hydrocarbon concentrations were measured in large urban areas with a high traffic density. Typical examples are New York, Los Angeles, Chicago, where a very wide variety of hydrocarbons was observed in the atmosphere, including alkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, aldehydes and ketones, etc. Concentrations of certain alkanes (e.g. ethane, propane, butane) at these localities were higher even by several orders of magnitude as compared to those reported for a polluted atmosphere. Of the aromatic hydrocarbons, toluene was most abundant, followed by benzene and xylene; acetylene was the main alkyne, and among the aldehydes and ketones, CH_2O and CH_3CHO were found in largest amounts.

From the standpoint of atmospheric pollution, hydrocarbon combustion is of major importance. Depending on conditions of the combustion processes, the balance of the proportions of final products may be considerable different. Particular differences are observed for mixtures containing different amounts of air. The composition of products changes also with temperature. At low temperatures (700 K) a slow combustion occurs, at temperatures from 700 to 1500 K, the process of the hydrocarbon oxidation is essentially more rapid with a tendency to explosion. In a comparison with the moderate combustion, the mechanism of the process is different. At very high temperatures (> 2300 K) an extremely rapid, explosive combustion is observed.

During moderate combustion, H_2O_2 is formed as a transient product in the first stages, and it enters into further reactions, forming free radicals. At temperatures below 700 K organic peroxides may be formed. Certain

Table 5.17. The estimate of emissions of hydrocarbons (except methane — NMHC[a]) in Europe in 1980 in thousands tons (total mass) [45]

Country	NMHC emissions
Albania	10
Austria	280
Belgium	390
Bulgaria	240
Czechoslovakia	600
Denmark	220
Finland	200
France	2000
FRG (east part)	680
FRG (west part)	2450
Great Britain	1158
Greece	260
Holland	600
Hungary	220
Iceland	15
Ireland	105
Italy	1750
Luxemburg	220
Norway	170
Poland	1000
Portugal	200
Roumania	460
Spain	1050
Sweden	380
Switzerland	260
Turkey	600
USSR	5000
Yugoslavia	210
European total	20538

[a] NMHC — non-methane hydrocarbons.

amounts of aldehydes (particularly CH_2O) and ketones are formed. Above 700 K reactions leading to the production of olefines, CH_4 and H_2 are of importance. For example for C_4H_9, the degradation reactions are:

$$\begin{aligned} CH_4H_9 &\rightarrow H + C_4H_8 \\ &\rightarrow CH_3 + C_3H_6 \end{aligned}$$

In a mixture enriched in fuel, new radicals may be formed together with further alkanes as follows:

$$CH_3 + RH \rightarrow CH_4 + R$$

or in the reaction with a hydrogen atom

$$H + RH \rightarrow H_2 + R$$

The hydrogen atom has a special position, since it can also react with O_2 with a simultaneous production of $O(^3P)$:

$$\begin{aligned} H + O_2 + M &\rightarrow HO_2 + M \\ H + O_2 &\rightarrow OH + O(^3P) \end{aligned}$$

The $O(^3P)$ atom undergoes a reaction with an alkane, producing two radicals, gives rise to which branching chain reactions:

$$O(^3P) + RH \rightarrow OH + R$$

Depending on conditions, in the course of the moderate combustion, organic acids may also be formed (at lower temperatures); in a thermal regime corresponding to 523–573 K, heterocyclic hydrocarbons are formed. The production of alcohols is sometimes also observed, particularly in fuel-enriched mixtures. Carbon monoxide, carbon dioxide and water are the main final products.

In the case of a rapid combustion at temperatures above 700 K, the reaction mechanism is different. H_2O_2 is no longer the initial intermediate product, since at these temperatures it starts to be thermally decomposed, yielding two OH radicals. The branched chain reaction becomes more extensive and it is originated via the HO_2 radical as follows:

$$HO_2 + RH \rightarrow R + H_2O_2 \rightarrow 2OH$$

The OH radicals react with alkanes or alkynes, producing organic radicals

$$\begin{aligned} OH + C_2H_4 &\rightarrow H_2O + C_2H_3 \\ OH + C_2H_2 &\rightarrow H_2O + C_2H \end{aligned}$$

Simultaneously with the oxidation reactions, a thermal splitting of hydrocarbons or pyrosynthetic reactions may also occur. In the case of acetylene, the pyrosynthesis starts at temperatures as low as 600 K and it is connected with the formation of low-molecular-mass polymers. In the temperature range from 700 to 800 K, benzene and polycyclic aromatic hydrocarbons may be formed. At temperatures of above 1300 K, in a mixture enriched in fuel, polyacetylenes may be stepwise reduced to soot.

At very high temperatures, the importance of the HO_2 radical decreases, since it is decomposed into a hydrogen atom and oxygen molecule. In contrast to this, the importance of the atom $O(^3P)$ increases with respect to its important role in the branching process of chain reactions. At temperatures of above 2300 K, it is necessary to consider reactions connected with splitting the final products, with the formation of $O(^3P)$:

$$\begin{aligned} M + H_2O &\rightarrow H + OH + M \\ M + CO_2 &\rightarrow M + CO + O(^3P) \\ M + CO_2 &\rightarrow M + 2O(^3P) \end{aligned}$$

so that the oxidation cannot be stopped as long as oxygen is available. Simultaneously with the oxidation cycle of hydrocarbons, an undesirable reaction, leading to the NO formation, also occurs:

$$\begin{aligned} O(^3P) + N_2 &\rightarrow NO + N \\ N + O_2 &\rightarrow NO + O(^3P) \end{aligned}$$

These reactions are of importance particularly in mixtures enriched in oxygen, since under these conditions the $O(^3P)$ atoms react more easily with N_2 than with hydrocarbons.

Since the hydrocarbons enter into the atmosphere (e.g. as products of the above combustion processes), they react with further components of the polluted atmosphere, or they participate in photooxidation or photolysis. The reactions resulting in photooxidation smog formation are the most important ones. The mechanism of this smog formation has been investigated by many specialists; the sequence of reactions described in Section 5.2.4.2 may be considered as the most reasonable one. The production of the photochemical smog is determined by conditions, in which the reactivity of hydrocarbons also plays an important role. It is characterized by the ability of hydrocarbons to participate in photochemical reactions in the presence of nitrogen oxides. According to this, hydrocarbons are divided into four classes of reactivity [34]:

(1) *high reactivity* — olefins, particularly tri- and tetraalkyl ethenes,

(2) *intermediate reactivity* — polyalkyl benzenes, monoalkyl ethenes,

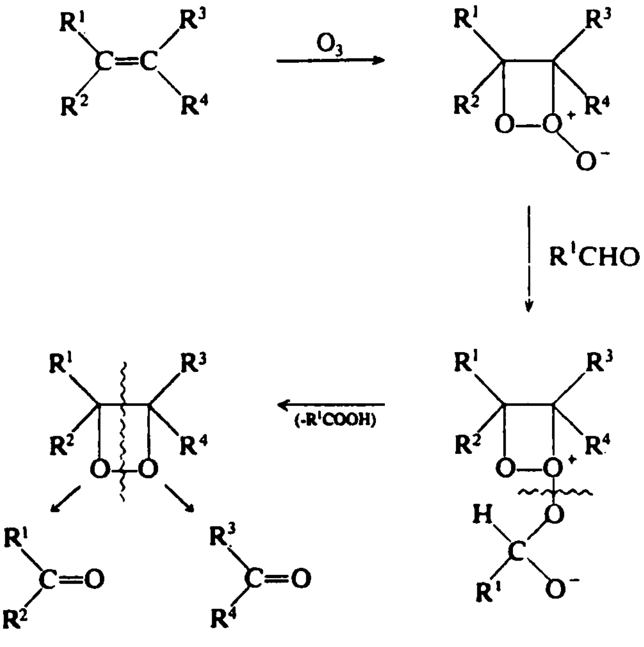
(3) *low reactivity* — ethene, monoalkyl benzenes, alkanes (C_4 and higher), and

(4) *negligible reactivity* — methane, ethane, propane, benzene, acetylene.

Of the range of reations of hydrocarbons in the atmosphere particularly important are those with ozone, which may be generated in the NO_2 photolysis process. It reacts readily with alkenes with producing different products, including lower hydrocarbons, aldehydes, organic acids, CO, CO_2 and H_2O. It is assumed that the initial reaction of alkenes with O_3 in the gaseous phase is accomplished in two steps as follows: the formation of an initial complex, which is further decomposed to an aldehyde or ketone and a peroxybiradical [8]:

$$\begin{aligned} O_3 + R^1R^2C{=}CR^3R^4 &\rightarrow \text{(initial complex)} \\ \text{(initial complex)} &\rightarrow R^1R^2C{=}O + R^3R^4COO \end{aligned}$$

The initial complex may be in the form of the four-membered cyclic system called molozonide; this may lead, in the presence of excess aldehyde, to the oxidation of aldehyde to acids. The reaction sequence is thus as follows:



The peroxybiradical decomposition may occur as follows:

$$\begin{aligned} R^3R^4CO_2 &\rightarrow R^3R^4 + CO_2 \\ &\rightarrow R^3R^4O + CO \end{aligned}$$

where R^3 or R^4 can represent a hydrogen atom.

The reactions of ozone with alkynes are essentially slower than those with alkenes. This is shown by the values of rate constants, which are lower in the case of alkynes due to the higher activation energy. Alkanes react very slowly with O_3 and thus, they are unimportant in atmospheric processes.

From the standpoint of air pollution, halogenated hydrocarbons are particularly significant, especially the group of chlorinated hydrocarbons from anthropogenic sources, which include chemicals for plant protection, industrial solvents, cleansers and fire extinguishing agents. Among natural sources, forest fires also contribute to the emissions of chlorinated hydrocarbons.

Halogenated hydrocarbons used as organic solvents are characterized by their remarkable volatility, chemical stability and low solubility in water. These characteristics also determine their behaviour in the ecosystem. They are supplied by evaporation into the atmosphere, which then serves as their main reservoir. The group includes chlorinated derivatives of methane such as CH_2Cl_2 and CCl_4, and ethylene ($C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4). The global annual CCl_4 production is approximately 1 Mt, 95% being used for the production of CF_2Cl_2 and $CFCl_3$. The annual world emissions of carbon tetrachloride, originating mainly from human activity, are considered to be in the range 5–8 $\times 10^4$ t yr^{-1} [47, 48].

From the atmosphere, CCl_4 is removed in reactions with free radicals by photolysis, hydrolysis and biological degradation after a preceding absorption (reactions with $O(^1D)$ are of particular importance [48]). Trichloroethylene and tetrachloroethylene are used extensively as industrial solvents of fats, waxes, bitumens, dyes, oils and paints.

The amounts of emissions of these vapours of solvents increased enormously particularly in the last decade. Data which estimate annual losses, considered as the difference between the world production and consumption, differ remarkably from each other.

Chloroform is one of the chlorinated derivatives of methane, supplied into the atmosphere only from anthropogenic sources. It may be formed as a side product during the water chlorination by the following reactions [49]:

$$Cl_2 + HCO_3^- \rightarrow HClO + Cl^- + CO_2$$

The hypochlorous acid reacts further with organic substances present in water, forming chlorinated compounds:

$$CH_3COR + 3HClO \rightarrow CCl_3COR + 3H_2O$$

Finally, chloroform is produced via hydrolysis:

$$CCl_3COR + H_2O \rightarrow CHCl_3 + RCOOH$$

A similar process may occur during the bleaching in paper manufacture.

Among various natural sources, the largest amounts of chlorinated hydrocarbons are supplied into the air by forest fires. In the combustion of cellulose, 2.2 mg of methyl chloride are formed per 1 g of substance burnt. Anthropogenic sources include the combustion of PVC (polyvinyl chloride) wastes, burning of plants in agriculture and uncontrolled fires resulting from human activity.

Out of the many chlorinated derivatives, vinyl chloride has been a focus of interest since its carcinogenic effects were discovered. Approximately 6% of its world production is assumed to escape into the atmosphere. Vinyl chloride is used for the production of different plastics and methylchloroform, and it is added to mixtures for the production of special packing materials. Until recently it has been used as a medium in aerosol sprays. The imission concentrations in the vicinity of production sources (0 to 8 km) are generally below 2.6 ng m^{-3}. In the literature, there are only few data about its atmospheric reactions. It is very probable that it participates in photooxidation reactions in the presence of nitrogen oxides. Carbon monoxide formaldehyde, formic acid and HCl are products of its photooxidation.

The very extensive use and high consumption of chlorinated hydrocarbons in plant protection resulted in a contamination of the whole environment. DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) is very dangerous on account of its toxic effects on all the living organisms. It is remarkably resistant, and its residence time in the atmosphere is considered to be several decades. Due to its method of its application, the atmosphere serves as its largest reservoir. Its vapour pressure at 273 K is 2×10^{-5} Pa, which represents about 3 μg m^{-3}. This concentration would correspond to a total amount in the troposphere of roughly 10^6 t. The other estimate is lower by about one half. From the atmosphere, it is removed only by the rain and the great majority is then transported into the oceans. It is nearly insoluble in sea water but is soluble in fats and thus, it is accumulated in organic matter (fishes, mammals, etc.). It is also accumulated in the soil, where the mean residence time is considered to be 5.3 years. It is assumed that on agricultural areas the amount of remaining DDT is as high as 0.17 g m^{-2}, in other areas 4.5×10^{-4} g m^{-2}.

In view of the seriousness of the environmental contamination with DDT, a number of models have been elaborated, describing the dynamics of its circulation in the ecosystem. On the basis of data obtained in this way, forecasts of this pollutant up to the year 2000 have been made. Mean concentrations calculated by Woodwell et al. [50] for the period 1940 to 2000 are plotted in Fig. 5.7. Two alternatives are considered in the model depending on wheather or not the production of DDT continues (curves A and B).

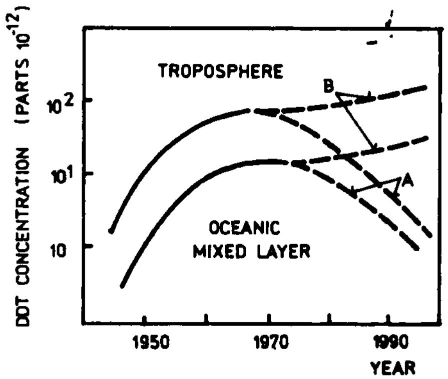


Fig. 5.7. Calculated average DDT concentration in the atmosphere and in the mixed layer of oceans: A — manufacturing of DDT ceases, B — manufacturing of DDT continues

The most studied members of the group of fluorinated hydrocarbons are the fluorochloromethanes, particularly CF_2Cl_2 (freon 12) and $CFCl_3$ (freon 11). Their use commenced 50 years ago, as cooling media, and recently they have found applications as media in aerosol sprays and their production has increased rapidly. These substances are characterized by a low reactivity, low solubility in water and no biological processes are known which would be able to remove them from the atmosphere. Thus, their residence time in the atmosphere is considered to be at least 20 to 30 years, however, maximal times may be as long as hundreds of years (depending on the height above sea level).

With their high chemical stability, the freons are able to diffuse gradually from lower layers of the atmosphere into the stratosphere, where they reduce the ozone layer by photodissociation reactions (this layer is of vital importance for the life on the Earth, since it helps to filter high-energy components of the solar radiation, which have detrimental effects on living organisms). According to Molina and Mutchler [51] at altitudes of 20 to 30 km the photodissociation occurs via ultraviolet radiation ($\lambda < 230$ nm) as follows:

$$\begin{aligned} CF_2Cl_2 + h\nu &\rightarrow CF_2Cl + Cl \\ CFCl_3 + h\nu &\rightarrow CFCl_2 + Cl \end{aligned}$$

The chlorine atoms formed react with ozone, producing a diatomic oxygen molecule

$$\begin{aligned} Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + O &\rightarrow Cl + O_2 \end{aligned}$$

This first cycle including chlorine atoms leads to the second cycle, initiated by the ClO radical:

$$\begin{aligned} ClO + O_3 &\rightarrow OClO + O_2 \\ OClO + O &\rightarrow ClO + O_2 \end{aligned}$$

The ClO radical may possibly be decomposed during the photodissociation or by the reaction with NO:

$$\begin{aligned} ClO + h\nu &\rightarrow Cl + O \qquad \lambda < 265 \text{ nm} \\ ClO + NO &\rightarrow Cl + NO_2 \end{aligned}$$

Since at these altitudes, OH, $O(^1D)$, H_2 and CH_4 are present, hydrogen chloride may be formed from atomic chlorine:

$$\begin{aligned} Cl + CH_4 &\rightarrow CH_3 + HCl \\ Cl + H_2 &\rightarrow H + HCl \end{aligned}$$

The HCl represents a temporary escape from the cycle since it enters into further reactions with OH or $O(^1D)$ with a regeneration of atomic chlorine.

The simultaneous presence of ClO and NO_2 at these altitudes presents a problem of $ClONO_2$ production, which could affect the amount of ClO and NO_x, reducing their effect on the ozone layer.

The main processes involving the reactions of freons in the stratosphere are shown in Fig. 5.8.

Many models have been elaborated, describing the diffusion and reactions of CF_2Cl_2 and $CFCl_3$ in the stratosphere. Based on these models,

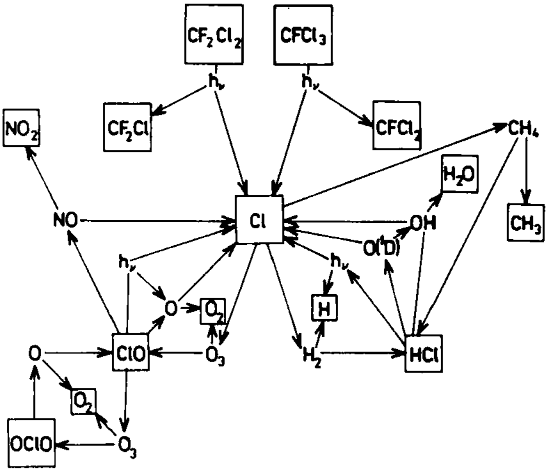


Fig. 5.8. Atmospheric reactions of freons

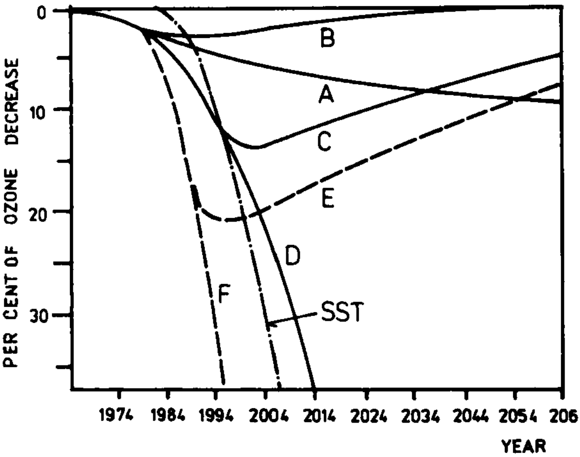


Fig. 5.9. Calculated effect of freons on stratospheric ozone: A — production held constant at level of 1975, B — production ceases in 1978, C — production increases 10% per year, ceases in 1995, D — production increases 10% per year, E — production increases 22% per year, ceases in 1987, F — production increases 22% per year, SST — estimate for upper boundary on NO injection from future supersonic fleets

dependences were established (in 1975) for changes of the amount of ozone with time, for different assumptions about increases of freon emissions; the results are plotted in Fig. 5.9 [52]. Curve A shows a situation, where freons enter into the atmosphere at a constant rate, corresponding to the level of the production in 1975. Curve B was calculated assuming the production to increase at a constant rate up to 1978, when it was supposed to be stopped (which, however, was not the case). Curve D assumes a 10%

growth of the production annually, curve C the same growth with stopping of the production in 1995. For curve F an annual increase in production of 22% was considered and curve E was calculated for a 22% annual increase, interrupting the production in 1987 (this again was not the case). The graph also presents a curve depicting a decrease of the ozone level caused by flights of supersonic aircraft in the stratosphere.

The carbon cycle. The carbon cycle shown in Fig. 5.10 contains the total material balances and the carbon flow in the atmosphere, lithosphere and hydrosphere [11].

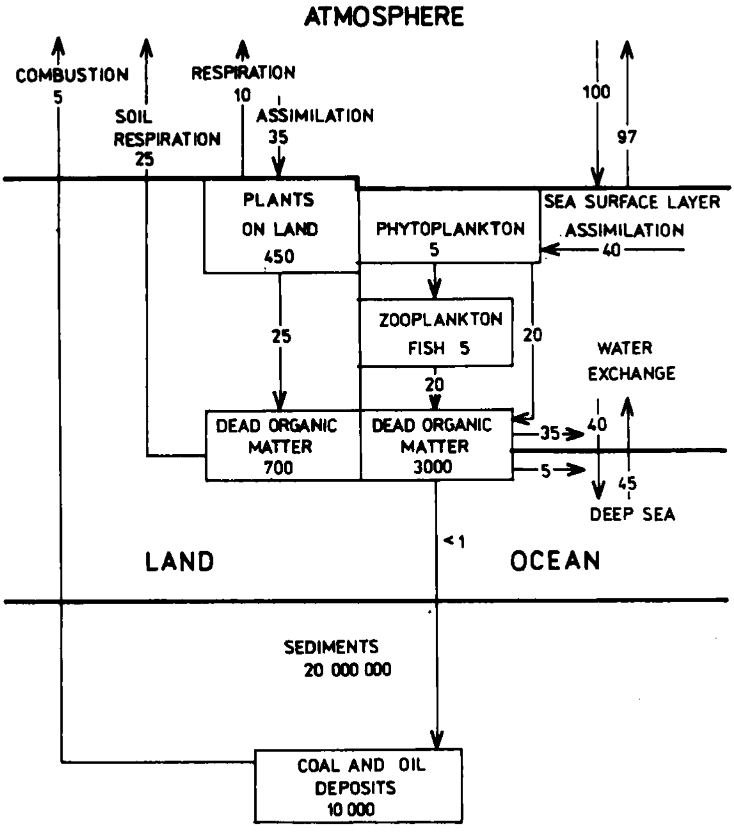


Fig. 5.10. Carbon circulation in the biosphere (kg $\times 10^{12}$ yr^{-1})

The core of the carbon cycle in the nature lies in the conversion of inorganic carbon (CO_2) to biological material and a reverse flow of carbon into the atmosphere after the decomposition of organic compounds to CO_2. The carbon circulation occurs in two independent cycles on the dry land and in the oceans, interconnected dynamically through the atmosphere.

The carbon cycle in seas involves the assimilation of carbon dioxide dissolved in sea water by the phytoplankton with a simultaneous oxygen release. Zooplankton and fish use this oxygen for the respiration. During the organic matter decomposition, CO_2 is supplied into the atmosphere. On land, the exchange of carbon dioxide with the atmosphere is accomplished by respiration, photosynthesis and by the combustion of fossil fuels.

From the total balance of the flows in the atmosphere, it follows that the main contribution to the increasing CO_2 concentration in the air comes from the fossil fuel combustion. At a rate of consumption of 5 milliard t annually, the CO_2 concentration in the atmosphere would increase by 0.7%. The actually measured annual increase is, however, only 1/3 of this value. This means that the remaining 2/3 are rapidly removed from the atmosphere, partly by dissolution in the oceans and partly by consumption for the production of the biomass on the earth's surface. The flow of carbon dioxide is partially maintained in a state of dynamic equilibrium through these autoregulation processes.

5.2.4.4 Halogens and halogen compounds

From the whole range of substances of this group, chlorine, hydrochloric acid, hydrofluoric acid and silicon tetrafluoride are the most important with respect to the amounts released into the atmosphere and to their toxicity. These harmful substances can enter into the atmosphere from natural sources as well as from industrial sources.

Fluorine compounds are emitted into the atmosphere in different states of matter from several industrial processes, from the combustion of coal, and a portion is supplied from natural sources (volcanic activity). In the case of industrial sources, the major contributions come from the production of aluminium, phosphate fertilizers, phosphoric acid, from the silicate industry, steel production and production of compounds containing fluorine. In most cases the emissions contain gaseous HF and SiF_4. For example, during the combustion of coal containing 0.001–0.048% of fluorine, about one half of the fluorine content is released in the form of HF and SiF_4. In the silicate industry, during the production of bricks, ceramics, cement and tiles, clay containing 0.02–0.3% of fluorine is used and by action of the firing or sintering process 30–90% of the original content are released in the form of HF and SiF_4. The petroleum refineries may also contribute to the amounts of gaseous emissions containing fluorine. In the production of petrol with high octane number, HF and BF_3 are used as alkylation catalysts; these are volatile compounds, which can escape into the atmosphere during the transport pumping and manipulation of wastes. Cigarettes are a source of fluorine-containing compounds, which may directly threaten the human health. In 1000 g of tobacco, there are of about 25 mg of fluorine. A consumption of approximately 25 cigarettes daily, results in the inspiration of about 0.4 mg fluorine per day.

The fluorine concentrations in a clean atmosphere are low; in polluted regions, in the vicinity of emissions, for example close to aluminium works, the values are as high as 0.02–0.22 mg m^{-3} [53], and in city areas the values range between 0.2 and 1.9 μg m^{-3} [54].

The spread of emissions of compounds containing fluorine in the atmosphere depends on different factors, such as meteorological conditions, state of the fluorine-containing matter, etc. Many inorganic fluorine compounds in the atmosphere are rapidly hydrolysed and converted to less volatile substances, which are removed from the atmosphere during condensation processes. Hydrogen fluoride in the atmosphere reacts with water vapour, producing an aerosol or droplets, which further react during their contact with solid particles containing e.g. $CaCO_3$ or CaO, producing fluorides. In the reaction of silicon tetrafluoride with water vapour, hexafluorosilicic acid is produced

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

In the course of reactions with hydroxides or carbonates, fluorosilicates are formed, which are mostly readily soluble in water.

Some fluorine compounds enter into the atmosphere in the form of solid particles, such as cryolite, fluoroapatite, aluminium fluoride and sodium fluoride.

Chlorine and chlorine compounds are supplied into the atmosphere from natural as well as from anthropogenic sources. Volcanic gases make a substantial contribution to the gaseous emissions of chlorine — the annual estimate is 7.6×10^6 t yr^{-1} [55, 56]. Chlorine and chlorine compounds of anthropogenic origin are encountered in chlorination and bleaching processes, in water chlorination and in the combustion of plastics based on chlorinated hydrocarbons (see Section 5.2.4.3). Cl_2 and HCl are the most important species in this group. Significant concentrations of these molecules occur in the vicinity of their sources. Their global values are low, in non-polluted atmosphere of the Northern Hemisphere the HCl concentration is 2–8 μg m^{-3} [57].

In the case of bromine compounds, ethylene dibromide is a component of the pollutants in a city atmosphere. It is added to petrol containing tetraethyllead to fulfil a capturing function in the engine cylinder. During the reaction, volatile $PbBr_2$ is produced from $C_2H_2Br_2$, and enters the atmosphere together with exhaust gas. Analyses of the air of certain big cities have demonstrated that the bromine concentration may be 0.12–0.45 $\mu g\ m^{-3}$ [58].

5.2.4.5 Radioactive substances in the atmosphere

Within a wide range of physical, chemical, biological and other processes, radioactive substances are produced, accumulated, transported and continually converted in the atmosphere. The radioactivity of the atmosphere was observed as early as at the beginning of this century. A deeper, systematic study in this direction has been, however, performed on a global scale only in the last twenty years, particularly as regards the quantification of the negative contribution from experimental nuclear explosions to the biosphere. At the present time, attention in the research into atmospheric radioactivity is also focused on the study of characteristics of gaseous emissions from nuclear reactors and from plants for nuclear fuel treatment. The study of radionuclides encountered in the atmosphere is also used advantageously for the study of complex atmospheric transport mechanisms.

The radioactivity of the atmosphere is due particularly to radioactive aerosols and gases; the characteristics of these correspond to those of non-radioactive aerosols and gases. Radioactive substances may form solid or liquid particles either directly or by sorption on the surface of non-radioactive particles. It is possible to tell very simply that aerosols may be affected by the wide range of various characteristics of components of particular particles, whereas the behaviour of gases is given by the simple characteristics of atoms and molecules present in their free state.

The radionuclides encountered in the atmosphere are of either natural or artificial origin — produced by human activity during controlled or uncontrolled nuclear reactions. On the basis of this, the topic may be considered in two parts, concerning *natural* and *artificial* radionuclides.

Natural radionuclides. The natural radionuclides may be divided into three basic groups:

(1) *Radioactive nuclides with half-lives comparable with the age of the Earth.* These are particularly ^{235}U (T = 7.13 × 10^8 years), ^{238}U (T = 4.51 × 10^9 years), ^{40}K (T = 1.27 × 10^9 years), ^{232}Th (T = 1.39 × 10^{10} years), ^{176}Lu (T = 2.1 × 10^{10} years), ^{87}Rb (T = 4.7 × 10^{10} years) and ^{138}La (T = 1.1 × 10^{11} years). Most of these radionuclides are isotopes

of remarkably lithophilic elements. They enter into atmosphere only in negligible amounts from minerals and rocks containing relevant elements.

(2) *Radionuclides* with half-lives much shorter as compared to the earth's age. *These are formed by nuclear transmutations from primary radionuclides*, and are members of three naturally occurring genetic sequences of stepwise nuclear decays, called decay series:

— the uranium series starting from ^{238}U and terminating by stable ^{206}Pb;
— the thorium series starting from ^{232}Th and terminating by stable ^{208}Pb;
— the actino-uranium series starting from ^{235}U and terminating by stable ^{207}Pb.

These include several tens of radionuclides, which may be divided into two groups from the standpoint of the occurrence of radioactive substances in the atmosphere.

(a) The *first subgroup* is given by *members of decay series with proton numbers 92 to 87*, which enter the atmosphere from the earth's surface, as do their sources — uranium and thorium radioisotopes. Coal is an appreciable source of these primary radionuclides and thus also of all the radionuclides of the group described. Depending on its origin, different types of coal contain measurable amounts of ^{226}Ra — 0.04–50 Bq kg^{-1}. The concentration of ^{226}Ra in fly ash may be as high as 40–290 Bq kg^{-1}. Among the radionuclides of the first subgroup, we can consider ^{234}U ($T = 2.5 \times 10^5$ years), ^{234m}Pa ($T = 1.1$ min), ^{234}Pa ($T = 6.6$ days), ^{231}Pa ($T = 3.4 \times 10^3$ years), ^{230}Th ($T = 8 \times 10^4$ years), ^{234}Th ($T = 24.1$ days), ^{228}Th ($T = 1.9$ years), ^{227}Th ($T = 18.2$ days), ^{231}Th ($T = 25.6$ hours), ^{228}Ac ($T = 6.1$ hours), ^{227}Ac ($T = 21.6$ years), ^{226}Ra ($T = 1620$ years), ^{228}Ra ($T = 6.7$ years), ^{224}Ra ($T = 3.6$ days), ^{223}Ra ($T = 11.7$ days), ^{223}Fr ($T = 22$ min).

(b) The *second subgroup* contains the *three radon isotopes* coming from particular decay series and *their products*, i.e. radioisotopes of radon, astatine, polonium, bismuth, lead and thallium. They are supplied to the atmosphere quite readily as gaseous radon, which thus serves as a source of its genetic products directly in the atmosphere. Rocks containing thorium and uranium, certain natural waters and also some types of coal may serve as sources of radon supplied to the atmosphere. The specific activity of gas obtained from coal ranges between 4×10^{-2} and 4×10^{-3} Bq l^{-1}. It is also of interest that a portion of 70 to 80% out of the total amount of radon contained in coal and in gas produced from this coal enters the atmosphere after combustion.

On account of this phenomenon, radioisotopes of this subgroup represent a major portion of the natural radioactivity of the atmosphere, the prevalent components being ^{222}Rn ($T = 3.82$ days) and ^{220}Rn ($T = 55.3$ s). Contributions from ^{119}Rn (T = 3.9 s) and from its decay products are negligible. Further important radionuclides of this subgroup are as follows: ^{218}Po (T = 3 min), ^{210}Po (T = 138 days), ^{241}Bi (T = 19.7 min), ^{210}Bi (T = 5 days), ^{212}Bi (T = 60.5 min), ^{211}Bi (T = 2.2 min), ^{214}Pb (T = 27 min), ^{210}Pb (T = 19.4 years), ^{212}Pb (T = 10.6 hours), ^{211}Pb (T = 36 min), ^{210}Tl (T = 1.3 min), ^{206}Tl (T = 4.2 min), ^{208}Tl (T = 3.1 min), ^{207}Tl (T = 4.8 min).

(3) *Radionuclides produced* directly in the atmosphere *during nuclear reactions of cosmic rays.* This group includes the radionuclides ^{3}H (T = 12.3 years), ^{7}Be (T = 35.5 days), ^{14}C (T = 5570 years), ^{22}Na (T = 2.58 years), ^{32}Si (T = 710 years), ^{32}P (T = 14.3 days), ^{33}P (T = 25 days), ^{35}S (T = 87 days), ^{36}Cl (T = 3.1 x 10^5 years), ^{38}Cl (T = 37.3 min), ^{39}Cl (T = 56.5 min), ^{37}Ar (T = 35 days), ^{39}Ar (T = 265 years), ^{81}Kr (T = 2.1 x 10^5 years), ^{85}Kr (T = 10.65 years).

Under normal conditions, the natural radioactive substances are present in an atomic state in the atmosphere. The natural activity of atmospheric air varies, depending particularly on the content of radioactive substances in the soil and on the intensity of the exchange of substances between the atmosphere and the earth's surface. The process of the release of gases is accelerated in general by an increase of temperature and decrease of the atmospheric pressure. These factors, together with the direction and velocity of the wind, affect the radon concentration in the layer adjacent to the earth's surface and thus also the main source of the natural activity in the atmosphere.

Artificial radionuclides. Artificial radionuclides observed in the atmosphere may be divided into four basic groups as follows:

(1) *Experimental explosions of nuclear bombs* are direct as well as indirect sources of numerous radioisotopes corresponding to many elements. During the fission of ^{235}U with thermal neutrons, about 60 radioisotopes are produced primarily and this number is increased stepwise by radioactive decays to 180 radioisotopes of 35 elements with proton numbers of 30 to 65 and nucleon numbers of 72 to 161. Further radioisotopes are produced indirectly, i.e. by the activation of structural materials of the bomb, and of the the dust and common components of the atmosphere. The intensity of a nuclear explosion has no essential effect on the qualitative problem of the radioactive aerosols formed, however, it contributes significantly to their distribution in the atmosphere. The heat energy released in the explosion of smaller bombs (up to tens kt TNT) is rapidly dispersed and the convective air motion driving radioactive particles is usually arrested prior to a possible transport of the fission products beyond the tropopause. Explo-

sions of larger bombs (0.1 Mt TNT) are, however, accompanied by slower and more powerful release of the thermal energy and as a result of this, most fission products are transported even into the stratosphere. As a result of the distinctively different physical characteristics of the troposphere and stratosphere, the radioactive aerosols exhibit different residence times in these regions. From the troposphere, one half of the radioactive particles is deposited onto the earth's surface within 20 days, whereas the removal of particles from the stratosphere takes several years and thus, the stratosphere is a long-term reservoir, supplying radioactivity to the atmosphere. Based on this, the concept of *tropospheric* and *stratospheric fall-out* were established.

The tropospheric fall-out contains a rich mixture of radionuclides, its essential portion being formed by isotopes with rather short half-lives, such as ^{106}Ru (T = 1.02 years), ^{144}Ce (T = 285 days), ^{95}Zr (T = 65 days), ^{89}Sr (T = 54 days), ^{140}La (T = 40.2 hours), ^{95}Nb (T = 35 days) and ^{140}Ba (T = 12.8 days). The stratospheric fall-out is characterized by a more restricted variety of radionuclides and longer half-lives, such as ^{90}Sr (T = 28 years) and ^{137}Cs (T = 30.4 years). Further important radioisotopes, which belong to fission and activation products of nuclear explosions are the following: ^{85}Kr, ^{55}Fe (T = 10.6 years), ^{60}Co (T = 5.29 years), ^{65}Zn (T = 245 days), ^{3}H and ^{14}C.

(2) *The treatment of nuclear material* is an increasingly important source of the radioactivity in the atmosphere. The radionuclides ^{85}Kr, ^{241}Pu (T = 13.3 years) and ^{241}Am (T = 458 years) belong to basic radionuclides of this group. Of these, particularly ^{85}Kr is a focus of interest, since its concentration in the atmosphere is continually increasing. The reason for this is not only its long half-life, however, but also the fact that it can be removed from the atmosphere only by its spontaneous decay.

(3) *The operation of nuclear power plants* should become, according to reliable forecasts, the most important source of the pollution of environment with radioactive substances in the near future. Besides the above-mentioned radionuclides ^{85}Kr, ^{90}Sr, ^{137}Cs, ^{14}C, ^{3}H, the radioisotopes of iodine ^{129}I ($T = 1.6 \times 10^7$ years) and ^{131}I (T = 8.05 days) are obviously the most important.

(4) *The use of radioisotopes in the national economy* is strictly and efficiently controlled and thus, it makes no important contribution to the atmosphere radioactivity in spite of the great variety of radioactive substances used.

In addition to common aerosols and gases, mentioned at the beginning of this section, radioactive substances in the atmosphere also occur, although very rarely, in a special form — as so-called *hot particles*. These are special aerosols first observed in 1953, with activities as high as 40 Bq. This activity might appear to be negligible, but considering the fact that the mass of these particles ranges between 10^{-15} and 10^{-8} g, it is obvious that the specific activity of hot particles is extraordinarily high. A particle with a mass of 10^{-10} g has a specific activity of about 4×10^{11} Bq g^{-1}. The activity of 40 Bq corresponds to a large number of radioactive atoms, e.g. 8.2×10^6 atoms of ^{140}La, 6.3×10^7 atoms of ^{140}Ba or even 1.7×10^8 atoms of ^{95}Nb. What is the mechanism of the accumulation of this number of radioactive atoms in one particle? In the case of commonly encountered values of the dust nuisance and natural activity, the formation of this particle is impossible, since even at high concentrations of radioactive substances and extremely low dust nuisance, there is only of the order of 1 radioactive atom per 10^6 dust particles in the air. The situation is different during the formation of radioactive aerosols after nuclear explosions, during work with high-activity burnt up nuclear fuel and during any handling involving radioactive materials.

The mechanism of the formation of hot particles, and their physical and chemical characteristics, are still not exactly known. Different authors report their sizes to be in the range 10^{-7} to 10^{-5} m, with specific masses of 2000 to 3000 kg m^{-3}. The hot particles are very variable as regards their shape and colour. The connection between their origin and nuclear explosions is also emphasized by the fact that particles occurring as a result of underground explosions have a spherical shape and smooth surface, while those observed after atmospheric explosions, are characterized by an irregular shape and rough surface. Different colours of hot particles are connected with their chemical composition. Iron, aluminium, calcium and silicon are predominant in the particles, however isotopes of uranium, plutonium, neptunium, titanium, manganese and many other elements are also important components.

The tiny concentration of hot particles in the atmosphere as well as the obvious connection between their occurrence and experimental nuclear explosions indicate their minor importance from the standpoint of research into the chemistry of the air; their study is, however, very important from the standpoint of the radiobiology. The reason for this lies in their extraordinarily high specific activity, which presents a potential possibility of the initiation of malignant changes in organs encountered after particle penetration into the organism.

5.2.4.6 Primary and secondary particles in the air

Liquid and solid particles enter the air predominantly from natural sources; only 11% comes from human activity. From these particles, so-called *secondary particles* are formed directly in the atmosphere, either during a change in the state of matter or in interactions of emissions connected with a formation of liquid and solid products.

The scale of natural sources of particles is very wide. They enter into the air during volcanic activity, via wind transport from the earth's surface, during forest fires, by sea water spray, and they can also arrive from the interplanetary space in the form of meteorites. The group of particles of the natural origin also includes microorganisms, spores and pollen.

Table 5.18. Global emissions of particles from natural and anthropogenic sources [59]

Source	Percentage of total amount	Production (t 10^6 yr^{-1})
Natural sources		
Salt from sea spray	44	908
Nitrates from NO and NO_2	18	390
Ammonia	11	245
Sulphates from H_2S	9	182
Terpenes	9	182
Dust particles from the earth's surface — transported by wind	9	182
Volcanic activity		4
Forest fires		3
Natural activity total	100	2096
Anthropogenic sources		
Particles directly from sources		84
Secondary particles formed from gaseous pollutants		
Sulphates from SO_2		133
Nitrates from NO_x		27
Substances formed by photochemical reactions from hydrocarbons		25
Human activity total		269

Among the various anthropogenic sources, the transport and domestic sources are most important, energy production and industry being second to them as regards contributions to emissions of particles. Relative contributions vary considerably depending on the locality (industrial centres, large urban areas, etc.). In cities, the first two sources may yield more than 60% of all the emissions of particles; on the other hand, in large industrial regions, as much as 25% may be attributed to production processes and about the same portion to the industrial fuel combustion. Global sources, together with an estimate of particles annually polluting the atmosphere, are summarized in Table 5.18 [59].

The chemical compositions of particles may be very different, depending on their origin. Of the natural particles, sulphates, nitrates, different silicates, carbonates, chlorides, fluorides and also particles of metals and metal oxides, hydrocarbons, and bacteria, moulds and pollen are most frequently represented. Particles from anthropogenic sources are soot, fly ash, and in cities with a dense traffic hydrocarbons, lead compounds and metal oxides. Large amount of particles from human activity is formed in the atmosphere as a result of the interactions of primary polluting components.

The size of atmospheric particles ranges from molecular dimensions up to a diameter of above 10 μm. Since particles with diameters below 0.1 μm (molecules and Aitken's nuclei) present no important problem and particles with diameters exceeding 10 μm are simply removed from the atmosphere by gravitational sedimentation, particles with diameters between 0.1 and 10 μm are the main focus of interest. They can affect the reflection and scattering of the incident solar light, the local cloudiness and precipitation.

The concentrations of particles in the air may be very different depending on conditions. Pure air contains particles to the extent of about 300 particles cm^{-3} (very small particles below 0.02 μm in diameter). In very polluted air, the content of particles may be as high as 10^4 to 10^5 particles cm^{-3}. Imission values of the concentration are about 10 μg cm^{-3}. In a city atmosphere, there is a typical concetration of particles of 60 to 220 μg cm^{-3} and in very polluted air it may be as high as 2000 μg cm^{-3}. The diurnal maximum is achieved at the morning traffic peak. The highest annual values of the concentration may be observed in the middle of the winter due to the greatest consumption of coal and heating oil. The monthly fall-out of particles with diameters exceeding 10 μm is 0.35–3.5 μg cm^{-2}, in the vicinity of sources it may be as high as 70 μg cm^{-2}.

The particles become dispersed in the atmosphere and they may form different aerodispersion systems. Depending on the state of matter of particles, a smoke or fog may be formed. Aerosols are systems in which the particle diameter is below 2 μm.

A fog is formed when the atmosphere becomes supersaturated with water vapour (usually during a temperature decrease). It contains particles with diameters between 7 and 15 μm, with a density of 50 to 100 particles per cm^3 for light fog and 500 to 600 particles per cm^3 for dense fog. The fog formation may be affected to a considerable extent by solid particles present in the polluted atmosphere. These form condensation nuclei, which facilitate the condensation of the water vapour. Particles with diameters below 1 μm may act as centres during the formation of droplets in clouds. The droplets produced start to sediment by the action of the gravitational force, they coagulate to form larger particles, which strike the earth's surface as rain drops. The presence of particles of the mentioned diameter in the atmosphere of industrial centres and large cities is one of reasons for increased cloudiness and precipitation in these regions.

Particles present in a polluted atmosphere exert further effects on climatic conditions. If their diameter is comparable with the wavelengths of the solar light, they are able to scatter the radiation. Larger particles partially absorb and partially reflect the light. As a result of these phenomena, the mean annual intensity of solar radiation above polluted areas may be reduced by 15%.

The effects of particles polluting the air can also be adversely manifested in other directions. Some of them may lead to the corrosion of metals, and many particles serve as a reservoir of adsorbed gases such as SO_2, H_2S, H_2SO_3 and H_2SO_4. Irreparable damage may result from the deposition of such aggressive particles on surfaces of paintings, sculptures and other works of art, and on ancient buildings.

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5.3 The formation of pollutants in industry and transportation

The overall problem of air pollution is very closely related to the development of industry and transportation, which make the major contributions to air pollution.

5.3.1 Air pollution due to emissions from industrial sources

5.3.1.1 Power production

Worldwide, a portion of about 75% of energy is obtained by burning fossil fuels.

In the direct combustion of fossil fuels (coal, petroleum and natural gas), very large amounts of gaseous emissions are formed, polluting the environment. The amount of these emissions depends on the type of the fuel used, on its composition and on provisions adopted with aim of minimizing their amounts.

In complete combustion, carbon is oxidized to carbon dioxide. During incomplete combustion, carbon monoxide is produced with accompanying energy losses. Carbon dioxide formed during the initial complete combustion, flows through layers of hot coal to be reduced to carbon monoxide. Independently of this process, at high temperatures, carbon dioxide is dissociated to carbon monoxide and oxygen ($2CO_2 \rightarrow 2CO + O_2$). Under normal combustion conditions, 98% of carbon present in the fuel is oxidized to carbon dioxide.

During fossil fuel combustion, sulphur is oxidized to sulphur dioxide, however, a small amount of sulphur trioxide is also formed. Sulphur trioxide is formed in combustion products by the dissociation of sulphate, by the reaction of sulphur dioxide with oxygen in the flame and by a heterogeneous catalytic oxidation of sulphur dioxide. The content of sulphur dioxide in combustion products is, at most, 5 to 10 vol.% out of the total amount of sulphur compounds. A portion of sulphur (of about 5%) is retained in the ash in the form of sulphates.

The production of nitrogen oxides in the course of combustion is a complex process, depending on the combustion temperature, design of the combustion chamber and the availability of excess air for the combustion. During the combustion, nitrogen oxides are formed from nitrogen contained in the fuel as well as from the atmospheric nitrogen. Nitrogen oxide is predominantly formed, starting at temperatures of about 100°C and achieving a maximum at about 2700°C. The NO_x formation can be controlled to a certain extent by regulating the amount of the air for the combustion, or by adjustments to the combustion chamber.

Lignite from certain localities has enhanced contents of arsenic, which is partially retained in the ash and partially emitted into the atmosphere. Some types of coal contain low amounts of fluorides and thus, the combustion of large amounts of these coals may serve as a source of the emission of fluorine compounds [1–3].

Table 5.19. Gaseous exhalates from power plants based on fossil fuels [4]

Pollutant	Power plant		
	coal	heating oil	natural gas
SO_2 emission without desulphurization (t yr^{-1})	120 000	38 600	20
SO_2 emission when using desulphurization equipments (t yr^{-1})	24 000	21 000	0
NO_x emission without purification equipments (t yr^{-1})	27 000	26 000	13 400
Solid particle emission (without separating devices) (t yr^{-1})	270 000	26 000	518
Solid particle emission with separating devices (t yr^{-1})	2 000	150	4
Emission of radioactive substances (MBq yr^{-1})	740	18.5	Negligible
Waste heat released into the atmosphere (mld kWh yr^{-1})	1.64	1.71	2.2

Table 5.19 presents data concerning emissions of gaseous pollutants during the production of the electric energy in power plants burning fossil fuel

(power output of 100 MW_e, efficiency 75%, electric energy production 6.57 milliard kWh [4]).

Power plants which burn coal release larger amounts of SO_2, NO_x and soil particles per unit of energy as compared to power plants using other fossil fuels. Power plants burning natural gas are characterized by low initial costs and a minimal impact on the environment. Power plants which burn heating oils occupy a position between the above-mentioned two types as regards their ecological effects.

The emission of sulphur oxides may be controlled by adding substances into the combustion chamber, which are able to bind sulphur dioxide (additive method). Finely group limestone, calcium hydroxide, calcium oxide or sometimes dolomite may be used for this purpose. Limestone is calcinated at high temperature, yielding calcium oxide, which binds the sulphur dioxide. Sulphate, sulphite, non-reacted adsorbent and fly ash are separated in a separating system. The disadvantage of this process is its low efficiency (only about 20 to 40% SO_2 are retained).

From the standpoint of improving the efficiency of the combustion and reducing the amounts of emissions it is advantageous to burn the coal or liquid fuel in a fluid layer, which is formed by solid particles of the heat carrier (e.g., ash, sand or other inert materials). The basic factor of the combustion in a fluid layer is the intensification of all the physico-chemical processes, occurring in particular stages of the combustion. Solid fuel particles are very rapidly dried, gasified and heated to the fluid layer temperature. During the combustion of liquid fuel, the fuel injected is rapidly degraded thermally with a possible evaporation of its lighter fractions. By the action of the turbulent flow of the fluidizing medium and the combustion air, an intense reaction of oxygen with fuel occurs. The heat released during the combustion in the fluid layer depends on the pressure; the amount of the heat released increases with increasing pressure. In this method of the combustion, the amount of soot formed is negligible, since larger particles are burnt as compared to the situation in powderized-fuel-fired boilers. The separation of residual larger inorganic particles from the stream of the combustion products, their transportation, storage or possible use are more favourable.

The parameters of the fluid combustion are very advantageous for the trapping of sulphur in the combustion process. Instead of the inert carrier of the heat in the fuel fluid layer, it is possible to use substances which bind sulphur oxides, such as ground limestone or dolomite. Thus, this is essentially a variant of the additive method, however, the conditions are essentially better [3, 5, 6].

The following processes may be employed for the separation of sulphur oxides from the combustion products.

- adsorption processes, where sulphur dioxide is bound to solid adsorbents (such as $CaCO_3$, charcoal, coke),
- absorption processes, where sulphur oxides are absorbed in an aqueous solution (e.g. Na_2CO_3) or a suspension of a appropriate substance (e.g. an aqueous suspension of ground calcium carbonate or magnesium oxide),
- catalytic processes, where SO_2 is first oxidized catalytically to SO_3, which is subsequently separated by different methods, and lastly
- combined processes, which may employ several principles [7–9].

The problems of separating nitrogen oxides are not as important as those concerned with separating sulphur oxides. In small combustion units, the NO_x emission is low and in large facilities, SO_2 emissions are predominant with respect to their amounts and detrimental effects.

The emissions of nitrogen oxides may be restricted by controlling the combustion process as follows: by using as low an excess of air as possible, by maintaining a proper ratio of the primary and secondary air for the combustion, by reducing the formation of deposits on the walls of the fire chamber; and in fire chambers which burn gas or heating oil, also by the recirculation of combustion products. Apart from this, when separating sulphur oxides by an absorption method, then a portion of about 20 to 40% of nitrogen oxides is also retained [6].

From the standpoint of environmental protection, the gasification and liquefaction are good approaches to the utilization of coal (particularly lignite) and materials containing carbon. During coal gasification, the main purpose is to obtain high-heating-value and low-heating-value gases. The low-heating-value gas may be employed as raw material or as a fuel for producing electric energy in combined steam cycles. The high-heating-value gas can be used instead of natural gas and it is finding wide applications as a fuel and raw material for industry. The advantage of the liquefaction is that by using different catalysts and under suitable operating conditions it is possible to obtain from coal different products, such as heating oils, petrol, aircraft fuel and diesel fuel, etc. The aim of the procedure is to obtain products with low contents of sulphur and ash, which may be easily stored, transported and burnt as liquids. Table 5.20 gives estimates of gaseous wastes during the gasification and liquefaction of coal (calculated according to EPA data for an energy production of 1000 $MW_e\ yr^{-1}$).

Nuclear fuel, comparing equal weights, has an energy content several orders of magnitude higher than fossil fuels. The potential energy of 1 kg

Table 5.20. An estimate of gaseous wastes during the gasification and liquefying of coal (t yr^{-1})

Gaseous wastes	Coal gasification		Coal liquefaction
	Gas of a low heating capacity	Gas of a high heating capacity	
Solid particles	0.75	820	529
SO_x	1 960	9 061	1 706
NO_x	928	6 771	7 409
CO	28	356	291
Hydrocarbons	28	108	2 268
NH_3	40	49	—

of uranium corresponds to that of 3 million kg of coal with a heating value of 29.3 MJ kg^{-1}. Even in the case of a low utilization of the uranium energy in the current reactor types (1–2%) 1 kg of uranium is equivalent to 20,000 kg of coal, however, in fast breeder reactors 1 kg of uranium corresponds to 1.9 million kg of coal. The high energy content of the nuclear fuel essentially decreases the required volume of mining and the transport, which cause considerable problems in the case of coal and petroleum, with a marked impact on the environment.

As compared to power plants based on fossil fuel, in nuclear power plants, the amount of harmful emissions is very low, producing no CO_2, SO_2, NO_2, CO or fly ash. The amounts of radioactive substances released into the atmosphere by nuclear power plants are also less than those emitted by plants operating with fossil fuel. Surprisingly the local low exposure of the environment surrounding the power plant to radioactivity may be higher by a factor of 400 in the case of power plants burning coal than that in the case of nuclear power plants, since coal contains natural radioactive elements.

The total costs for the electric energy production in nuclear power plants are lower than those in power plants burning fossil fuels. The cost of the fuel represents only 33% in the case of nuclear power plants, 80% in the case of power plants burning fossil fuels [3].

Nuclear power engineering is the main source of gaseous radioactive wastes. They are released from fuel assemblies, which have become non-gas-tight during the operation, and further from a residual contamination of the surface of fuel elements resulting from the production and from the activation of the primary coolant and its admixtures. The contributions from these sources are remarkably variable, depending on the type of the reactor, energy power output of the reactor core, its operating regime and other factors [10].

Depending on the physico-chemical composition, the gaseous radioactive products released may be divided into four groups as follows:

(1) Radioactive rare gases of fission (Xe, Kr) and activation (Ar) origin, which are dangerous to the human organism as sources of external beta and gamma irradiation. The data available, however, have demonstrated that even at a maximal value of annual emissions of radioactive rare gases, the individual and collective dose from the exposure of inhabitants living close to nuclear power plants does not exceed 1% of the natural radiation background.

(2) Radioactive isotopes of iodine (^{129}I, ^{131}I, ^{132}I, ^{133}I, ^{134}I, ^{135}I) are volatile components at the operating temperatures of the nuclear fuel. They are dangerous to the human organism on account of their concentration in the thyroid gland after being ingested with air or milk.

(3) Radionuclides with long half-lives (^{3}H, ^{14}C), which are incorporated into important structures in the organism, particularly into the genetic material of cells.

(4) Radioactive aerosols (particularly aerosols of fission products) which fall out from smoke containing radioactive gaseous products and enter nutritional chains.

Nuclear power plant facilities should be equipped with suitable devices for removing radioactivity from the air. The radioactive emissions should be released via a special, sufficiently high chimney, which could provide an efficient dispersion of radioactive substance in the atmosphere [11, 12].

5.3.1.2 Metallurgy

In metallurgy, metals and their alloys, different metallurgical by-products and final products are produced. The industry is divided into two parts, the metallurgy of ferrous and non-ferrous metals. The metals are extracted from their ores by hot processes (pyrometallurgy), wet processes (hydrometallurgy) and by the use of electric current (electrometallurgy). All the processes for obtaining raw iron and steel are of the pyrometallurgical type. Non-ferrous metals are produced by all three of the above-mentioned processes.

Metallurgical plant assemblies are among the most serious industrial sources polluting the atmosphere, particularly from the standpoint of solid emissions. The main metallurgical processes and plant producing dust particles are as follows: the production of raw iron (blast furnaces and associated units), production of steel (oxygen converters and double hearth furnaces) coking plants, foundries, cupola furnaces, plants for the production of iron alloys and auxiliary plants. Harmful gaseous emissions are produced on the one hand during combustion processes and, on the other, in the course of industrial processes. In the majority of processes, the most important harmful substance is sulphur dioxide produced during the combustion of sulphur contained in raw materials and fuel. Blast furnaces and other auxiliary plants involved in ferrous metal metallurgy have also been the most serious polluting agents in the past. With the modernization of iron production, the problems of the pollution become increasingly complicated, since at particular stages of the production, further specific sources of the pollution are encountered.

During the ore treatment, particularly in the course of its drying, storing and handling, a considerable dust nuisance occurs as a result of raw material transport by the wind. During the agglomeration and grading, dust is formed, containing particularly Fe, oxides of Fe, Si, Ca, Al and Mg; CO and SO_2 are the most important of the toxic gases.

Gas leaving the blast furnace is purified and burnt. In spite of this, a certain fraction escapes, entraining fine particles of different metal oxides. When oxygen is being used in the melting process, characteristic red smoke escapes from the furnace, containing very fine dispersions of iron oxides. The escape of the dust from the blast furnace depends on the efficiency of the gas purification, on the technical conditions and the extent of sealing of the furnace. Under unfavourable conditions (using poor ore and during a high-intensity operation of the furnace) the dust escape may be as high as 200 kg per ton of raw iron produced.

The amount of SO_2 produced in the blast furnace operation depends on the sulphur content in the treated raw material and in the fuel. The emissions escape into the air, particularly due to the furnace not being gas-tight. The blast furnace is also a source of other gaseous pollutants, particularly nitrogen oxides and hydrocarbons.

During steel production in Siemens-Martin furnaces, dust is released from the furnaces, containing especially iron oxides and many other compounds of Si, Mn, P, Al, Ca, Mg, Sn, and other elements. When using oxygen, a large amount of SO_2 is released, its content in reaction products during the steel production being dependent on the sulphur content in the fuel oil or coke. The dust nuisance is essentially lower as compared to the blast furnace process. The dust is very fine and thus, high-performance separators are required for its removal.

The converter procedure for the steel production with the use of oxygen reduces the time of the melting process to as little as 20 min, however, it also results in an increased escape of dust and harmful gases. As regards the chemical composition of the dust produced during the converter method of steel production, particularly iron and iron oxide dust and oxides of Si, Mn, Ca, Al are present. Among the gaseous components, especially CO and CO_2 are released from oxygen converters.

Combustion products from ferro-alloy furnaces contain extremely fine dust, formed particularly by Fe, Si, Al, Mg, and gaseous harmful substances SO_2, CO and sometimes also H_2S and other gases.

During the production of cast iron in foundries, solid emissions are produced in some quantity. Dust particles (generally SiO_2 and Fe and Ca oxides) are mainly macroscopic and they can be efficiently separated in cyclones. The SO_2 emission depends on the sulphur content in the coke and it does not represent a serious danger.

In electrolytic aluminium production (involving the electrolysis of aluminium oxide to aluminium) gases containing fluorine are formed during the melting process at temperatures of about 950°C. They are present in anodic gases, which are produced at the anode/electrolyte interface. Besides fluorine compounds, the anodic gases contain carbon monoxide and carbon dioxide, tar and other electrolyte components. A total of 17 kg of fluorine compounds per 1·t of aluminium produced is released in the electrolysis. The amount of fluorine compounds emitted into the atmosphere depends on the type of the electrolyser used and on the type of anodes. With the present technical possibilities, the amount of fluorine compounds released can be reduced to 1 to 2 kg per 1 t of aluminium produced, which is only 1/10 as compared to production units with no provisions for reducing the emissions.

In the production of lead, this element enters into the atmosphere from the metallurgical plant in the form of particles of sizes between 0.001 and 100 μm. The particles present in the smoke are of sizes between 0.01 and 2 μm. Besides the air, they also pollute the soil and water, since larger particles sediment on areas adjacent to the works. The production of lead-containing alloys contributes about 2% to the total air pollution with lead.

During the pyrometallurgical production of copper, zinc, antimony, etc. by calcination, gases are produced, containing particularly sulphur oxides. The gases entrain harmful oxides of volatile metals (As_2O_3, Sb_2O_3, PbO, $PbSO_4$, ZnO, etc.) in the form of a pale smoke. After reduction calcination the gases contain carbon monoxide, which is poisonous. The reduction gases also give rise to an explosion hazard.

Table 5.21. Average amounts of exhalates formed in coke production (per 1 t of coal treated)

Emissions	Amount (kg)
SO_2	1.40
CO	0.86
H_2S	0.2
NO_2	0.7
Tar	1.0
Aromates	0.43
Solids	0.91

Coking plants, which are an important part of a metallurgical complex, are also an important source of air pollution. There is the problem of a considerable dust nuisance during unloading and grinding of coal, in filling the chambers and furnaces with coal, during the removal of coke from furnaces and its quenching with water. The coke treatment during grading and grinding processes is a further source of dust pollutants. Gaseous emissions from coke production contain many toxic components such as H_2S, HCN, SO_2, CO, aromatic, polyaromatic and aliphatic hydrocarbons and their derivatives, which exert detrimental effects on the health of workers in coke plants and of inhabitants in the vicinity of the plants. Table 5.21 presents average amounts of exhalates per 1 t of coal treated. During the use of phenol water for quenching, one can assume the formation of about 0.8 kg of phenol, 0.4 kg of ammonia and 2 kg of hydrogen sulphide per 1 t of coal [3, 6, 12–17].

5.3.1.3 The silicate industry, building industry and the production of building materials

The silicate industry, building industry and production of building materials are important sources of solid pollutants. Their contributions to gaseous pollutants are, however, fairly low.

As a source of the dust, it is necessary to consider all the various loose building materials (sand, gravel, cement, lime, bricks, etc.). When handling dry material, the dust nuisance is much greater than when handling moist material. Boiler houses and plants for producing bituminous mixture are source of gaseous emissions.

The most important source of the dust and gaseous emissions comes from the actual production of building materials, which includes the following steps: mining of raw materials → transportation → grinding → drying → calcination → addition of admixtures → mixing → storing of final products → packing and expedition.

Particular attention should be paid to cement works as regards air pollution. The main technology operations involved in cement production are as follows: drying of raw material (when performed in special furnaces), drying of the furnace product, sintering of raw materials and cooling of the sintered material. Cement works give rise to detrimental effects on the environment of the works as well as on the works area itself, particularly with respect to a high dust nuisance. In cement works, the sources of the dust nuisance are as follows:

(1) *Technological equipment* emitting into the environment large amounts of dust: rotary and shaft furnaces, polluting the air over a large area around the cement works; and milling plants for raw materials, cooling equipment for sintered material, milling devices for cement, etc., which pollute the atmosphere in the near vicinity of the cement works. These dust sources may be isolated from the surrounding atmosphere only by a perfect sealing of the whole process.

(2) *Local sources of the dust* unfavourably affect particularly the working environment in the plant itself (storage of dry materials, handling, transportation, bins for these materials).

The dust from the furnaces is mainly formed by the cement raw material, particularly limestone. The weight concentration of the dust per volume of combustion products is typically 2–7 g m^{-3} in the case of shaft furnaces, 3–75 g m^{-3} in the case of rotary furnaces using the wet production process, and 10–100 g m^{-3} in the case of rotary furnaces using the dry method with a stream preheater.

Gaseous exhalates SO_2, SO_3, CO_2, CO and H_2S can be formed during the cement production. The sulphur dioxide concentration is typically about 0.2 g m^{-3}, the concentration of carbon monoxide in the case of shaft furnaces is 0.6–3.5 vol.%. Sulphur oxides (produced from sulphur present in the fuel and raw material) are neutralized to a considerable extent by calcium carbonate and alkalies in the production process itself and thus, they bring no greater problems. Rotary and shaft furnaces are sources of nitrogen oxides, since temperatures in these units are appropriate for nitrogen oxide formation. It is important to monitor the content of carbon monoxide in the furnace aggregate continuously, since under certain unfavourable conditions an explosive mixture of hydrocarbons and CO may be produced, which may result in explosions and damage to electrostatic separators and other devices.

Heating of raw magnesite is the main technological operation in the production of magnesite products. Sintering furnaces are the chief sources of harmful substances, where the combustion products are in the form of a dispersion of solids in a gaseous phase containing nitrogen oxides. The secondary processes leading to the formation of harmful substances are as follows: drying of raw material, transportation, and grinding, all of which lead to dust production. The problems of air pollution from magnesite production are similar to those of cement production, however, the extent of emissions (particularly MgO) is essentially higher.

During the production of a bituminous mixture (for road surfacing) gaseous as well as solid emissions are emitted. The gaseous emissions are formed on the one hand from the combustion process (SO_2, NO_x) and, on the other hand, from heating and evaporating the binder (hydrocarbons). Among the gaseous emissions, SO_2 may be partially trapped or its emission may be reduced by using fuels with low contents of sulphur. Solid emissions are formed by soot from the combustion of oil for the drying cylinder and for heating tanks for binder, and there is also dust, which is produced mainly in the drying cylinder. Further sources of the gas nuisance come from operations involving raw material, from unloading up to the charging of the drying cylinder, transportation routes from the cylinder to the mixer, screening, and the eventual transport of the bituminous mixture obtained. The problem of the soot emission may be solved by adhering to a correct combustion regime with the use of a suitable fuel. The limitation of dust emissions is particularly dependent on the number and technological sophistication of separating units used.

Drying furnaces are the main sources of solid (dust) emissions from the production of expanded perlite. The secondary technology operations of the production, accompanied by the formation of harmful emissions are as follows: mechanical treatment of the raw perlite and its transportation.

Fluorine admixtures used in the production of certain types of glasses cause the occurrence of hydrogen fluoride emissions. Hydrogen fluoride is also released during polishing or etching of glass. In glass works, emissions of nitrogen oxides are also formed, particularly in glass furnaces operating at high temperatures. During the production of lead-containing glass, lead also enters the atmosphere, resulting in significant pollution, particularly of the working environment. Plants for brick production, and brick raw materials containing higher amounts of fluorides and low amounts of alkaline components, can be sources of low amounts of hydrogen fluoride or silicon tetrafluoride.

5.3.1.4 The chemical industry

Measured by the amounts of emissions polluting the air, the chemical industry occupies the third position after energy production and transportation, however, it is at the top of the list as regards the toxicity and mutagenicity of exhalates.

For the industrial wastes polluting the air it is possible to consider emissions from chemical plants or from joint ventilation systems. They may be divided into two basic groups as follows:

(a) emissions containing toxic components in the form of gases and vapours,

(b) emissions containing toxic components in the form of solid or dust particles.

Special attention is paid to gaseous emissions from chemical plants particularly for the following reasons:

- they contain predominantly irritating or toxic substances,
- they may contain high concentrations of polluting substances formed in accident situations, as well as during normal operations,
- they can enormously deteriorate the environment by their smell.

Oxides of sulphur and nitrogen, hydrogen sulphide, chloride, hydrogen chlorine, fluorine and hydrogen fluoride are the most serious gaseous emissions (as regards their amounts and detrimental effects). Harmful organic substances are represented by hydrocarbons, halogenated hydrocarbons, thiols, aldehydes, ketones and acids.

The second group (b) is of lower importance from the standpoint of the amounts and toxicity. Solid particles are emitted particularly during the production of mineral fertilizers, calcium carbide, soda, pigments and in other processes involving the handling and transport of loose substances [18, 19].

In view of the very wide variety of chemical plants and thus also emissions produced, it is useful to divide the pollution sources according to the types of the production in order to facilitate their inspection, control and recording. According to the register of emissions and sources of the air pollution (REZZO), in the Czechoslovak chemical industry more than 20 groups and types of plants are recorded as producing the emissions, as presented in Table 5.22 [6].

In the production of inorganic compounds, the atmosphere is predominantly polluted by plants for the production of acids (H_2SO_4, HNO_3, HCl, HF, H_3PO_4), fertilizers, halogens and their derivatives. Serious ecological problems may be encountered in processes for sulphuric acid production.

Table 5.22. Classification of chemical industry plants for recording emissions and source of air pollution

Groups and types of productions	REZZO code
Production of chlorine and hydrogen chloride	38
Production of bromine	39
Production of hydrogen fluoride, fluorine and fluorine compounds	40
Production of sulphur, sulphur dioxide and sulphuric acid	41
Production of sulphur compounds	42
Production of fertilizers	43
Production of calcium carbide and phosphorus	44
Production of ammonia	45
Production of nitric acid	46
Production of electrographite	47
Production of soda and alkali	48
Production of pigments	49
Production of rubber	50
Production of synthetic materials (plastics, synthetic fibres)	51
Production of soot	52
Production of viscose and cellulose	53
Production of film raw materials and foils	54
Production of pharmaceuticals	55
Production of lacquers, enamels and varnishes	56
Production of synthetic leathers	57
Production of glue and gelatine	58
Production of soap and detergents	59
Petroleum refining plants and production of oils	60

Even when adhering to technological parameters, certain amounts of sulphur dioxide, unreacted in the oxidation step (as much as 0.3 to 0.4% by volume in the final gases) may be released into the atmosphere. The final gases also contain sulphur trioxide and sulphuric acid aerosol, particularly in the case of inefficient operation of absorption and drying equipment.

Plants for the production of nitric acid are serious sources of atmospheric pollution in spite of many improvements and the development of numerous combined procedures. As much as 0.30% by volume of oxides of nitrogen may occur in the final gases, even in the case of properly operating absorbers; even higher concentrations are sometimes encountered. Nitrogen oxides can also enter into the atmosphere during nitration processes.

Plants for superphosphate production represent the main sources of fluorine emissions. The inital raw materials (natural phosphates) always contain small concentrations of fluorine compounds (e.g. CaF_2) and in the process of the decomposition with sulphuric acid, hydrogen fluoride is released which reacts with silicates present. In this reaction system, extraordinarily aggressive hydrogen fluoride enters the environment besides silicon dioxide and fluorosilic acid. Hydrogen fluoride is similarly released from fluorides contained in raw materials for phosphoric acid production by the wet process. Hydrogen fluoride also enters the atmosphere in the production of this substance from imperfectly operating absorption systems. Fluorine emissions are also formed in plants for the production of combined fertilizers and technical fluorides.

The electrolytic production of chlorine and the production of hydrochloric acid are the main sources of chlorine and hydrogen chloride emissions. Modern processes are safe during normal operation, larger emissions being present particularly when starting the process or, of course, in the case of accidents. Many processes for the production of chlorinated hydrocarbons in liquid or gaseous phases also present no serious danger for the atmosphere during normal operation.

The petroleum and natural gas industries are the most important sources as regards air pollution by organic substances. In spite of the fact that alternative sources are increasingly being used, the exploitation of petroleum and natural gas is growing on account of the increasing demands of the petrochemical industry. The improvements in the production of primary petrochemical substances (hydrocarbons, synthesis gases) allows an ever more rapid development of the production of plastics, synthetic fibres, surface active compounds, paints, plant protection agents, dyes, pharmaceuticals, explosives and other products involving organic synthesis; all this, however, generates ecological problems.

Hydrocarbons (particularly aromates and polycyclic hydrocarbons, but also *n*-alkanes, isoalkanes, cycloalkanes as well as unsaturated hydrocarbons), which enter the atmosphere in the course of petroleum and natural gas exploitation, during their treatment, transportation, storing and utilization of products, are important sources of air pollution. In the developed industrial countries the portion of hydrocarbon emissions constitutes as much as 9% of the total amount of emissions [20]. Table 5.23 presents data concerning emissions of hydrocarbons from a hypothetical refining plant with a treatment capacity of 5 million t yr^{-1}, related only to storage and transport of petroleum and by-products in the refining plant [21].

Emissions of sulphur oxides, particularly SO_2, present a serious problem in the industry of the petroleum and natural gas treatment. The SO_2 concentrations in the atmosphere depend on the sulphur content in the raw

Table 5.23. Hydrocarbons emissions from a hypothetical refinery

	Uncontrolled hydrocarbon emission		
	Annual throughput $(m^3\ yr^{-1})$	Vol.% on throughput[a]	$(t\ yr^{-1})$[b]
Ballasting crude tankers			1500[c]
Tankage			
Crude oil (EFR)[e]	5 170 000		88
Condensate (EFR)	360 000		20
Residue (fixed roof)	255 000		11
Blend stocks (EFR)	1 715 000		41
Intermediates (fixed roof)			10
Naphtha (EFR)	465 000		4
Gasoline (EFR)	1 740 000	0.003	35
Naphtha loading			
Rail	46 000	0.020	6
Ship/barge	186 000	0.017	22
Gasoline dispatch			
Pipeline	500 000	—	—
Truck loading	520 000	0.055	172
Rail loading	160 000	0.061	59
Ship loading	400 000	0.034	82
Barge loading	160 000	0.052	50
Wastewater treatment			200
Fugitive losses			1250[d]
Total			3540

[a] Losses from tanks depend on perimeter, vapour pressure, wind velocity and throughput.

[b] Density of vapour emissions is 600 kg m^{-3}.

[c] From 75% of crude tankers not at present equipped with segregated ballast tanks. Assumes crude oil washing of tanks prior to loading ballast and 30% ballast.

[d] Assumes fugitive emissions 0.025 wt% on refinery intake.

[e] EFR — external floating roof.

material treated, on the type of the fuel used in the refining plant and on the efficiency of desulphurizing processes.

Durinig the last few decades, by introducing new technologies of desulphurization and by adhering to relevant regulations, the content of sulphur in heating media has decreased by 62%, the sulphur emissions in petroleum refining plants were reduced by 40% and, in 1985 for example, in western Europe they represented only 6.5% of the total estimate of emissions [22].

Table 5.24 presents potential sources of emissions during refining and petrochemical processes involved in crude petroleum treatment and Table 5.25 shows an estimate of gaseous wastes from petroleum refining plants with a capacity of 2.5×10^7 t of raw petroleum (which is equivalent to 1000 $\mathrm{MW_e\ yr^{-1}}$).

Table 5.24. Potential sources of emissions during refining and petrochemical processes involved in crude petroleum treatment

Type of exhalates	Potential sources
Sulphur oxides	Boilers, regenerators of catalysts, flame heaters, combustion furnaces, destruction of acid sludges
Hydrocarbons	Barometric condensers, blow-through processes, boilers, regenerators of catalysts, compressors, cooling towers, flames, heaters, containers, pumps, tanks, vacuum nozzles, and equipment for treating liquid wastes
Nitrogen oxides	Boilers, catalyst regenerators, compressor motors, flames
Solid particles	Boilers, catalyst regenerators, coking processes, heaters, combustion furnaces

Table 5.25. Emissions from the petroleum refining plants

Type of emission	Amount (t/1000 MW $\mathrm{yr^{-1}}$)
SO_x	21 000
Organic compounds	23 000
NO_x	18 000
CO	4 300
Ammonia	2 230

The malodorous smell is another unpleasant phenomenon in the vicinity of petroleum refining plants, and it is caused by compounds contained in raw petroleum or formed in the technological process. Particularly unpleasant smells are due to hydrogen sulphide and mercaptans, such as ethyl mercaptan, which causes a noticeably bad smell in a concentration as low as 1 to 10^9.

Many organic synthesis processes follow the primary petroleum and natural gas treatment. A simplified schematic diagram of the petrochemical petroleum treatment (Fig. 5.11) illustrates the great variety of intermediate and final products formed in the processing of hydrocarbons, so the formation of different organic emissions is not surprising. Some examples of harmful organic compounds present in emissions from the synthesis of important synthetic organic products are summarized in Table 5.26. The

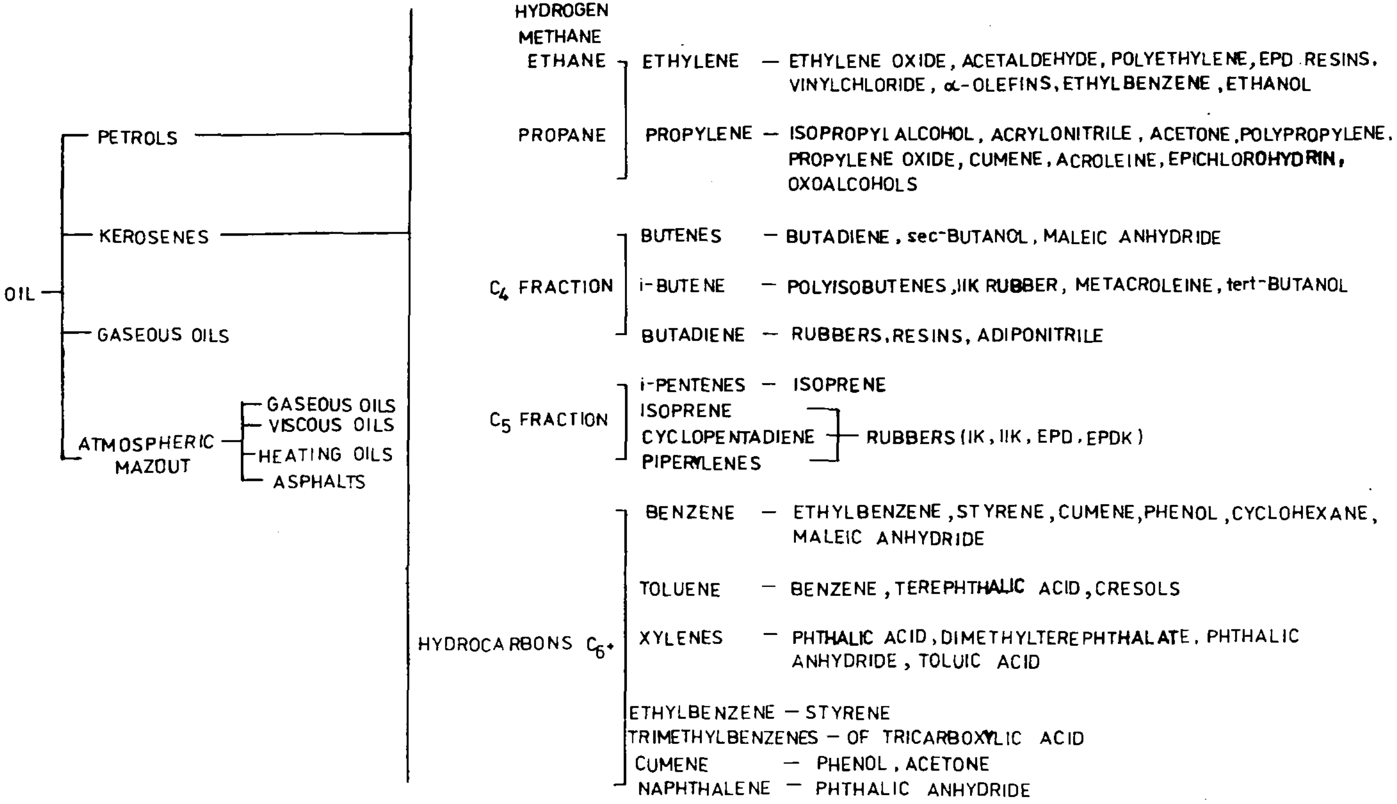

Fig. 5.11. Petrochemical processing scheme

Table 5.26. Harmful organic substances contained in emissions from the production of important compounds in industrial organic synthesis

Product	Emission
Methanol	Methanol
Caprolactam	Benzene, toluene, phenol
Adipic acid	Cyclohexane, formic acid, acetaldehyde
Phthalanhydride	Phthalanhydride, maleic anhydride
Vinyl chloride	Vinyl chloride
Hexamethylenediamine	Adiponitrile
Pesticides	Hydrocarbons, phenols, different pesticides, ethyl dichlorothiophosphate, diethyl chlorothiophosphate
Alcohols, fatty acids, fats	Aldehydes, amines
Dyes	Aldehydes, ketones, phenols, terpenes, thiophene, alkyl sulphates, polychlorinated biphenyls
Pharmaceuticals	Formaldehyde, acetaldehyde, acetone lower alcohols, phenols, organic acids
Plastics	Phenols, organic compounds containing sulphur, acrolein, formaldehyde, urea, melamine, different polymers
Synthetic fibres	Carbon disulphide
Polyisocyanates	Phosgene, chlorobenzene, 2,4-diphenylmethanediamine, methanediamine
Acrylates	Methyl acrylates, methanol, acetone, butanol
Polystyrene	Styrene, ethylbenzene, xylenes, cumene, benzene
Polyethylene	Hydrocarbons
Polyvinylchloride	Vinyl chloride, vinylidene chloride, vinyl acetate
Synthetic rubbers	Butadiene, butenes, pentane, pentadiene, acrolein, acrylonitrile, dichloroethane, methyl methacrylate, methanol, phosgene, chlorobenzene, caprolactam, cyclohexane
Rubber products	Soot, benzene, chlorides, naphthylamine
Textile materials	Formaldehyde, hydrocarbons

production of synthetic polymers occupies a special position in organic syntheses, since at the present time it is one of the most dynamically developing areas of industrial production. Toxic monomers, auxiliary substances or other possible compounds can enter the air of the working environment. The degradation of polymers may also be an important source of emissions. For example, during the decomposition of fluoroplastics, fluorine compounds are released, hydrogen chloride is released from polyvinyl chloride, hydrogen cyanide is released from polyacrylonitrile, etc. A serious pollution of the working environment can also come from organic solvents used in the production of synthetic polymers. Vapours of organic solvents can undergo photochemical reactions leading to a photochemical oxidation of the solvents, forming dangerous, harmful substances in the presence of nitrogen oxides and involving an active participation of atmospheric oxygen.

Gaseous emissions from the paper and cellulose industry represent a special group, particularly causing emissions containing sulphur trioxide, hydrogen sulphide and strongly smelling organic substances, such as methane thiol, dimethyl sulphide, dimethyl disulphide, etc., formed in the course of cellulose production by the sulphate process. In the case of the sulphite process for cellulose, emissions of sulphur dioxide are formed, especially during the regeneration and combustion of sulphite extracts.

5.3.1.5 The foodstuff and pharmaceutical industries

The sources of harmful emissions in the foodstuff industry are usually not the technological process itself, but auxiliary plant, particularly boiler houses and power plants. In certain branches of the foodstuff industry there are, however, sources of dust, during the preparation of raw materials or treatment of the final product.

In flour production, the dust is formed during the transport of cereals, during their rough cleaning, as well as in the course of the milling process itself. The dust from the transportation systems (conveyers, elevators, etc.) and from the rough cleaning of grains is mainly composed of fine soil particles, fragments of grains and chaffs, chaffs, light seeds of weeds, etc. In further cleaning of the grains, finer dust is formed, containing fine particles of the external shell, fragments of chaffs, etc. The air leaving the mill, containing considerable amounts of fine flour is extracted by a central extraction pipeline passing through a high-pressure ventilator into textile filters, sometimes also after a passage through cyclones.

In meat production, different problems of a sensorial character are particularly encountered. For example, the wastes (the blood, parts of animal bodies and further wastes) rapidly decompose, resulting in a strong smell. Pathogenic microorganisms can also enter the atmosphere, which may lead to a propagation of different infections. Similar problems may also be encountered in the milk industry, in the course of an inefficient waste treatment.

In installations of the edible-fats industry, the working air is polluted particularly by dust, by solvent vapours and by volatile substances from the fat materials treated. The dust is mainly small particles of the raw material, which enter the air at particular stages of the treatment. The dust gets into the atmosphere during the pneumatic transportation and drying of seeds, during the removal of shells from the seeds and also in the course of the transport and cooling of ground materials after the extraction process. The pollution of the air with vapours of solvents (particularly petrol and n-hexane) used for the oil extraction is important not only from the standpoint of their direct harmful effect on the health of workers, but also from the standpoint of a possible fire and explosion. Volatile substances from treated fat material, which enter the atmosphere in the course of the fat refining and degrading and during fatty acid distillation, etc., are sources of unpleasant smell, which is unpleasant not only for the employees, but also for inhabitants in the vicinity of the plant. Most of the malodorous substances are released from the deodorization equipment. The major portion of them may be removed in cooling towers and the residual amounts can be retained in charcoal filters or in wet washing towers. Volatile substances from other refining plants, from the fatty acid distillation are mostly efficiently trapped in special spiral absorbers containing NaOH solution. Another approach is to burn these substances, by blowing the air from the plant into heating equipment. In certain plants of the pharmaceutical industry, problems are encountered similar to those occurring in the edible-fat industry.

The pharmaceutical industry produces a very wide variety of pharmaceuticals, antibiotics, vitamins, hormones, extracts and tinctures from plant materials, infusion solutions, etc. for human and veterinary use. The production processes involve chemical, biochemical and biological operations. In a number of processes, harmful or malodorous substances are formed which can enter the atmosphere in the form of gases, vapours, fogs or dust. Out of the high number of these substances only a limited group need to be considered from the standpoint of atmosphere protection. Many of the substances undergo only small emissions, so that during their spread in the atmosphere the concentration formed is non-harmful from the health standpoint, or it causes difficulties only in the plant itself, or possibly in its close vicinity, so that this is a problem of the working environment rather than a matter for wider concern.

In the pharmaceutical working environment there is particularly a danger of air pollution by vapours of organic solvents, acids, alkalies, etc., by microorganisms and by dust of various chemical compositions. These air pollutants exert detrimental effects on the human organism, especially on the skin and mucous membranes and they can often induce poisoning with serious consequences to the human health. Thus, production methods need to include as efficient a separation of the harmful substances as possible, often via a combination of different separation methods [23–25].

5.3.2 Air pollution by emissions from combustion engines

In addition to industry and energy production, transport is a field of the human activity seriously affecting quality of the environment due to the emissions of gaseous pollutants. These, together with dust particles are produced by rail, road, and air transport and also by shipping.

Rail transport, which formerly was a significant contributor to air pollution, due to the use of steam locomotives, is now of minor importance. The change to the diesel and particularly electric motors has considerably reduced the amounts of harmful emissions. Electric locomotives are environmentally excellent. In the future, this form of transport may be transferred into underground vacuum tunnels, where the trains will move on electromagnetic cushions, thus providing the cleanest transport of all. Besides the low degree of air pollution, rail transport possesses economic advantages, including its high capacity and low costs.

Shipping transport is characterized by low costs and the capability of transporting large and heavy objects as compared to other types of the transport. The possibilities of river transport are, however, obviously restricted by the geographic location of rivers and canals. Shipping is particularly dangerous as regards the pollution of rivers, lakes and seas by petroleum substances, and in the case of tankers, by the petroleum itself. Water-borne transport sometimes also gives rise to serious problems of air pollution, particularly in the close vicinity of rivers and channels, in the countryside as well as in the urban environment. From high-power diesel engines, particularly carbon monoxide, aldehydes, sulphur dioxide, nitrogen oxides and non-combusted hydrocarbons enter the atmosphere. A good example is the international waterway at Detroit, where the shipping caused considerable pollution of the atmosphere by emissions of black smoke, fly ash and harmful gaseous substances from combustion of coal and oil. The emissions deteriorated the human environment in housing and recreational areas at many localities along the course of the river. The authorities of the cities of Detroit in Michigan and Windsor in Ontario asked the Departments for Foreign Affairs of the USA and Canada for assistance in the solution of this serious problem. After relevant provisions and proposals of a mutual international commission, the situation was improved. The air pollution along the river was much reduced by strict observation of the accepted plan to restrict the emissions by employing more efficient devices for the combustion of fuels.

Air transport is clearly the most rapid (and the most comfortable) but it gives rise to many negative effects, including air pollution. Exhaust gases from aircraft directly threaten human health in the vicinity of airports, where it is possible to observe the air pollution visually; during take-off and landing, one can see smoke emission containing harmful polluting substances (gases, soot, solid particles). The smell of fuels can be noticed along the runways. In the vicinity of large international airports, this pollution results in fog formation, reduced visibility and thus also in manoeuvering problems. Aircraft pollute the air with carbon monoxide, nitrogen oxides, non-combusted hydrocarbons, aldehydes, solid particles and soot, etc. Both piston and turbine engines of aircraft produce 2–4 mg of benzo[a]pyrene per minute in normal operation.

A possible danger of disturbing the natural equilibrium the planetary scale has been discussed. Large amounts of oxygen are consumed, with a consequent production of large amounts of harmful substances. A total of 35 t of oxygen is consumed during the flight of a jet airplane over the Atlantic Ocean. Combustion products from the engines of supersonic aircraft react with ozone at high levels in the atmosphere, thus reducing the thickness of the protective layer of this gas.

In the case of *road transport* it is not possible to conceive any substitute for motor vehicles. Motor vehicles are used to a huge extent for collective transport, individual transport and freight. They deteriorate the quality of the environment in cities with dense traffic. At the present time, in industrially developed countries, motor vehicles contribute more than 50% to the amounts of anthropogenic gaseous emissions polluting the atmosphere. In certain big cities and industrial agglomerations, this contribution exceeds 90%.

Even after the year 2000, motor vehicles will be the main means of transport. According to studies, the number of motor vehicles in the world will increase to 600 millions by the year 2000, and the annual rate of increase of their production is 2.5%. A total of approximately 3.7 million workers are employed in the automobile industry in countries making major contributions to the world production of motor vehicles. This number is predicted to decrease to 2.3 millions by 2000.

With the rapid expansion of the number of motor vehicles based on combustion engines, in certain parts of some countries the problem of the air pollution is even reaching catastrophe levels. One car produces approximately 1 t of harmful gases annually, containing 700 kg of carbon monoxide, 100 kg of hydrocarbons, 35 kg of nitrogen oxides and uncertain amounts of other highly toxic substances such as benzo[a]pyrene or lead. A striking illustration of the scale of the problem comes from the USA: a child is born every 12 s; a car is produced every 5 s. It has been considered that air pollution will increase absolutely as well as relatively unless there is an effective control of the production of motor vehicles [26, 27].

5.3.2.1 Combustion engines and combustion processes

For road (and partially also railway, boat and air) transport, piston combustion engines are used most frequently. In these the chemical energy of the fuel is changed directly in the combustion space of the engine into thermal energy, which is converted by the engine into mechanical work.

In such engines, petrol and less frequently alcohol–benzine and benzol mixtures are used. In the engine a compression occurs in cylinders of the mixture of petrol and air, which is ignited after the compression.

The stoichiometric amount of the air necessary for the complete combustion of 1 kg of petrol amounts to 14.6–15 kg (depending on the fuel composition). The fuel is, however, never perfectly mixed with the air and the ratio is not always stoichiometric. A mixture is typically used, which is richer by 50% as compared to the ideal mixture. These circumstances, together with the short time of the combustion itself, result in an incomplete burning of hydrocarbons, so that aldehydes and other organic compounds are produced, which can further react with burning products. Thus, in exhaust gases of a petrol engine, there is always a certain amount of non-combusted fuel, and products of incomplete combustion.

The composition of exhaust gases of petrol engines varies over a wide range, depending on the operation conditions and on the adjustment of a given engine. The most harmful substances are emitted during idling, acceleration, during maximal power output and when braking with the help of the engine.

Disregarding the presence of nitrogen oxides, sulphur-containing substances and compounds of lead in petrol, it is possible to write the following equation for the combustion

$$C_xH_{2y} + \left(x + \frac{y}{2}\right) O_2 = n.xCO + x(1 - n)CO_2 + yH_2O + \frac{nx}{2}O_2$$

where n is the fraction of carbon in the fuel oxidized only to CO. From this equation it is possible to establish the composition of the mixture and the efficiency of the combustion process when performing a chemical analysis of exhaust gases. The combustion is invariably imperfect, since the relatively cool walls of cylinders arrest the various reactions.

The composition of the mixture has a major effect on the harmful substances formed. The mixture burns with the highest efficiency only in the presence of a certain excess of the air. The air excess also determines the rate of the combustion, which is the highest for a moderately rich mixture.

In diesel engines, diesel fuel, containing higher molecular mass hydrocarbons, is used instead of petrol. Air is drawn into the cylinder. By a rapid compression, the air is heated up to the ignition temperature of the fuel. The fuel is injected into the cylinder, and it ignites in the presence of the excess heated air. The burning mixture yields mechanical work via the action of its pressure on the piston.

Diesel engines require a considerable excess of air; even with an excess of about 20%, the engine usually emits smoke (a fuel:air ratio of 1:14.7 should be sufficient theoretically). The smoke results from the fact that the non-combusted substances from diesel engines also contain carbon besides $C_xH_y + CO$. White smoke, containing mainly water vapour, non-combusted fuel and oil, is obtained when starting up, during idling and during a moderate load. With increasing load the emission of the white smoke disappears. The smoke becomes gray due to increase of the amount of non-combusted fuel in the exhaust gases. Black smoke is formed during the highest engine loads or during imperfect combustion (it contains non-combusted carbon — soot).

With a large excess of air in the combustion chamber (20–600%), the combustion becomes more complete. At high temperatures and in the presence of excess nitrogen, nitrogen oxides (NO_x) are produced. Since diesel fuel, in contrast to petrol, contains higher amounts of sulphur, larger amounts of sulphur dioxide are also produced. At the high temperatures of diesel fuel combustion, complicated cracking reactions, production of aromatic substances, aldehydes (particularly acrolein), soot and smoke are formed.

In exhaust gases of diesel engines, lower amounts of CO and C_xH_y are found as compared to those from petrol engines, the amounts of nitrogen oxides being about the same in the two types of engine.

5.3.2.2 Exhalates from combustion engines

During the operation of a combustion engine, harmful substances are produced essentially from four main sources of the motor vehicle:

(1) exhaust gases (60%),
(2) crankcase ventilation (20%),
(3) losses by the evaporation from the carburettor (10%),
(4) losses by evaporation from the petrol tank (10%).

The main problem is to decrease the amounts of harmful substances in the exhaust gases. The exhaust gas composition depends on a number of factors:

- the type of the combustion engine (petrol, diesel),
- type of fuel used,
- design characteristics of the engine and accessories,
- precision of the production and adjustment of the combustion engine,
- operating conditions (idling, deceleration, acceleration, etc.).

The following substances are all present in exhaust gases of combustion engines:

- nitrogen and oxygen from the air,
- water vapour and carbon dioxide from a complete combustion of the fuel,
- carbon monoxide, non-combusted, partially oxidized or degraded hydrocarbons from an incomplete combustion of the fuel, nitrogen oxides via direct synthesis from the oxygen and nitrogen from the air in the engine combustion space,
- products of the conversion of compounds added to the fuels for improving their quality, particularly lead aerosols ("fuel additives"),
- sulphur compounds (sulphur dioxide), compounds of calcium, manganese, etc., depending on the composition of the fuel and the additives in the fuels and lubricants.

Table 5.27 shows the limit values for contents of the main components in exhaust gases from petrol and diesel engines.

Some of the substances mentioned are concerned in the formation of secondary harmful species: ozone, peracyl nitrate, singlet oxygen and solid aerosols in the atmosphere, which are components of the white photochemical smog of the California variety. Sulphur dioxide in the air is partially further oxidized to sulphur trioxide and hence sulphuric acid. These substances, together with soot are components of the black smog of the London type.

In Table 5.28, relative abundance is given of main components of exhaust gases for characteristic conditions of the petrol and diesel engine load.

Carbon monoxide is considered to be the most harmful component of the exhaust gases. It is produced mainly in petrol engines operating with a rich mixture. The preparation, distribution and composition of the mixture are the decisive factors for the amount of carbon monoxide produced. Exhaust gases contain typically as much as 12% of CO during idling, 8% during acceleration and partial load and 3–5% during deceleration. Two-stroke

Table 5.27. Composition of exhaust gases (vol.%)

Component	Engine		Toxicity
	petrol	diesel	
Nitrogen	74–77	76–78	Non-toxic
Oxygen	0.3–8.0	2–18	Non-toxic
Water	3.0–5.5	0.5–4.0	Non-toxic
Carbon dioxide	5.0–12.0	1.0–10.0	Non-toxic
Carbon monoxide	0.0–12.0	0.0–0.5	Toxic
Nitrogen oxides	0.0–0.8	0.002–0.5	Toxic
Non-carcinogenic hydrocarbons	0.2–3.0	0.01–0.5	Toxic
Aldehydes	0.0–0.2	0.001–0.01	Toxic
Soots (g cm^{-3})	0.0–0.4	0.01–1.1	Toxic
Polyaromatic hydrocarbons ($\mu g\ m^{-3}$)	100–400	0–100	Carcinogenic

Table 5.28. The relative abudance of certain harmful substances in exhaust gases during characteristic conditions of the load (vol.%)

Type of engine	Component of exhaust gas	Idling	Acceleration	Partial load	Deceleration
Petrol	CO	11.7	8.0	8.4	5.5
	C_mH_n	0.47	0.096	0.032	1.675
	NO_x	0.0033	0.135	0.0653	0.0018
	Aldehydes	0.003	0.0016	0.0007	0.0286
Diesel	CO	0	0.050	0	0
	C_mH_n	0.039	0.021	0.009	0.033
	NO_x	0.0059	0.0849	0.0237	0.003
	Aldehydes	0.0009	0.0017	0.0011	0.003

engines produce higher amounts of CO, whereas diesel engines produce much lower amounts (0–0.06%).

Of the total amounts of *hydrocarbons* entering the atmosphere during motor vehicle operation, 60–70% come from exhaust gases, a further 15–30% from the crankcase, the remaining portion being evaporated from the carburettor and petrol tank. The number of different hydrocarbons in exhaust gases is estimated to be about 200. All the processes leading to carbon monoxide production also lead to the release of non-combusted hydrocarbons.

Non-combusted hydrocarbons in exhaust gases consist most frequently of four-carbon-atom species, nitroparaffins and aldehydes. These moderate the burning process of hydrocarbon fuels, they are broken down in the presence of metals at higher temperatures, however, following this they are incompletely burnt, due to an insufficient amount of oxygen. They are always intermediate products of burning. Non-combusted hydrocarbons represent a great danger particularly in regions where oxidation photochemical smog may be produced. They are also associated with unpleasant odours.

Special attention is paid to *polyaromatic hydrocarbons*, since some of them are carcinogenic. Benzo[*a*]pyrene is the most typical of such species. Its greatest amounts are formed during engine idling at minimum rpm.

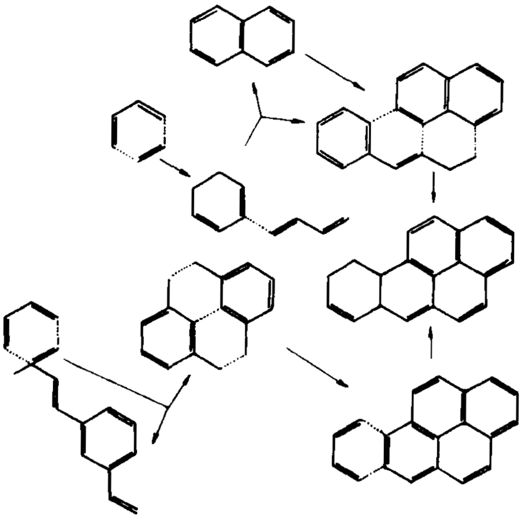

Fig. 5.12. Formation of benzo[*a*]pyrene by pyrosynthesis

Figure 5.12 is a schematic diagram of benzo[*a*]pyrene formation via pyrosynthesis [1]. Approximately 40 and 50 g of benzo[*a*]pyrene are obtained from 1 t of petrol and diesel fuel, respectively. The total amount of polyaromatic hydrocarbons in exhaust gases of petrol engines is roughly 100–400 μg m^{-3}, with higher amounts in two-stroke engines than in four-stroke ones; in the exhaust gases from diesel engines these amounts range from 0 to 100 μg m^{-3}. The amount of polyaromatic hydrocarbons in exhaust gases increases particularly as a result of a frequently changing operating regime in city traffic. The petrol composition, type of lubricating oil and condition of the engine are most probably also of importance. Polyaromatic hydrocarbons from exhaust gases of petrol engines are absorbed to a certain extent on soot particles, thus increasing their carcinogenic activity.

Sulphur oxides SO_x from emissions of combustion engines are of negligible importance in comparison with the amounts from industrial air pollution. They are produced particularly in diesel engines (as much as 0.5% SO_x). The sulphur content in the diesel fuel is continually being decreased (at the present time it is 0.2–0.3%) and thus, the contribution from combustion engines to pollution with sulphur oxides is also declining.

Nitrogen oxides NO_x are present in exhaust gases of both petrol and diesel engines. Nitrogen monoxide is produced by a reduction of higher nitrogen oxides in the presence of metals. At higher temperatures, it starts to split into its elements and at 900°C it is completely decomposed. Nitrogen monoxide may be an intermediate product at the beginning of the combustion, however, it is not a significant component of exhaust gases. Nitrogen oxide NO is obtained during combustion processes at sufficiently high temperatures. At first stage of the process atomic oxygen is produced by dissociation of O_2:

$$O_2 \rightarrow 2O$$

or during the interaction of CO with $OH^{\bullet}$ radicals (occurring during combustion processes) according to the scheme:

$$CO + OH^{\bullet} \rightarrow CO_2 + H$$

after which a reaction of atomic hydrogen with the O_2 molecule occurs:

$$H + O_2 \rightarrow OH + O$$

The atomic oxygen generated in the system initiates a chain reaction connected with the nitrogen oxide production:

$$\begin{aligned} O + N_2 &\rightarrow NO + N \\ N + O_2 &\rightarrow NO + O \end{aligned}$$

The following side reaction can occur simultaneously:

$$\begin{aligned} N + NO &\rightarrow N_2 + O \\ O + NO &\rightarrow N + O_2 \end{aligned}$$

The reactions involved in NO formation occur particularly in a mixture rich in air, since atomic oxygen reacts more easily with N_2 than, for example, with hydrocarbons.

The remaining oxides dissociate, e.g. nitrogen trioxide N_2O_3 is dissociated by action of the humidity, nitrogen dioxide NO_2 is dissociated at temperatures of about 600°C and nitrogen pentaoxide dissociates at normal temperatures and thus, these oxides cannot be important components of exhaust gases, as is the case also for nitrogen peroxide NO_3.

Thus, nitrogen oxide NO is the most important oxide of nitrogen in exhaust gases, its amount being dependent on the mechanism of the fuel combustion, air humidity and pressure in the combustion space.

Nitroparaffins may be formed by a reaction of nitrogen oxide with hydrocarbons of the fuel, which are decomposed only at the end of the combustion process with increasing concentrations of nitrogen oxide and non-combusted hydrocarbons.

Free OH radicals formed in the combustion space during the combustion process lead to the formation of the aldehydic group — CHO, which may replace hydrogen in the chain process producing an aldehyde. The formation of nitrogen oxide as well as burning of hydrogen and carbon contribute to the OH radical formation. Aldehydes (formaldehyde, acetaldehyde, acrolein, etc.) are produced by the petrol as well as diesel engine in concentrations of 60 to 100 mg m^{-3}.

In general, when the amount of non-combusted hydrocarbons and carbon dioxide decreases, then the amount of aldehydes increases and vice versa, for a given excess of the air in petrol engines. The nitrogen oxide concentration varies depending on the amount of excess air and the rpm value. The formation of harmful substances is affected by all the parameters influencing the pressure; a pressure increase, the combustion temperature and the particular branch of fuel can also affect the concentration of NO.

From the above-mentioned facts we can see that not only non-combusted hydrocarbons, carbon monoxide, carbon and aldehydes are formed by the imperfect combustion, reactions yielding nitrogen oxide also occur. This means that the restriction of the nitrogen oxide formation may result in a reduction of the amount of products of incomplete combustion.

Besides harmful gaseous substances, combustion engines also produce solid and liquid particles of various dimensions, consisting of a mixture of organic and inorganic compounds. The smaller particles may reside in the atmosphere even for several months. In urban areas with a high traffic density, their concentrations in the atmosphere can be very high.

The amount of these particles in exhaust gases depends on the design, maintenance, operation, type of fuel and oil, condition of the engine, etc. For example, during acceleration, the amounts of these particles are increased several times; under conditions of a steady state of the engine operation, this amount is reduced and stabilized; the amount of the particles emitted also increases with the driving speed.

In these particles, *lead* is present, which is added to petrol in the form of tetraalkyllead (most frequently tetraethyllead) as an admixture for increasing the octane number ("ethylized fuel").

The amount of lead, which enters into the atmosphere with exhaust gases is different according to data from different sources. It is particularly dependent, as for most exhaust pollutants, on the composition of the fuel, vehicle speed, engine operation regime, etc. In an average sized city approximately 10 t of lead per year enters the atmosphere just from exhaust gases of motor vehicles. The size of lead particles in exhaust gases ranges between 0.01 μm and several micrometers.

In ethylized fuels, the total volume of emitted particles is smaller than that in fuels containing no tetraethyllead, and their average diameter is larger. The portion of particles with a diameter below 2×10^{-6} m is about 80%, and in ethylized fuels approximately 40% of the particles are characterized by a diameter below 0.1×10^{-6} m, the fraction of particles with this diameter in non-ethylized fuels being only 10%.

Imperfect combustion of rich mixtures leads to *soot* formation. The basic substance is carbon, and on its surface various harmful substances are adsorbed, particularly carcinogenic hydrocarbons. Petrol engines produce as much as 0.4 g m^{-3}; diesel engines as much as 1.1 g m^{-3}, i.e. 17 kg of soots per 1 t of fuel [26–28].

5.3.2.3 Possibilities of reducing harmful exhalates from exhaust gases of combustion engines

The attempts to reduce amounts of harmful substances in the exhaust gases of motor vehicles and the possible future lack of sufficient reserves of petroleum have prompted the search for other types of engines for cars and for design improvements of the petrol engine. At the present time, only two types of other driving units are available (the Wankel rotary combustion engine and the diesel engine). Other types of motors are being studied and developed such as combustion turbine, steam engine, the Stirling motor, the electric motor, etc. Their production on a large scale can be, however, hardly envisaged in the near future.

The main trends of research into design adjustment of the present combustion engine from the standpoint of reducing amounts of harmful substances are mainly as follows:

- adjustment of the composition of fuels and the development of new fuels (propane-butane, methanol, ethanol, hydrogen, etc.),
- combustion of poor mixtures in petrol engine,

— injection of volatile fuels,
— control of the exchange of gases in the cylinder,
— programmed combustion process,
— additional combustion of carbon monoxide and hydrocarbons and degradation of nitrogen oxides in exhaust gases (introduction of air into the exhaust channel, the use of thermal and catalytic reactors).

The diesel engine is the most suitable alternative for cars. The extent of the air pollution by exhalates from combustion engines can also be reduced by the drivers, particularly by maintaining the car in a good technical condition, by a proper method of driving especially when the engine is warming up, and particularly by a proper carburettor adjustment. Large amounts of toxic carbon monoxide are produced by an incorrect adjustment of the idling regime [27].

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5.4 Emission control

The restriction of emissions into the air and reduction of their undesirable effects on the environment can be achieved by several methods. The most important of these are self-evident, as follows:
— elimination of the emission sources,
— minimization of the amount of harmful substances directly in the source,
— capture and destruction of polluting components from exhalates.

5.4.1 The elimination of emission sources

The most efficient method for reducing the amounts of emissions is obviously by eliminating their source. This may be achieved by changing the technology, raw materials, fuels or simply by changing the products produced, or in the limit, stopping the production processes leading to the exhalations.

An example of a technology change is the shutting down a power station based on fuels of a poor quality, replacing it by a hydroelectric power plant. In the chemical industry sources of emissions of nitrogen oxides during the production of sulphuric acid were eliminated by replacing the producing technology based on the tower method by that based on the contact method. This was achieved by replacing the catalyst for the sulphur dioxide oxidation to sulphur trioxide; in the former method, nitrogen oxides were used, giving an undesirable emission source and in the latter process, a solid catalyst based on vanadium pentaoxide is used.

The change of raw material or fuel can be an important method for eliminating an emission source. For example, it is advantageous to use preliminarily desulphurized gaseous fuels instead of solid fuels. However, in times of global lack of resources, the use of more advantageous raw materials is the exception rather than the rule.

A typical example of replacing the products is the fairly recent production of bioinsecticides instead of the production of chemical insecticides. In agriculture, the replacement of powdered fertilizers (causing many problems during their application into the soil) by liquid fertilizers is also important.

In connection with the problem of the destruction of the ozone layer (discussed in Section 5.2.4.3) it is of enormous importance to stop completely the further production of aerosol sprays using freon as the spraying agent and to replace it with a non-polluting agent.

5.4.2 Minimization of amounts of pollutants in the source

In cases where it is impossible to eliminate completely the formation of harmful substances in the source itself, it is necessary to look for the solution in minimizing their amounts. A considerable decrease may be achieved by various methods, depending on the type of source. Procedures aimed at the development of technologies with small amounts of wastes are the most promising. Good results are also achieved by adjusting current production processes, particularly in combination with the adjustment of production equipment. The processing of fuels, especially the reduction of contents of sulphur and volatile substances, also represents successful approach. Modifications of technologies and equipment have met with success in many fields in recent years. In energy production, one should mention the fluid technology using solid fuels with a low combustion temperature, ranging between 800 and 900°C. At this temperature, the melting point of the ash is not reached and a portion of the original content of sulphur compounds remains undecomposed in the fuel. This makes it possible to decrease the sulphur dioxide content in the combustion products. Good results were achieved with the use of two variants of the fluid combustion approach: (a) a fluidized bed furnace with non-clinkering fluid layer and a two-stage burning process; and (b) a fluidized bed furnace with a non-clinkering fluid layer and a one-stage burning process in two fluid layers [1]. The use of two-stage oxidation and the associated absorption process in sulphuric acid production [2] can be mentioned as an example of a simple technology adjustment in the chemical industry, which achieved a remarkable decrease of SO_2 emissions (below 0.03% SO_2 by volume). Adjustments of production equipment may help to reduce considerably the amount of emissions. In this direction, the minimization of NO_x emissions in combustion equipment is of a great interest at the present time. This is achieved by reducing the temperature of the flame core, either by forming the reduction atmosphere in the burner space or by gradual introduction of air into the burner or possibly into a further stage in the combustion chamber. An additional supply of fuel and air into the combustion chamber above the zone of the main burners also gives good results. By applying design changes it was possible to decrease the NO_x content in combustion products down to a maximum of 300 mg m^{-3} [3]. It is assumed that for burners using coal, the NO_x concentration can be decreased even below 0.01 vol.%, and in burners of fuel oil, below 0.005 vol.%.

In connection with the problems of emissions of fluorine compounds from the electrolytic production of aluminium, as a further example, we can mention the exchange of electrolysers with self-sintering electrodes for those with preliminarily calcinated anodes, which enabled the hermetic sealing of electrolytic vats and the complete withdrawal of the produced exhalates into separators.

The treatment of fuels, particularly desulphurization and the removal of volatile inflammable substances belong to successful approaches providing a remarkable decrease of emissions. In the case of solid fuels such as coal, it is possible to use grading, floating, carbonization (particularly a low-temperature one) or further thermal treatments. The hydrogenation desulphurization process is highly efficient, but, it is very expensive for coal and in practice it is feasible only for the desulphurization of heating oils.

5.4.3 Capture and destruction of pollutants

The capture of pollutants from final gases is mostly less suitable than the adjustment of technologies or types of equipment. This approach is frequently more expensive and it brings many technical complications and ecological problems in the case where gas purification is connected with the formation of undesirable side products or wastes.

During the separation of solid, liquid and gaseous pollutants from exhalates, different processes may be used. Solid and liquid particles (dust, fly ash, aerosols) are retained in different types of separators. In the capture and destruction of gaseous pollutants, many chemical and physico-chemical principles are used. Separation equipment for solid and liquid particles are characterized by a higher degree of development than those for the separation of gases and vapours, which are still in the course of development.

5.4.4 Processes and equipment for decreasing the emissions of solid and liquid particles

5.4.4.1 Physical principles used for the separation

Principles of basic importance during the separation are based on the effect of *inertial and electric forces, gravity*, and the *resistance of a fluid medium.* Besides this, the *diffusion*, the *interception principle* and other effects find application. In particular types of industrial separators, a combination of these principles is usually used and, in addition, the particle motion may be affected by further transport phenomena, such as *thermophoresis, diffusion* and *coagulation.* The separation process is naturally affected by characteristics of the particles to be separated, by the technical operating parameters of the gas to be purified, and also by certain characteristics of the separator itself. Thus, the separation process can hardly be exactly described mathematically, and most separators are designed on the basis of experimental data rather than pure theoretical principles.

The *gravitational principle* can be applied during horizontal flow of a mixture of gas and particles, where the gas velocity is almost zero in a limiting layer of the gas at the boundary surface, so that the motion of particles induced by gravity can occur. The motion of particles in a stationary medium reaches a steady state and the velocity of fall results from an equilibrium between gravitational and aerodynamic effects. The quantity of particles separated on the given areas is determined by the particle concentration in the limit layer and by the velocity of fall.

The effect of external forces on the motion of bodies, which tend to remain in the original dynamic condition, is the basis of the inertial principle. In the presence of a force, the motion of a body is changed in direction of action of the force. When polluted gas flows around a curved separating area, then it is possible to observe different curvatures of the paths of particles and the carrying gas trajectory, with a retention of the particle on a given area. This principle may be used in different types of dry mechanical separators.

Particle motion in a real gas is affected by the molecular structure of the gas and by turbulence. These two characteristics are considered as *diffusion phenomena.* During the separation of particles from a pure gas, molecular as well as turbulent diffusion may occur. *Molecular diffusion* is the motion induced by action of molecular phenomena due to the characteristic random motion of molecules. The action of molecular forces is clearly manifested for particles smaller than 1 μm. The diffusion phenomenon connected with the turbulent state of the gas stream is termed *"turbulent diffusion"*. On account of the turbulence, vortex elements are formed in the streaming gas, which induce the motion of gas and particles in various directions, different from the basic vector of the stream velocity. Turbulent diffusion occurs mainly for particles larger than 1 μm. The diffusion principle is utilized particularly in filtration through fibrous filtration layers.

The *screen effect (interception)* may be used for the separation of particles from a gas when there are other bodies in the flow comparable with the size of particles driven by the gas.

The pollutant particles may then be directly captured on the body in the flow.

During the separation of particles in electric precipitators, the *effects of an electrostatic field* are used, with a deposition of electrically charged particles on collecting areas of electrodes. A more complete separation is achieved with artificial charging of particles. The separation of charged particles can, however, also occur in the absence of the electrostatic field by inducing charges of opposite sign on the collecting area.

5.4.4.2 Technical operating characteristics of separators

The *separation capacity, pressure losses* and *energy consumption* are the most important *parameters of separators*, and these can help to establish relevant characteristics for the choice and evaluation of separators. They are dependent on a number of factors, of which the following are the most important: dirty gas inlet flow rate, its composition and conditions concentration of the particles in the gas together with their physical and chemical characteristics and the operating regime of the separator.

The separation efficiency is a measure of the performance of a given separator, and both *total and fractional separation efficiencies* can be considered. It may be expressed in mass units or in terms of the numbers of particles, so that the separation efficiency expressed in mass or in a number of particles is obtained.

The *total separation efficiency* S_t is the ratio of the amount of dust retained in the separator per unit time $\dot{M}_r$ to the amount of the particles entering the separator per unit time $(\dot{M}_e)$. It is thus possible to write

$$S_t = \frac{\dot{M}_r}{\dot{M}_e}$$

Since $\dot{M}_e = \dot{M}_r + \dot{M}_g$, where $\dot{M}_g$ is the amount of dust remaining in the purified gas, it follows that

$$S_t = 1 - \frac{\dot{M}_g}{\dot{M}_e} = \frac{\dot{M}_r}{\dot{M}_e + \dot{M}_g}$$

The total separation efficiency cannot express differences between separations of particular dust fractions. This value varies depending on the granulometric composition of the dust entering the separator, since the efficiency is dependent on grain size.

The fractional separation efficiency S_f is defined in the same way as the total separation efficiency, but it is related to particles of a certain size. In industrial practice, a curve of the fractional separation is used, which presents the separation efficiency of a given separating unit for different particle sizes (dependence $S_t(d)$, where d is the equivalent diameter of the particle).

As a further parameter of the separation efficiency, we can consider the *penetration* P defined as $P = 1 - S_t$ and degree of separation $D = 1/P$. The penetration is used for expressing the separation efficiency in the case where the separation efficiency is very close to unity, such as in the case of filtration.

The separator pressure losses are defined as the difference between the sums of static and dynamic pressure before and after the separator. To express the characteristic parameter corresponding to the pressure loss of a separator, *the pressure loss coefficient* is frequently used ξ_D, where the subscript D is related to the characteristic dimensions of the separator. The pressure loss coefficient depends on the pressure loss of the separator, gravitational acceleration, flow rate gas density and separator dimensions.

The pressure losses of electric separators in comparison with the other types are very low, ranging between 60 and 250 Pa. A good separation efficiency with saving optimum operation conditions may be achieved in mechanical dry separators as well as wet separators at pressure losses of 600 to 1200 Pa (except for Venturi and slot separators). Considerable pressure losses occur in the filtration layer. Their values depend on the layer porosity ε, diameter of filtration material fibres, layer thickness, gas dynamic viscosity and the velocity of the streaming gas.

The pressure losses in separators are chosen in range which provide an optimal separation efficiency and good functional characteristics for the separator.

The energy consumption in separators is frequently evaluated from the specific consumption of energy, which is established from the separator power input per 1000 m^3 of gas to be purified.

5.4.4.3 Industrial separators

The industrial separators may be divided, according to physical principles, into three main groups as follows: *mechanical separators (dry or wet), electrostatic precipitators, and industrial filters.*

5.4.4.3.1 Dry mechanical separators

The group of dry mechanical separators include sedimentation chambers, inertial, vortex and centrifugal separators. For dust separation in these units particularly gravitational and inertial forces are used.

These separators are characterized by a fairly low separation efficiency for particle sizes below 5 μm. The separation limit, defined by a size of particles a_m for which the fractional separation efficiency $S_f = 0.5$, ranges between 3 and 30 μm. Such devices are characterized by simple design, operation and maintenance, and by low initial and operating costs, low pressure losses and energy consumption.

Settling chamber. The settling chamber is a large piece of equipment (in the case of considerable quantities of gas a length of chamber of 10 to 20 m is by no means exceptional), where the mean velocity of gas is lower than 1 m s^{-1}. Depending on the density of the dust to be separated, a good fractional separation efficiency is obtained for particles in a range of 50 to 70 μm. On account of its simplicity it is usually used as the first step of the separation before more efficient separators, thus making it possible to reduce the sizes and operating costs of later stage. The separation efficiency may be improved by including partitions for repeatedly changing the direction of the gas flow, which helps to separate the particles by action of their impact on the partition surface.

Dry inertial separators. The louvre separator, whose principle is illustrated in Fig. 5.13, is a typical representative of this group. In the course of the dust separation, inertial forces act during a change of direction of the streaming carrying gas. The separation limit ranges between 10 and 12 μm. The separator is suitable for relatively low input concentrations of dust — about 1 g m^{-3}. It is unsuitable for sticky, fibrous or abrasive types of dust. It is used most typically as the first separation step. It is characterized by its relatively small volume, simple construction, low pressure losses and small initial costs.

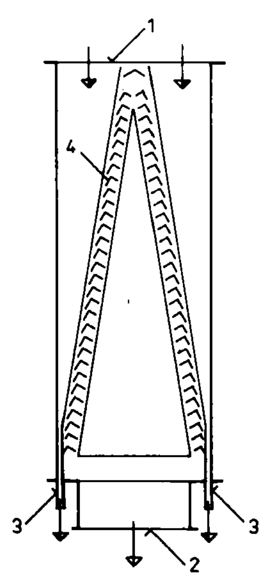

Fig. 5.13. Louvre separator. 1 — dusty gas, 2 — clean gas outlet, 3 — dust out, 4 — louvres

Dry vortex separators (*cyclones*). These are among the most extensively used mechanical separators. The principle of a cyclone operating with a tangential input is as follows: gas polluted with dust enters a cylindrical vessel tangentially, where it is forced to move in a rotational, spiral motion. Dust particles are retained on the cyclone wall by the action of the centrifugal force. The purified gas is released from the middle of the cyclone via an outlet. The rotational motion of the gas in axial cyclones may be achieved either by the tangential inlet or by fitting a spinners. For these separators, the lower limits of separation are between 2 and 10 μm. The cyclone operation is deteriorated by abrasive and sticky particles and, it is less efficient at higher temperatures.

From the principle of the cyclone function it follows that smaller particles may be separated in cyclones with smaller diameters. The separation efficiency of cyclones depends on a number of factors, the most important of them being defined by the relationship

$$S_{\mathrm{f}} = \frac{2CAv_{\varphi}^{2}\tau}{C_{\mathrm{d}}Sv_{\mathrm{a}}D}$$

where S_{f} is the fractional separation in the separator, C_{d} is the dust particle concentration at the point of input into the separator, C is the concentration in the limit layer, v_{a} is the mean axial velocity in the centrifugal chamber of the cyclone, S is its cross-section and D is its diameter, v_φ is the gas velocity at the chamber circumference, A is its surface area and τ is the time of particle relaxation.

It is obvious that higher separation efficiency may be achieved in cyclones with larger ratios $A/S = 4h/D$, where h is the chamber height. Higher values of the separation efficiency are also achieved for smaller diameters D, higher flow rate and a smaller input opening.

The separation efficiency of cyclones is further dependent on temperature; it decreases by 1 to 5% with increasing temperature. This effect is more marked in the case of particles of smaller diameters.

By increasing the cyclone diameter, the centrifugal force acting on the particle is decreased, which also means a decrease of the particle separation efficiency and thus, it is undesirable to use large-diameter chambers for high flow rates. In this case, it is necessary to use a system of parallel cyclones, which may be divided into (a) *group cyclone separators* (2–16 cyclones, usually in a circular arrangement), and (b) *multicyclones* (systems of tens to hundreds of cyclones of smaller diameters arranged in an enclosed housing).

For practical reasons it is not recommended to use cyclone elements < 200 mm in diameter, since they tend to cause sticking and higher abrasion.

Both types of systems are available in different design variants. Figure 5.14 is an example of a system of parallel operating elements, showing an installation of a bank of cyclones with an axial inlet.

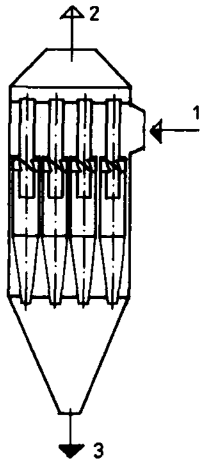

Fig. 5.14. Typical bank of small diameter high efficiency cyclones. 1 — dirty gas inlet, 2 — clean gas outlet, 3 — dust withdrawal

In present times, with the higher requirements for separation efficiency, such cyclones are rarely installed independently. They are rather used under particular operating conditions, which would make the other types of separators unsatisfactory. Their particular attraction is the ability to operate in variable conditions, at high temperatures, at high dust concentration (as high as 400 g m^{-3}, and in the presence of corrosive gases.) If the gas contains sticking hygroscopic dusts, it is possible to inject water at the point of the input into the cyclone, which rinses the dust from the walls. Advantages of cyclones are in their simple design, simple operating requirements and the smaller space required as compared with certain other types of separators. More detailed data concerning the operating parameters and design characteristics of cyclones can be found in the literature [4–12].

The type of separators has probably reached the limit of development, apart from minor operating improvements and increase of the service time.

Rotational separators. During the separation of particles in a rotational separator, both centrifugal and Coriolis forces are used. In contrast to other types of dry mechanical separators, a part of the separator — the rotor — is given a rotational motion. Depending on the different functions of the rotor, the separators may be divided into two basic types: the *ventilator type* (the separator rotor serves as a moving wheel of the ventilator) and the *centrifugal type* (rotation in the rotor itself).

The separation efficiency of such a unit is high, and is comparable with values achieved with the best cyclones. These separators, however, have higher maintenance requirements and they are unsuitable in the case of abrasive and sticking dusts.

5.4.4.3.2 Wet mechanical scrubbers

In wet mechanical scrubbers, particularly inertia is used in the separation process and, to a lesser extent diffusion processes and the condensation effect. The separating areas are formed by a water curtain, water drops, a liquid surface or the surface of bubbles. During the separation involving water drops, their mass and diameter has to be much larger than those of the particles to be separated. The efficiency of the separator is governed by relation between the velocity of the droplets of the washing medium and that of the particles in the gas to be purified, and the time of contact between the liquid and gaseous phases.

In comparison with dry mechanical separators, the wet separators exhibit a higher separation efficiency. High values can also be achieved for fine dusts. The separation efficiency of wet separators depends on the wettability of the dust with water, which can be partially adjusted by adding suitable additives or finely dispersed solid particles.

The limit of the separability of wet separators varies from several micrometers down to 0.1 μm. Wet mechanical separators have many advantages, including a functional reliability in the case of abrasive and sticking dusts, the possibility of trapping gaseous mixtures from the gas to be purified, and good separation efficiency for fine dusts. They are used advantageously for explosive and inflammable substances. In spite of these advantages, they are not used very widely, due to the high corrosion risk (resistant material and anti-corrosion treatment of the water should be employed — e.g. neutralization and inhibitors of corrosion) and partly to problems with freezing water in cold periods (in the case of an outdoor situation of the separator). A further disadvantage may be the cooling of gases and their consequent saturation with water vapour, which deteriorates their spread during the release. Considerable disadvantages are the necessary treatment of the resulting sludge and a high water consumption. For more details see references [6, 7, 9, 11].

The wet mechanical scrubbers include simple shower, vortex, foam, inertial, stream and rotational separators.

Spray scrubbers. The group of spray scrubbers includes the following two types: spray towers and spray chambers. Inertial forces are used during the dust separation. The separation efficiency in the spray chamber is increased by the long time of contact between the phases. It is affected by the height of the spray tower, which usually exceeds 15 m and by the gas stream velocity, varying between 0.1 and 1 m s^{-1}. The specific water consumption (expressed in l per 1 m^3 of gas to be purified), ranging between 1 and 5 l m^{-3}, is high. The separation efficiency does not exceed values of 90%.

In spray chambers, the drops are injected into the gas stream at a high velocity. The gas streams through the equipment at a velocity up to 3 m s^{-1}. The specific water consumption is lower than that in towers, ranging between 0.2 and 1 l m^{-3}.

Wet spinner scrubbers. Wet spinner scrubbers operate on the basis of the same principle as dry vortex separators, however, they are equipped with jets to spray water. The jets form a continuous film of water on the walls of the cyclone, thus making possible a removal of captured solid particles to the outlet neck of the scrubber. The gas temperature must not exceed 150°C. Types with an tangential inlet of the gas as well as those with an axial inlet (with the use of a spinner) are used. The specific water consumption is between 0.1 and 0.4 l m^{-3}, in the case of wet scrubber with the spinner, the separation limit is below 1.5 μm. The maximal input dust concentration is essentially lower as compared to dry vortex separators; and a value of 30 g m^{-3} should not be exceeded.

Wet foam scrubbers. In wet foam scrubbers, the gas streams through a gridded or perforated plate, on which the water is poured. At a certain stage in the operating regime, foam is formed and particles from the gas to be purified are retained on the surface of bubbles. The velocity of the gas stream through the perforated plate ranges from 0.5 to 2 m s^{-1}. The separation limit is between 2 and 3 μm. The specific water consumption is 0.1 to 5 l m^{-3} and the recommended dust concentration is 400 to 500 g m^{-3}. For intermediate sizes of dust particles, as high an efficiency as 97 to 99% is achieved.

The wet foam scrubbers can be used advantageously for retaining dust as well as gaseous pollutants. For this reason their wide use in the future is to be expected. For a more detailed description of their function see references [5, 6].

Wet inertial scrubbers. The inertial principle is used for the separation of dust particles in this type of scrubber. Sprayed layers of small objects or sprayed rods are used. This type of scrubber also includes units, where the stream of purified gas and a pressure difference force the water from the open surface into S-shaped slit, where it is mixed with purified gas.

The scrubber with a sprayed layer operates at gas velocities of about 3 m s^{-1} with a specific water consumption up to 1 l m^{-3} for dust concentrations up to 20 g m^{-3}.

In scrubbers with a liquid surface, the gas stream may be provided by the following two methods: in the first method, the flow direction is governed by paddles, onto which a portion of water from the level is transported by the action of the stream, and in the second method gas flows through slits to the liquid level. Advantage of these scrubbers are their high separation efficiency for submicron particles and low specific water consumption, usually 0.03 l m^{-3}.

Wet flow-through scrubbers. In wet flow-through scrubbers, also referred to as *Venturi scrubbers*, high separation efficiencies may be obtained even for particles of size 1 μm or even smaller. During the separation, the mutual agglomeration of two aerosols is used — dust particles in the polluted gas and the drops used for their separation. The process is accomplished in a Venturi tube (Fig. 5.15) into which water is supplied through jet or by a flow onto the walls of the tube. High relative velocities between the gas to be purified and water drops allow the achievement of high separation efficiencies. Uniform spraying of water over the whole cross-section is a basic requirement for a reliable functioning of the separator, but this

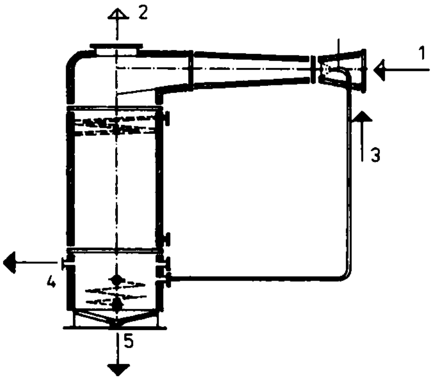

Fig. 5.15. Venturi scrubber. 1 — dusty gas inlet, 2 — clean gas outlet, 3 — water in, 4 — water out, 5 — dust

cannot be achieved in Venturi tubes of large diameters used for large flow rates, where it is necessary to use Venturi separators with a larger number of parallel Venturi tubes of small diameters. The separators are able to provide gas purification up to a temperature of 500°C. The considerable energy required, high water consumption and sludge formation are their disadvantages.

Wet rotational scrubbers. These operate on the basis of the same principle as dry rotational separators. Water is supplied into the rotor centre and it is sprayed by a perforated disc forming the rotor hub. They are characterized by a high separation efficiency for particles of a size of several micrometers. Their disadvantages are the high energy consumption, complicated design and problems with operating reliability. For these reasons they are seldom used and they are being gradually replaced by other types of separators.

5.4.4.3.3 Electric precipitators

In electric precipitators solid or liquid particles from gases are retained by the action of an electrostatic field. This field acts on charged particles, which are deposited on collecting electrodes. The particles gain their charge from gas ions formed in the precipitator during a corona discharge at sites with a high field intensity. The corona discharge is formed by applying high-voltage (40–80 kV) direct current to electrodes with different radii of curvature. The total separation efficiency in the electric separator (in the common planar arrangement) can be calculated from the semi-empirical Deutsch relationship

$$S_t = 1 - \exp\left(-\frac{LU_0}{Rv}\right)$$

where L is the precipitator operating length, R is the distance of the high voltage electrode from the collecting electrode, u is the mean separation velocity and v is the velocity of the gas flow in the precipitator. The separation velocity ranges between 0.03 and 0.3 m s^{-1}, depending on the granulometric composition of the dust to be separated.

Electric precipitators have many advantages and they are frequently used for the purification of gases from combustion and technology processes at high flow rates. They exhibit a high separation efficiency even for fine particles, a low energy consumption, low sensitivity to abrasion, and they can also be used at relatively high gas temperatures. Suitably qualified personnel for operating and maintenance are required. A disadvantage of these separators is their sensitivity to changes in the composition of particles to be separated, and they are unsuitable for the separation of dust with a high specific electric resistance. The input concentrations of the dust are about 20 g m^{-3}.

The *chamber precipitator* is the most frequently used type of electrostatic precipitator, as shown in Fig. 5.16 [13]. The gas polluted with dust enters into the space between the high-voltage and collecting electrodes. Here the particles acquire an electric charge and travel to the collecting electrode, from which they are removed by mechanical striking. Besides the electric chamber precipitators, *tubular electric precipitators* are also used. In this type, the high voltage electrode lies along the axis of a circular cross-section tube and the particles to be separated are deposited on the wall.

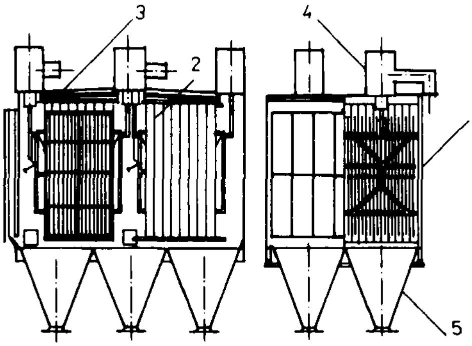

Fig. 5.16. Parallel-plate electrostatic precipitator. 1 — chamber, 2 — collector plate, 3 — discharge electrode, 4 — section switch box, 5 — dust collector

5.4.4.3.4 Industrial filters

Filtration is a process in which particles carried by a gas flow are retained on filtration material, and the purified gas after the passage through the filtration layer enters into the stack for emission into the atmosphere. Essentially all the physical processes involved in particle separation occur during the passage of the polluted gas through porous layers. Besides effects of inertial and gravitational forces, interception and electrostatic principles may be used. A coagulation of particles can also occur, which leads to a change of the dust granulometric composition at higher concentrations.

The filtration layer is characterized by the main functional parameters, i.e. pressure losses (including their changes with time, depending on the dust content) and total or fractional separation efficiency. The efficiency depends on the characteristics of particles to be retained, on the parameters of the gas to be purified, on the physical and chemical characteristics of the filtration layer and on its structure. It is represented by complicated functions of several variables. For the fractional separation efficiency of the filtration layer of a fibrous structure it is possible to write

$$S_t = 1 - \exp\left[-\frac{4(1-\varepsilon)S_{\mathrm{fi}}s}{\pi\varepsilon a}\right],$$

where ε is the layer porosity, S_{fi} is the separation efficiency of the fibre (determined from criterial dependences), a is the diameter of the filtration material fibres and s is the filtration layer thickness.

Filters may be divided into two basic types, depending on the method of the filtration material recovery — primary and secondary. *Primary filters* work under conditions of a continuous regeneration of the filtration material (input dust concentrations in g m^{-3}), and *secondary filters* operate with periodic exchanges of the filtration material after clogging (input concentrations in mg m^{-3}).

The structure of the filtration layer may be of various kinds, depending on the material and method of its treatment. Fibrous materials, granular layer and porous materials are used. Woven or bonded textile materials are used most frequently. Depending on the thickness of the filtration fibre, they are used for the retention of submicrometer to micrometer diameters of particles, the fibre thickness being in the range 2 to 10 μm. The filtration rates in the filtration layer are low, varying for different types between 0.01 and 1 m s^{-1}

Besides textile materials, wire mesh, perforated foils or mats consisting of woven fibres are used.

Simple filtration devices use an assembled arrangement of particular chambers, where the filtration material is situated in a suitable manner, or as plugs inserted into the polluted gas outlet tubing. The method of placing the filtration textile materials in filters and removing the retained layer of the dust considerably affects the design solution of main parts of the filter. Depending on the filtration material arrangement, *bag filters* may be classified *as pocket (sail), sleeve*, and *gusset.* During the filtration cycle the gas to be purified flows inside the tube, where it is filtered on the walls; during the cleaning cycle the filter is regenerated by reversing the air flow, by shocks of pressurized air or by combining various methods. For these reasons, interrupted operation of particular sections is necessary. For more detailed data on particular types of filters see references [4–6, 8].

The filters find their widest use when purifying waste gases as well as during the adjustment of the air quality for the ventilation and in industry. Due to the high separation efficiency achieved (usually of above 99.5% even for fine dusts), they are among the most efficient types of separating equipment. In spite of large initial costs, high operating costs and problems connected with reliability when the allowed temperatures are exceeded, their use is on the increase.

5.4.5 Processes and equipment for reducing gaseous emissions

The destruction and removal of pollutants occurring in exhalates is performed by *adsorption, absorption* and *catalytic processes*, by *combustion* or by *specific chemical processes.* The capture of harmful substances is often complicated on account of both the low concentrations of these substances in the gas and high flow rates.

The choice of the most effective process for capturing gases and vapours depends on several factors. From the technical standpoint, it is necessary to take into account the operating characteristics of the gas to be purified, the concentration, chemical and physical characteristics of substances to be separated as well as those of the remaining admixtures in the gas to be purified. The cost-effectiveness of the process is an essential factor, particularly the operating costs, and the consumption of energy and water. The question of environmental protection is also of importance in making the choice. The type and quality of wastes obtained must be taken carefully into account as regards the possibilities of their further use or their disposal.

5.4.5.1 Absorption

Absorption is here taken to mean the capture of a gaseous component in a liquid absorbent. The gas to be purified, containing a mixture of gaseous components comes into contact with the liquid phase during the absorption and in this process the substance penetrates in a direction governed by the concentration gradient. In general, the absorption of one component is accompanied by a desorption of the remaining components. Thus, the absorption liquid has to be chosen in such a way as to provide a sufficient selectivity, absorbing only the component which is supposed to be removed from the gas. The desorption of the captured component can be accomplished by various methods, for example by increasing the temperature, reducing the pressure or by using water vapour. The recovered liquid is returned to the process and the released concentrated gaseous component can be further utilized. The absorption of the component captured may be associated with a chemical reaction producing a new compound, which is removed from the solution by settling, expelling by the use of other substance, precipitation or decomposition. During absorption connected with a chemical reaction, a solution or a suspension is frequently employed as the absorbing medium.

The following criteria should be considered when selecting the washing liquid. It should be non-toxic, it should exert a low vapour pressure under given operating conditions, and it should be stable and readily available. Absorption can be used for capturing sulphur dioxide, hydrogen chloride, hydrogen fluoride, hydrogen sulphide, chlorine and nitrogen oxides.

During the desulphurization of combustion products, absorption is the only method which is widely used in practice. Suspensions of lime, limestone, magnesium oxide or alkalies are used most frequently.

A further field of use for absorption is the removal of odoriferous substances from waste gases by washing them with oxidizing solutions containing, e.g., hypochlorites, ozone or potassium permanganate, which convert the substances absorbed to non-smelling oxidized products. For the removal of several substances a multistep absorption may be employed, using different solutions to retain selectively particular components from the gas to be purified. Efficient deodorization may be achieved also by washing with water, oxygen and alkaline solutions. The odoriferous substances can also be destroyed by biological methods. A packed absorber is used, operating under conditions of countercurrent washing with water from the sewage treatment plant. In this way, smelling substances are on the one hand absorbed in water and, on the other, oxidized by biological processes, yielding non-smelling products.

Different types of absorbers are used for absorption. The most simple unit is an *absorbing tower* with sprayed liquid, with countercurrent motions of the gas and liquid. The efficiency depends on the size of drops produced and on the uniformity of their distribution in the tower. The absorber should be equipped with a drop separator. Low pressure losses and simple design are the advantage of this type of equipment.

Packed absorbers are used most frequently; one is shown schematically in Fig. 5.17. The efficiency depends on the total contact area and uniformity of wetting of its surface. The formation of the surface layer of the washing liquid on the filling is affected by the velocity of the gas stream, the absorption process being intensified by enlarging the area. The absorbers are usually characterized by high efficiency; the gas flow rate varies, depending on the type of packing used, from 1 to 3 m s^{-1}.

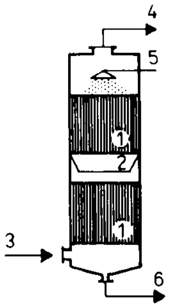

Fig. 5.17. Packed column. 1 — packing elements, 2 — gas distributor, 3 — gas in, 4 — gas out, 5 — liquid in, 6 — liquid out

Foam or plate absorbers are equipped with perforated plates, forming one or several stages. The washing liquid is maintained on the perforated plate by the gas streaming through it. At a certain gas flow rate a foam regime is established, providing a large contact area and thus also high separation efficiency. The absorbers operate with a water overflow, which may be achieved in the following two ways. The liquid streams down to a lower plate, either directly through the openings in the plate, or through an overflow opening connecting two neighbouring plates. With a sufficient number of plates and in the case of very soluble gases or in the case of absorption accompanied by a chemical reaction, a separation efficiency as high as 92 to 98% may be achieved.

A fairly considerable hydraulic resistance and sensitivity to fluctuations of the gas flow rate are disadvantages of the foam absorbers. The disadvantage may be partially overcome by using plates with adjustable openings, so that the free area of the plate is adjusted with respect to the amount of the gas to be purified. A more general use of these types of absorbers is forecast.

5.4.5.2 Adsorption

Adsorption is the process of concentration of gases, vapours or liquids on the surface of pores of solid materials, as a result of adsorption forces. Two types of the adsorption forces may be considered — physical and chemical. When the substance adsorbed is bound to the surface of the adsorption agent by intermolecular forces (particularly dispersion forces), the adsorption is of a physical nature. Chemisorption occurs when these forces have the character of chemical interactions. The adsorption process depends on the temperature, pressure and chemical composition of the adsorbed gas and adsorbing material. The adsorption is always connected with a release of adsorption heat (and thus an appropriate level of cooling should be provided for large adsorption units).

During the physical adsorption of a substance from the gas stream on the surface of porous sorbents several processes occur, the most important of them being as follows: The diffusion of molecules of substances adsorbed from the space between the granules to the external surface of the adsorbents — external diffusion, the diffusion of molecules of the substance adsorbed in the adsorbent pores — inner diffusion, and the adsorption itself. More details are given in the relevant literature [14].

The separation is not completed by the adsorption of a certain component from the gas to be purified; the second step is the recovery of the compounds from the adsorbent surface, accomplished by desorption. This involves the use of either water vapour, inert gas or the action of increased temperature and/or decreased pressures. All these effects may be used in combinations. The concentrate obtained is either returned to the production process or destroyed. In certain cases, the adsorbent is not recovered but is destroyed together with the substance adsorbed. The most extensively used *industrial adsorbents* are: charcoal, coke, semi-coke, natural zeolites, molecular sieves, silicagel, and activated alumina. The specific surface of adsorbents varies over a wide range, the common types of charcoal used, e.g., for capturing organic vapours having an active surface area of 600 to 1000 $m^2 g^{-1}$. In general, adsorbents used in technological operations, having a large specific surface, should have the following technical properties among others: Sufficient mechanical strength and wear resistance, and low pressure losses during the passage of the gas through the sorbent layer.

In practice, the adsorption process is used most typically for retaining vapours of solvents and different organic substances and it has also been applied for capturing SO_2, H_2S, CS_2, mercaptans, NO_x and HF. The adsorption is also frequently used for destroying odoriferous substances, where a very thin layer may be sufficient for their removal in the case of their low concentrations. Several types of unit are used for adsorption. As regards the sorbent layer and the recovery method, these may be divided into *adsorbers with a moving layer*, operating continuously, and *adsorbers with a discontinuous operation*, having a stationary adsorbent layer. The continuously operating adsorbent are designed with either a *moving or a fluidized bed adsorbent layer.* In the adsorbent with the moving layer, the adsorbent moves against the direction of the flow of the gas to be purified. The adsorbent recovery is provided for in a desorption section of the adsorption column or in an independent recovery unit, and the adsorbent recovered is transported to the initial section of the adsorption column. In the case of fluidized bed of adsorbent, the adsorbers are composed of two layers, one of them operating as an adsorption layer and the second as a recovery layer. A schematic diagram of the fluidized bed adsorber is shown in Fig. 5.18 [19].

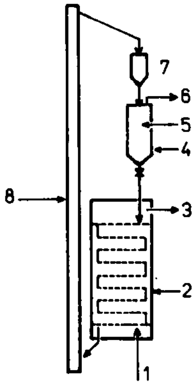

Fig. 5.18. Fluidized bed adsorber. 1 — impure gas inlet, 2 — adsorber, 3 — clean gas outlet, 4 — regenerating agent, 5 — regenerating bed, 6 — desorbed vapour, 7 — surge bin, 8 — elevator for saturated adsorbent

Adsorption units are usually not mass produced, they are supplied on the basis of experimental tests for the given technology. For the retention of organic substances, separation efficiencies exceeding 99% may be achieved [15, 16]. The input concentrations of the species to be extracted usually vary between several g per m^3 to several tens of g per m^3.

5.4.5.3 Combustion processes

Combustion processes may be used advantageously for the destruction of different organic, toxic or smelling substances, by their oxidation to carbon dioxide and water. They also find application for removing certain inorganic materials, which may be burnt to form other compounds which are non-hazardous from the hygienic standpoint. The combustion can be accomplished either directly or indirectly with the help of a catalyst.

Thermal combustion. In thermal combustion, the *combustion process* occurs either *directly or indirectly*, depending on the heating capacity of the mixture of the gases to be purified with air.

Direct combustion is achieved when the gas to be purified contains materials with heating capacity. The combustion process should be controlled in order to achieve complete combustion. This generally requires the presence of a sufficient excess of air, and temperatures above 800°C. Besides the excess air, which should constitute at least of 2 to 3 vol.%, the combustion also depends on the mixing ration gas/air, on the method of the air inlet and on the degree of mixing. In the case of burning organic substances with a high formula weight, hydrocarbons may polymerize and soot may be formed; this is limited by adding water vapour or water. Indirect combustion is brough about by adding an auxiliary fuel with a sufficient heating capacity or by preheating the gas to be purified to the combustion temperature.

If the efficiency of destruction of the harmful substance is to be above 90%, then the residence time of the pollutants in the oxidation zone should be approximately 0.5 s and the temperature must not decrease below its limit value (500 to 650°C for the combustion of hydrocarbons and 750°C in the presence of carbon monoxide); and the destruction of malodorous substances require temperature above 800°C. Such thermal combustion can be employed in petroleum refining plants and in the petrochemical industry, for removing hydrocarbons from final gases, for removing vapours of solvents in the chemical and woodworking industry, and in steel works, etc.

Catalytic combustion. In the course of catalytic combustion, complete and rapid combustion is achieved at essentially lower temperatures as compared to thermal combustion. High efficiencies (92–99%) are achieved at 400°C. Various types of catalysts are used during the combustion, either metallic catalysts (such as Pd, Pt) or different oxides deposited on carriers. The catalytic combustion process is very sensitive to operating temperatures, to the presence of catalytic poisons, and to the extent of dust removal from the gas to be purified. The effect of catalytic poisons depends on the type of the catalyst used; in general it can be said that catalysts are sensitive to the presence of compounds of arsenic, phosphorus, of halogens and their compounds, hydrogen sulphide, carbon monoxide, ammonia and other compounds. These factors can seriously affect the reliability of the operation.

The catalytic combustion processes may be used advantageously when removing smelling organic substances, for the destruction of vapours of organic substances used as solvents, and of phenol, formaldehyde, etc.

Catalytic reactions. Catalytic reactions in the gas phase are used for the oxidation, reduction or decomposition of many pollutants. The catalyst increases the chemical reaction rate, which makes it possible to reduce the temperature of the reaction and, depending on the conditions, to increase the reaction yield. The temperature decrease is of great importance, since in many cases it is unnecessary to supply heat to the system, thus significantly reducing costs.

Catalytic reactors are constructed either with the *catalyst fixed on a plate* or in *a fluidized bed.* For more detailed data concerning types and functions of catalytic reactors see, e.g., references [17, 18].

The catalytic processes are used for the gas purification in the chemical industry and in energy production. They have found extensive applications, for example, in the total or selective reduction for the removal of NO_x, when nitrogen oxides are reduced to form nitrogen. The efficiency of this process is high, in the case of removing NO_x in the production of nitric acid, it may be as high as 90–95%.

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5.5 The analysis of the atmosphere

Pollutants in the air are determined:
— in the free atmosphere,
— in enclosed spaces (housing, working areas), and
— at the localities of the release of harmful substances.

The determination of pollutants in the free atmosphere is the *analysis of imissions*; the determination at the locality of the harmful substance released is referred to as the *analysis of emissions.*

Analytical procedures used in these three fields of interest are very different from each other, particularly as regards the concentration ranges measured.

The imissions are measured at values in μg m^{-3}, mg m^{-3}, whereas in the case of the emissions the values are in g m^{-3}. The concentrations of pollutants in enclosed spaces (e.g. at work places) are between these two concentration ranges.

When following the emissions, the species and amount of the pollutant released from the source are determined, on the one hand depending on time (the periodicity of emissions) and, on the other hand, depending on the power output of the source (emission factor). It is assessed as follows:
— by a discontinuous measurement or continuous recording,

— by a calculation on the basis of the raw material or fuel balance or on the basis of average emission factors.

During the emission analysis itself, it is frequently necessary to analyse samples taken from flowing gas at a temperature of several hundred °C, under conditions of increased or decreased pressure, or possibly from a gas–dust system.

The imissions are measured under normal atmospheric conditions (pressure and temperature); the measuring conditions are determined by the ambient meteorological conditions.

In the measurement of imissions, problems of detection limits and of precision are encountered, and in the course of measuring emissions, it can be difficult to remove disturbing components, to establish temperature and pressure conditions and to take representative samples.

The choice of a suitable procedure is the first important step for obtaining accurate results in an air analysis (as is the case also for water analysis). The general procedure of analysis may be divided into the following stages:

- sampling and preliminary treatment of the sample for the analysis,
- a conversion of the component to be determined into the state where it can be detected or its concentration can be determined,
- the qualitative detection or quantitative determination itself,
- treatment of results obtained and their evaluation.

In this chapter, imission measurements will be the main focus of our interest.

5.5.1 Concentration units of gases and their calculation

In analytical practice, measurements in vol.% are most frequently used for expressing concentrations of gases in the air (or possibly their smaller analogues: ppm, ppb). Units of the type, weight per volume (g m^{-3}, mg m^{-3}, μg m^{-3}, ng m^{-3}) may also be used. In the case of all these concentration units, it is necessary to include data about the pressure and temperature in the record.

For a mass of gas of a volume V (m^3) and density ϱ (kg m^{-3})

$$m = V\varrho \qquad \text{(kg)}$$

The gas density ϱ may be expressed, from the equation of the state of an ideal gas, in the form

$$\varrho = \varrho_0 \frac{T_0}{p_0} \frac{p}{T} \qquad (\text{kg m}^{-3})$$

Table 5.29. Relationships between concentration terms for gases

	Vol. %	ppm	ppb	g m^{-3}	mg m^{-3}	μg m^{-3}	ng m^{-3}
Vol. %	1	10^4	10^7	$10^3 \cdot A \cdot \mathrm{const}$	$10^6 \cdot A \cdot \mathrm{const}$	$10^9 \cdot A \cdot \mathrm{const}$	$10^{12} \cdot A \cdot \mathrm{const}$
ppm	10^{-4}	1	10^3	$10^{-1} \cdot A \cdot \mathrm{const}$	$10^2 \cdot A \cdot \mathrm{const}$	$10^5 \cdot A \cdot \mathrm{const}$	$10^8 \cdot A \cdot \mathrm{const}$
ppb	10^{-7}	10^{-3}	1	$10^{-4} \cdot A \cdot \mathrm{const}$	$10^{-1} \cdot A \cdot \mathrm{const}$	$10^2 \cdot A \cdot \mathrm{const}$	$10^5 \cdot A \cdot \mathrm{const}$
g m^{-3}	$\frac{10^{-3}}{A \cdot \mathrm{const}}$	$\frac{10}{A \cdot \mathrm{const}}$	$\frac{10^4}{A \cdot \mathrm{const}}$	1	10^3	10^6	10^9
mg m^{-3}	$\frac{10^{-6}}{A \cdot \mathrm{const}}$	$\frac{10^{-2}}{A \cdot \mathrm{const}}$	$\frac{10}{A \cdot \mathrm{const}}$	10^{-3}	1	10^3	10^6
μg m^{-3}	$\frac{10^{-9}}{A \cdot \mathrm{const}}$	$\frac{10^{-5}}{A \cdot \mathrm{const}}$	$\frac{10^{-2}}{A \cdot \mathrm{const}}$	10^{-6}	10^{-3}	1	10^3
ng m^{-3}	$\frac{10^{-12}}{A \cdot \mathrm{const}}$	$\frac{10^{-8}}{A \cdot \mathrm{const}}$	$\frac{10^{-5}}{A \cdot \mathrm{const}}$	10^{-9}	10^{-6}	10^{-3}	1

$A = Mp/T$, where M is the formula mass in kg mol^{-1}, p — pressure in Pa, T — temperature in K, const = 1.203×10^{-6} K mol^{-1} m^{-3} Pa^{-1}.

where ϱ_0 is the gas density in the normal state, i.e. at $T_0 = 273.15$ K and pressure $p_0 = 101.325$ Pa.

The density ϱ_0 of an ideal gas, at normal temperature and pressure, can also be expressed as

$$\varrho_0 = \frac{M}{22.41} \qquad (\mathrm{kg\ m^{-3}})$$

This equation can also be used, with minor differences in practice, for non-ideal gases.

Combining the above three equations, the gas concentration c_m may be expressed as follows [1]:

$$c_m = \frac{c_{\%}}{100}\,\frac{M}{22.41}\,\frac{273.15}{T}\,\frac{p}{101.325} \qquad (\mathrm{kg\ m^{-3}})$$

and after a simple adjustment:

$$c_m = \mathrm{const}\ c_{\%}\frac{Mp}{T} \qquad (\mathrm{kg\ m^{-3}})$$

where const = 1.203×10^{-6} K kmol $\mathrm{m^{-3}}$ $\mathrm{Pa^{-1}}$, c_m is the gas concentration in kg $\mathrm{m^{-3}}$, $c_{\%}$ — the gas concentration in vol. %, M — the molar mass of the gas in kg $\mathrm{kmol^{-1}}$, p — the gas pressure in Pa, T — the gas temperature in K. The concentration of the gas in volume % may then be calculated as

$$c_{\%} = c_m\frac{T}{\mathrm{const}\ Mp} \qquad (\mathrm{vol.\%})$$

With respect to the fact that in analytical practice involving atmosphere analysis the volume % is too high a concentration unit, the units ppm (parts per million) and ppb (parts per billion) are still used. When presenting the gas concentration without a further specification, then by ppm we mean one millionth of the volume per total volume and by ppb we mean one milliardth of the volume per total volume. Thus, % by volume = 10^4 ppm = 10^7 ppb. Table 5.29 shows the relationships between the various units of gas concentration.

5.5.2 Air sampling

The accuracy and representative character of the eventual analytical results obtained depends considerably on the first stage of the analytical procedure — thorough and precise sampling. The fact that the total error of the determination E has a cumulative character which includes errors of particular operations $E_1, E_2, \ldots, E_n$ is a general feature of most analytical procedures, valid not only for air analysis [2]

$$E = \sqrt{E_1^2 + E_2^2 + \cdots + E_n^2}$$

This is particularly important in the case of an air sampling procedure, since the proper sampling of a gas is a difficult procedure with a wide range of possible errors. When planning and carrying out the sampling procedure, it is necessary to adhere particularly to the following principles:

(a) the sample should be representative with respect to the actual condition at the sampling site;

(b) the sampling method chosen should provide

— reliable measurements of the whole volume or flow rate of the air;
— efficient and stable absorption, adsorption, binding or fixation of the component to be determined (the absorption efficiency should not be less than 90%),
— a simple means of concentrating the component to be determined should be available,
— the method should have as high a selectivity as possible with respect to the component to be determined;

(c) the choice of the site, time and duration of sampling should correspond to the planned interpretation of results obtained.

Particular sampling methods are most frequently divided according two essential criteria. The first criterion is governed by the characteristics of the medium to be analysed and depending on this, we can consider *imission* and *emission* sampling methods. The second criterion is the characteristics of the substance to be determined; there are significant differences between the sampling of *gaseous components, solid particles* and *aerosols.*

A sampling device, regardless of the character of the carrying medium and component determined, should provide the following functions:

— an inlet for the air to be analysed,
— absorption, fixation or retention of the component to be determined,
— measurement of the total amount of the air analysed,
— an effective exhaust of the sampled air.

The arrangement of functional parts of a typical sampling device is obvious from the block diagram in Fig. 5.19.

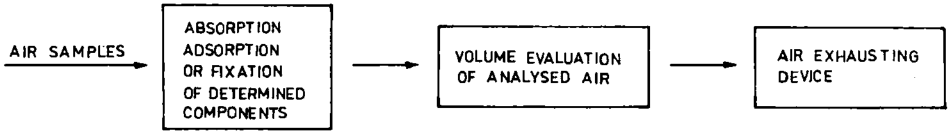


Fig. 5.19. Configuration of the sampling device

5.5.2.1 The imission sampling procedure for gaseous pollutants in the air

5.5.2.1.1 Analysed air inlet

The analysed air enters the sampling apparatus by as short a path as possible. The length of the inlet should not exceed 2 m. The material of the inlet pipeline or tube, with a common internal diameter of 5 to 10 mm, should be inert with respect to the component to be determined and it should not be charged electrostatically during the sampling procedure (to avoid dust deposition). Silica glasses, refined steels and glasses such as Rasotherm or Pyrex are most suitable for these conditions; teflon, polyethylene, polypropylene, poly(vinyl chloride) or silicon rubber can be used, but they are less suitable. The use of common rubber tubes is not permissible. The opening of the inlet pipeline or tube should be at a level of at least 1.5 m above the ground.

In certain cases it is necessary to include a filtration tube into the inlet pipeline. Its purpose is to prevent an entry of solid particles, to increase the sampling selectivity or to remove water from the sample analysed. The filling of usually small glass or polyethylene filtration tubes (150 mm long and 10 mm in diameter) is adjusted to the requirements of the analysis or possibly of the calibration of recording instruments. Different types of charcoal and silica gel are generally used.

5.5.2.1.2 Absorption or storage of the component to be determined

For the absorption of the component to be determined, liquid absorbents or solid adsorbents are used. The storage of the sample, mostly in a glass tube, is used less frequently.

For a good quality sampling procedure it is desirable to achieve the most efficient and most selective absorption or adsorption of as large volume of the component to be determined as possible in the shortest possible time.

Where *absorption solutions* are employed, they are contained in absorption vessels of different shapes and sizes to make the most effective contact between the absorbent and air sample. In recent times, for high quality sampling procedures, many types of glass impingers and sintered-glass or spiral absorbers have been proposed. Impingers and sintered-glass absorbers are essentially modified types of wash bottles.

Impingers make use of the inertial mass of the sample components to be separated, which strike either a perpendicularly oriented plate wetted with the absorption solution or the impinger bottom after their passage through a narrowed opening (nozzle), i.e. after acquiring a higher velocity. The distance between the nozzle opening and wetted target surface should be optimal in order to achieve as high an absorption efficiency as possible with a simultaneous maintenance of as high flow rate as possible; this distance is typically 2 to 5 mm.

Several types of impingers are used in different laboratories throughout the world. Some of them are named according to particular workers, such as the Polezhaev, Greenburg–Smith, Wilson and Zaitsev impingers [3, 4].

Absorbers with sintered glass make it possible to break up the sample into a large number of small bubbles released in the close vicinity of the moistened absorber bottom, thus providing the most efficient contact of a large number of bubbles of the air with the absorption medium.

It is also desirable to maintain as high a flow rate as possible.

Spiral absorbers are used less frequently; in their use, the air sample is moistened on the surface of a spiral glass tube filled with the absorption solution. Some new designs of spiral absorbers allow for a repeated absorption of the sample in a fairly small volume of the absorption solution, which makes it possible to concentrate the component to be determined.

By using appropriate absorption solutions, it is possible to retain and concentrate not only gases, but also finely dispersed solid and liquid particles, on the basis of different physico-chemical processes: by dissolving, chemical reaction, moistening, etc. The advantages of this method are as follows:

— the possibility of concentrating the components to be determined, which are usually present in low original concentrations,

— the possibility of selecting an absorption mechanism, which enables one to determine directly the concentrated component in the sample (titration, spectrophotometry, electroanalytical methods, etc.).

Figure 5.20 shows frequently used types of impingers. On the left, there is a low-volume microimpinger with an internal diameter of the sprayer of 1.0 ± 0.25 mm and with a distance between the sprayer opening and bottom 5.0 ± 0.5 mm. The maximal flow rate through different types of microimpingers does not exceed 5 l min^{-1}. On the right, there is a large-

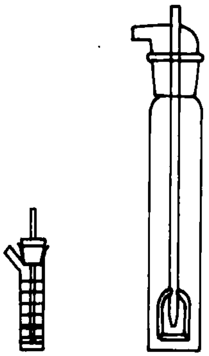


Fig. 5.20. Midget impinger and Greenburg–Smith impinger [5]

volume impinger with a moistened plate, developed by Greenburg–Smith, with an internal diameter of the sprayer of 2.3 mm and distance between the opening and target plate of 5 mm. A flow rate up to 20 l min^{-1} can be obtained in this impinger.

Figure 5.21 shows a standard Czechoslovak impinger and standard Czechoslovak absorber with sintered glass.

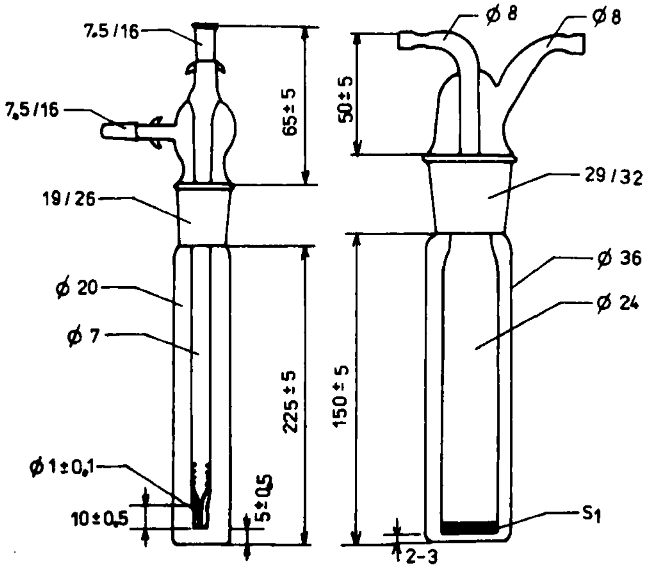


Fig. 5.21. Standard Czechoslovak impinger and standard Czechoslovak absorber with sintered glass (S_1). Dimensions in mm

In recent years, automatic sampling equipment has come into general use, and these include several absorption vessels generally eight in number connected in series, where the sampling procedure starts and terminates according to an automatic present programme, not requiring the presence of an operator.

Capturing the component to be determined on *solid adsorbents* has a number of advantages as follows:
- simple handling and transportation,
- high efficiency and selectivity in certain cases,
- the possibility of concentrating the component to be determined,
- the possibility of obtaining the component to be determined in its initial state.

Tubes 200 to 400 mm long and 5 to 10 mm in diameter are generally used as adsorption vessels. The choice of the adsorbent depends on the component to be determined and on the degree of moisture in the air sampled.

Among the various *polar adsorbents* metal oxides, particularly alumina and silica gel are used. Polar adsorbents are suitable for capturing the gases to be determined and vapours from the air in the case of low humidity. *Non-polar adsorbents*, particularly different types of charcoal may be used advantageously for long-term sampling of moist air, due to the low hydroscopicity and high adsorption capacity of charcoal. The adsorption capacity of charcoal depends on the critical temperature and boiling point of the gas to be retained [2].

Charcoal cannot be used for the adsorption of gases with a critical temperature below $-50°C$ and boiling point below $-150°C$; such gases include oxygen, nitrogen, hydrogen, and carbon monoxide. Gases with critical temperature between 0 and 150°C and boiling points between -100 and 0°C are adsorbable, although with a low efficiency (ammonia, hydrogen sulphide, hydrogen chloride, ethylene, formaldehyde, etc). In these cases the adsorption efficiency is increased by cooling the adsorption tube or the air sampled and by increasing the volume of the adsorbent. Vapours with boiling points above 0°C (inorganic as well as organic) are sorbed with a high efficiency on charcoal.

The efficiency of the adsorption of many gases on solid adsorbents may be increased by using specific impregnation substances. These are applied onto carriers or directly onto the charcoal. In this way it is possible to increase strongly, for instance, the adsorption efficiency for ammonia (with the help of bromine), formaldehyde (with the help of sodium sulphide) and hydrogen sulphide (with the help of silver cyanide or lead acetate).

The sampling procedure can also be performed by the simple *sucking of air into a gas tube* (volume generally below 2000 ml). The gas tubes are equipped by perfectly tight taps at both ends and they may be filled by one of two methods. The first method involves suction with the help of aspirators or more simple pumps. In this method of sampling it is usual to specify that at least a tenfold volume of the sample should be allowed to pass through the tube before sampling. The second method is based on filling a preliminarily evacuated tube with the sample. For this, tubes with smaller volumes are used and the air at the selected locality is sampled merely by opening one of the taps.

One of the most practicable procedures for analysis with the use of the gas tubes involves the addition of the reagent solution into the tube filled with the sample. After subsequent shaking of the contents of the tube, the component to be determined can be absorbed in the reagent solution and/or a chemical reaction may occur, making possible, for instance, a colorimetric determination. The absorption is frequently facilitated by addition of an inert foaming substance, such as certain arylalkylsulphonates and butanol.

In recent years, inflatable gas-tight plastic bags of volumes of 1 to 100 l are also used for taking and storing samples. The use of these bags has several advantages including their low weight, simple sampling and dosage of the sample, and lack of fragility. The selection of the plastic material presents certain problems, since besides possessing suitable physical characteristics it has to be inert with respect to the air components to be determined. Several materials are used in practice, however, each of them is characterized by certain drawbacks. The frequently used polyethylene and polypropylene films are not sufficiently inert to SO_2 and nitrogen oxides. A product of the Dupont Company is also used; this is a polyester foil, known under the commercial name Mylar, in which samples of air containing hydrocarbons, sulphur dioxide, ozone and nitrogen dioxide may be stored for several hours without observable changes.

When taking air samples which are not to be analysed immediately, then the sample temperature and water vapour concentration should be sufficiently far from conditions of the dew point. Water vapour would be otherwise condensed on the inner walls of sampling vessels, which could lead to a distortion of the analytical results.

5.5.2.1.3 The determination of the amount of the air analysed

The amount of the air analysed, i.e. the air drawn through the sampling apparatus, may be established in the following ways:

— by measuring the velocity of the air flow,
— by measuring the air flow rate,
— by measuring the air volume passed through the apparatus.

The amount of air measured in any of these ways is then re-calculated with respect to standard conditions, i.e. the corresponding dry air volume at 273.15 K and 101.325 Pa.

The velocity of the air flow is measured most frequently by thermo-anemometers. A sensitive semiconductor or resistance thermometric sensor is situated in the flow of the air sampled. The resistance of the sensor depends on the velocity of the air flow and the calibration is provided at a constant temperature with the help of a suitable flow meter. The disadvantage of the thermo-anemometers is the necessity for constant temperature for the period of particular sampling procedures and also the need for a time consuming calibration. Connection to a recorder is advantageous.

The measurement of the air flow rate is the most common method in practice, by using rotameters and cross-sectional or bubble flow meters.

The measurement of the flow rate by *rotameters* is based on measuring the position of a float, suspended by the flowing medium in a conically widened tube. The use of the rotameter in the system of a sampling apparatus carries several advantages including the minimal space it occupies, simple reading off of the measured value and negligible pressure losses. For these reasons, rotameters are the most frequently used devices for establishing the amount of the air analysed in commercially available instruments. The only problem is the need for extraordinary precision in making the float and calibrated tube to exact sizes. For this reason, the rotameter can be produced only in highly specialized workshops. The commercially supplied rotameters are mostly calibrated at 273.15 K and 101.325 Pa. Changes of temperature of the aspirated air by 1 K result in an error of approximately 0.4% in determining the flow rate.

Cross-sectional flow meters operate on the basis of determining a pressure difference between two positions with different cross-sections. The cross-sectional flow meters used in the laboratory consist of capillaries (cross-sections of 0.5–10 mm^2) and different types of open manometers filled with water, silicone oil or mercury. The flow rate of the measured medium through the capillary is essentially directly proportional to the pressure drop measured provided that the length of the capillary is greater than its diameter by a factor of at least 100.

Bubble flow meters are the simplest laboratory flow meters, suitable particularly for the calibration of the other instruments at very low flow rates. They are based on the determination of the velocity of the motion of soap bubbles driven by the gas measured, in a calibrated tube. They can be easily prepared from commonly used pipettes. An advantage is that their incorporation into the apparatus leads only to a negligible pressure loss. Their discontinuous operation is a disadvantage.

Out of the various other types of flow meters, we should mention briefly *instruments* operating *on the basis of heat transfer*, and *turbine flow meters.* The measurement of the gas flow rate, on the basis of heat transfer, depends on determining a temperature difference at ends of a metallic tube, one end of which is electrically heated. The temperature difference, depending on the flow rate, is measured by two thermoelements.

The essential part of the turbine flow meter is a small ferromagnetic turbine of a minimal weight situated in the tube and its revolutions, caused by the flowing gas are measured electrically. These flow meters are not widely used in analytical practice because of their high cost.

For the last of the three main methods, *the volume of the air passing through the apparatus* is measured under laboratory conditions by either wet or membrane gas meters [6].

Wet gas meters operate on the basis of gradual filling and emptying of four identical chambers situated radially with respect to the gas meter axis. The wet gas meter is filled with liquid (water) up to half its height, i.e. up to the level of the axis. The height of the level can be easily controlled and it plays a decisive role in the correct installation of a gas meter. During stepwise filling with the flowing gas, the chambers are lifted out of the liquid and their motion is transferred to a counter. The wet gas meters are equipped with a water level (for establishing their correct position), a thermometer and an open manometer (for relating the measured values to normal conditions). The wet gas meters can be used advantageously under laboratory conditions for a calibration of the other types of flow meters and for measuring volumes at flow rates of 5 to 1000 $\mathrm{l\ h^{-1}}$. They are not generally used under field conditions due to the problems of their installation.

Membrane (dry) gas meters are used for measuring volumes at high flow rates and for the measurements under field conditions. They include two chambers with movable partitions forming four measuring spaces. The partitions are membranes supported by a metallic sheet and their motion is transferred mechanically to a distributing mechanism. The distribution of the gas into particular measuring spaces is provided by a valve distribution system. Commonly produced laboratory gas meters may be used for measuring volumes at flow rates up to 20 $\mathrm{m^3\ h^{-1}}$ at an operation pressure up to 5 kPa. One disadvantage is that they have to be calibrated from time to time, generally against a wet gas meter.

5.5.2.1.4 Suction equipment

The procedure for the suction of samples, depending on the requirements of the sampling apparatus, is effected by the following devices:
— hand pumps,
— aspirators,
— water pumps,
— membrane pumps.

For taking fairly small sample volumes (up to 2 l), which are generally analysed simultaneously with the sampling procedure, *hand pumps* are frequently used (such as those supplied by the company Dräger). Large-volume syringes may also be used for such volumes.

For taking volumes of approximately 10 l, different *aspirator* systems [7] are used. The principle of their design and function is shown in Fig. 5.22.

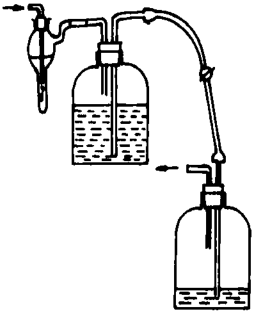


Fig. 5.22. Basic parts of an aspirator

The use of *water pumps* in sampling equipment presents no problems under laboratory conditions with respect to performance and the vacuum obtained. For safety reasons as well as the considerable water consumption, their long-term use is, however, avoided. Their principal disadvantage is that they cannot be installed under field conditions.

Membrane pumps are the most extensively used suction units commonly included in commercial sampling devices, and they operate with a range of power outputs. Czechoslovak membrane pumps (Chemoprojekt, Prague), Hungarian pumps of the type MIKI G-13 and membrane pumps from companies Hartmann–Braun and Austen are examples of such pumps in general use.

5.5.2.2 Sampling of solid pollutants and aerosols in imissions

The sampling of imissions for the determination of solid pollutants and aerosols is performed with similar instruments as for the determination of gases. The differences are only in the first two functional parts — in the method of providing the inlet of the air to be analysed and in the way of the absorption or fixation of the component to be determined (see Fig. 5.19).

The devices for imission sampling for the determination of solid pollutants can be divided into

- low-volume ones,
- high-volume ones,
- devices for capturing sedimenting dust (see Section 5.5.2.2.1).

The *low-volume sampling devices* are for aspirating similar amounts of the air analysed as those discussed in Section 5.5.2.1 in connection with sampling procedures for the determination of gaseous pollutants; the *high-volume* ones can handle 20 to 200 cm^3 of air per hour.

The inlet of the air to be analysed into the device should be as short as possible and it most frequently consists of only a sampling head with filter holders. The sampling head can be completely open so that the aspirated air passes through the filter without any inlet tubing. The size of the filter-holders depends on the size of filters used. Small-volume sampling devices are equipped with circular holders, 35, 50, 90 and 160 mm in diameter. Large-volume devices have larger holders. For example, the large-volume sampling device, type GMW 2000, made by General Metal Works, recommended by the World Health Organization and the World Meteorological Organization has a rectangular holder measuring 203 × 254 mm.

The holders and sampling heads are made of different alloys or plastics. The basic requirements for the holder quality are as follows:

- perfect sealing,
- analysis undistorted by the material used,
- sufficient mechanical support for the filter,
- simple connection to the suction device.

The absorption or *fixation* of solid pollutants and aerosols is generally accomplished on paper, membrane (nitrocellulose), polystyrene or glass-fibre filters. It should be noted that aerosols may also be sampled directly into absorption solutions (similarly as when sampling gaseous pollutants) and with the help of electrostatic precipitators; however, these methods are infrequently used in practice. Particular types of filters are selected depending on the type of the pollutants to be determined. The filter quality is considered from the standpoint of the pore size, efficiency of capture, hygroscopicity, resistance, content and type of impurities and method of the treatment prior to the analysis.

Membrane filters (Whatman 40, Whatman 41) have exceedingly low contents of impurities and ash. They can be easily mineralized and they exert a low filtration resistance. Their disadvantages are their high hygroscopicity and lower efficiency for the capture of particles of sizes below 1 μm.

Membrane filters (Sartorius SM, Synpor, Millipore) made of cellulose derivatives contain varying amounts of impurities and thus, before the sample analysis the given component should be determined in unexposed filters. Such membrane filters are very resistant to water, weak acids and bases, however, they are soluble in ketones, esters and alcohols. Their ashing is often carried out after solution in isopropyl alcohol.

Polystyrene filters (Microsorban-Sartorius) are characterized by a high efficiency of capturing particles below 1 μm, low filtration resistance and a fairly low content of impurities. Their disadvantage lies in their hygroscopic character.

Glass-fibre filters (Whatman GF-A, Sartorius SM 13 400, Gelman type A) are characterized by considerable mechanical strength and efficiency of capture, low filtration resistance and minimal hygroscopicity. For these reasons, they are considered high-quality filtration materials. Extraordinarily high contents of impurities, particularly of heavy metals can cause difficult problems, however, the use of glass-fibre filters is on the whole very advantageous and thus, they are widely used.

5.5.2.2.1 The capture of sedimenting dust

For the capture of the dust fraction from emissions with large particles (diameters of above 10 μm) it is possible to use:
— simple capturing devices with a horizontal opening,
— devices for capturing dust with an adhesive foil.

The equipment shown in Fig. 5.23 (a type standardized in England) consists of a funnel and collecting vessel. The instrument is fixed in a stand, so that the funnel opening is at a level of 1.5 m above the ground. The funnel is protected from birds by wire netting. Because the device also captures precipitations, the sample of solid particles is obtained by the filtration or by the evaporation of water.

Figure 5.24 is a schematic diagram of a device for capturing dust with an adhesive foil. A 0.07 mm thick aluminium foil 39 x 84 mm is fixed into a frame and vaseline is spread onto its surface (50 mg). The uniform spread

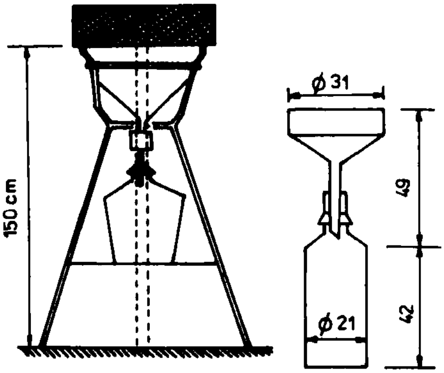


Fig. 5.23. Simple dust collector (English standard)

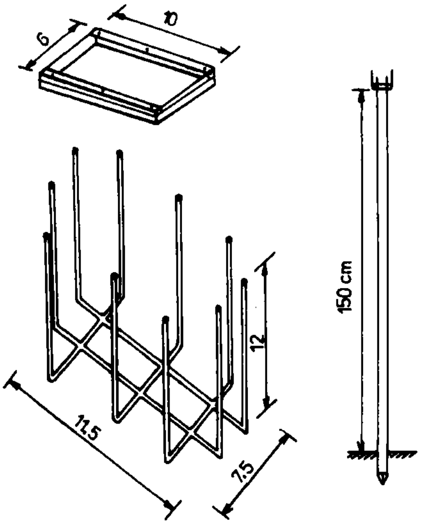


Fig. 5.24. Scheme of a dust collector with adhesive foil

of vaseline is facilitated by short heating. The foil is then exposed at the selected site.

5.5.2.3 Sampling of pollutants in emissions

Within the general field of analysis of air pollutants, we will mention only briefly the principles of air sampling for the case of emissions.

The basic condition for a correct sampling is its *isokinetic character*. This means that during the analysed air sampling procedure, the gas flow rate through the opening of the sampling apparatus (inlet tubing) should equal the gas flow rate at the site of the relevant industrial unit from which the sample is taken.

The sampling procedure calls first of all for determination of the streaming gas velocity profile. For this purpose, a dynamic velocity probe is used (Prandtl or Pitot tube). This determines the dynamic pressure value at a particular measured point of the given profile. The gas flow rate at the i-the point, v_i, is directly proportional to the square root of the dynamic pressure at the same point according to the relationship:

$$v_i = \sqrt{\frac{2}{\varrho} P_{\mathrm{d}_i}}$$

where ϱ is the streaming gas density, P_{d_i} is the dynamic pressure value at the i-th point of the tubing profile.

The cross-section of the tubing where the sample itself is measured and taken from is chosen at a position which is characterized by as steady and as uniform streaming as possible. Whenever possible, particularly a straight part of the tubing should be considered with a requirement that the smallest length of the direct tubing preceding the cross-section chosen should be twice as long as the internal diameter of the tubing (in the case of a circular cross-section) and that the length of the direct part of the tubing after the cross-section chosen should not be shorter than 1/2 of the cross-section.

5.5.2.4 The separation of aerosol fractions depending on particle size

In order to analyse particles of a certain size, which is frequently required, the sample should be divided into fractions immediately following the sampling procedure.

Cascade impactors are used most typically for this purpose. In such equipment, after an acceleration of the air stream in narrowed opening, the aerosol particles strike perpendicularly oriented plates and they are retained, depending on their mass, in particular stages of the impactor (Fig. 5.25). Larger particles and smaller particles are retained on higher and lower stages, respectively.

The Anderson cascade impactor (Fig. 5.26) is a well-known and frequently used device for the separation of aerosol fractions. Here, the aerosol passes stepwise through several plates with microscopic openings. After passing through a nozzle, the particle gains a high kinetic energy, depending on its mass. In this way, ever smaller particles are captured, the last

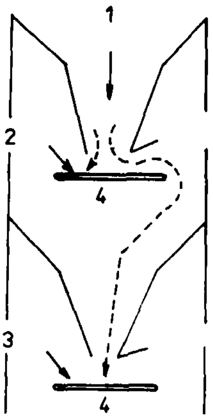


Fig. 5.25. Principle of a cascade impactor: 1 — aerosol particles, 2 —large particles, 3 — fine particles, 4 — collecting plate

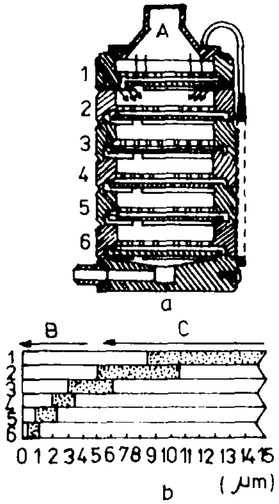


Fig. 5.26. Anderson cascade impactor: a — suctional view, b — characteristics of the separation of aerosol particles at different stages (1–6). A — air flow, B — health hazard region, C — safe area, penetration to lung is not likely

step being formed by a membrane filter, which retains the last fraction containing essentially only submicroscopic particles.

5.5.3 The determination of particular substances in the air

The sensitivities of classic analytical methods, particularly gravimetric and volumetric analysis are insufficient in the analytical chemistry of the atmosphere. Furthermore, in most cases, it is impossible to accumulate sufficiently large amounts of the sample, which would make it possible to use these classic methods. However, with the development of modern physical and physico-chemical methods of analytical chemistry it is now possible to perform very sensitive measurements of pollutants occurring in the atmosphere [16–19].

Colorimetric or *photometric measurements* are often used in the analytical chemistry of the atmosphere. *Chromatographic methods*, particularly *gas chromatography*, are used ever more frequently, being important particularly for the analysis of hydrocarbons and pesticides. *The emission spectral analysis* in the visible region, and in the infrared or ultraviolet regions of the spectrum may be used for as many as 70 elements. *Mass spectrometry* makes it possible to study new substances formed in the atmosphere by photochemical secondary reactions. The gas chromatographic method is often combined with mass spectrometry. *Atomic absorption spectrometry* is a very important development for the determination of metals. *Electrochemical analytical methods* (particularly coulometry and polarography) are frequently used for cases such as the determination of the whole spectrum of toxic metals in fly ash. *Stripping polarography* is very important. It may be used for determining trace amounts of elements that are able to form amalgams, such as copper, lead, thallium, zinc, cadmium, tin, antimony, gallium, germanium, and bismuth. Coulometry finds ever wider application in the determination of SO_2.

Nuclear analytical methods, particularly *activation analysis* and *radionuclide X-ray fluorescence analysis* are frequently used in the analysis of atmospheric aerosols.

The long-term goal of the chemistry of atmospheric aerosols is to establish analytical methods for determining the chemical composition of particular submicrometric particles. At the present time, this requirement is partially satisfied by two methods — *electron* and *ion microprobes*, which are based on the analysis of a point-concentrated electron or ion beam. By use of the ion microprobe it is possible to determine essentially all the elements, whereas the electron microprobe is suitable only for elements with a greater atomic mass than sodium.

The recommended units for expressing the levels of air pollutants are μg m^{-3} [8] for gases and vapours; μg m^{-3} for the weight of particulate matter; for particulate matter count, number per cubic metre; for visibility, kilometres; and for emission and sampling rates, m^3 min^{-1}. Air volumes should be converted to conditions of 10°C and 101.3 Pa, assuming ideal gas behaviour.

The air pollutants generally determined may be grouped into five categories [9]:

Table 5.30. National air quality standards [10]

Pollutant	Averaging time	Primary standard	Secondary standard
Sulphur dioxide	Annual arithmetic mean	80 μg m^{-3}	—
	24 hours	365 μg m^{-3}	—
	3 hours	—	1300 μg m^{-3}[a]
Nitrogen dioxide	Annual arithmetic mean	100 μg m^{-3}	100 μg m^{-3}
Carbon monoxide	8 hours	10 mg m^{-3}	10 mg m^{-3}
	1 hour	40 mg m^{-3}	40 mg m^{-3}
Hydrocarbons (exclusive of methane)	3 hours	160 μg m^{-3}	160 μg m^{-3}
Particulate matter	Annual geometric mean	75 μg m^{-3}	60 μg m^{-3}[b]
	24 hours	260 μg m^{-3}[a]	150 μg m^{-3}[a]

[a] Not to be exceeded more than once a year.

[b] Annual geometric mean, to be used in assessment of industrial plants to achieve the 24-hour standard.

(1) Pollutants for which ambient (surrounding atmosphere) standards have been set by the Environmental Protection Agency [10], as summarized in Table 5.30. The standards are classified as primary (defining the level of air quality necessary to protect public health) and secondary (designed to provide protection against known or expected adverse effects of air pollutants upon materials, vegetation, animals, etc.).

(2) Pollutants specifically hazardous to human health, for which ambient air quality standards are not applicable (asbestos, Be, Hg, etc.).

(3) Pollutants regulated in new installations of selected stationary sources, such as coal-cleaning plants, cotton gins, lime plants and paper mills (e.g. NO_x, SO_x, particulate matter, acid mist).

(4) Pollutants from the emissions of motor vehicles that are now regulated (CO, NO_x, hydrocarbons).

(5) Pollutants studied to determine the degree to which they should be controlled and the best method of control for each (As, Cd, Ni, Cr, V, Mn, Li, Cu, Zn, Ba, Sn, Se, F, Cl_2, HCl, H_2S, B, P, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, pesticides, radionuclides, etc.).

Much of the remainder of this chapter is devoted to a brief survey of analytical methods for most of the species mentioned above. A summary of instrumental techniques for air monitoring is presented in Table 5.31.

Table 5.31. Instrumental techniques for monitoring elements in atmospheric pollutants and gaseous air pollutants

Method Pollutant	Amperometry	Atomic abs.spectrometry	Chemiluminescence	Conductometry	Catalytic oxidation	Chromatography	Emission spectroscopy	Flame photometry	Infrared absorption	Manual wet chemistry	Mass spectrometry	Neutron activation analysis	Photometry	Potentiometry	Tape samplers	Ultraviolet absorption	Ultraviolet emission	Sulphation plates and PbO_2 candle	X-ray fluorescence
As		×										×	×						×
Ba		×					×												×
B		×																	
Be		×					×						×						
Cd		×					×						×						×
Cr		×					×					×							×
Cu		×					×					×							×
Fe		×					×					×							×
Li		×					×												
Mn		×					×					×	×						×
Pb		×					×						×						×
Ni		×					×												×
Hg		×										×	×						×
Sb												×	×						×
P		×																	
Sn							×												×
Zn		×					×												×
V							×					×	×						×
Se												×	×						×
F																			×
CO					×	×			×										
CO_2						×			×										
SO_2	×			×		×		×	×				×	×		×	×	×	
NO, NO_2	×		×						×				×	×		×			
Oxidants (O_3)	×		×										×			×			
Hydrocarbons	×					×			×		×		×			×			
H_2S						×									×				
Mercaptans						×													
HCl										×									
Cl_2										×									
NH_3										×			×	×					
Gaseous fluorides														×					
Gaseous PAH						×					×								
Gaseous silicates						×													
Volatile pesticides						×					×								

5.5.3.1 Sulphur dioxide

The *Weast-Gaek method* [2, 11–13]. Sulphur dioxide is absorbed in $Na_2(HgCl_4)$ solution with an admixture of chelaton III (to prevent the catalytic oxidation of sulphur oxide, catalysed by heavy metals) in the form of a dichloro–sulphito–mercurate complex:

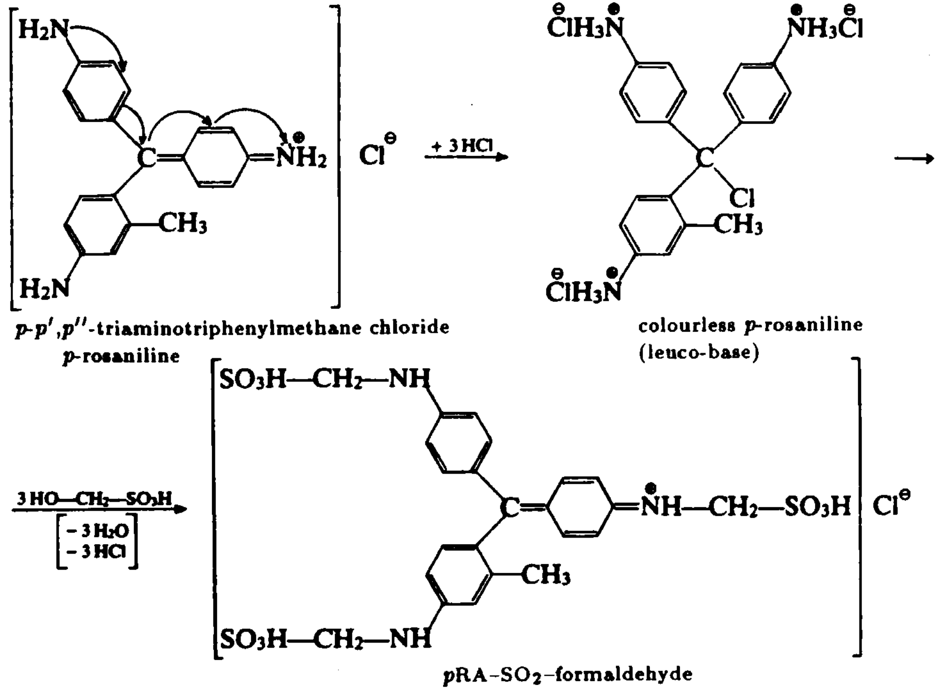
$$(HgCl_4)^{2-} + \overset{1.}{\boxed{SO_2}} + H_2O = (HgCl_2SO_3)^2 + 2Cl^- + 2H^+ \qquad \text{(I)}$$

This complex with *p*-rosaniline or *p*-fuchsine and formaldehyde yields a red-violet colour, which may be used for a spectrophotometric measurement

$$[HgCl_2SO_3]^{2-} + \overset{2.}{\boxed{HCHO}} + 2H^+ = HgCl_2 + \underbrace{HO\text{-}CH_2\text{-}SO_3H}_{HM\text{-}SO_2} \qquad \text{(II)}$$

$$\overset{3.}{\boxed{pRA}} - HM\text{-}SO_2 pRA\text{-}(HM\text{-}SO_2)_2, pRA\text{-}(HM\text{-}SO_2)_3 \qquad \text{(III-V)}$$

Structural formulae:



p-*p*′,*p*″-triaminotriphenylmethane chloride
p-rosaniline

colourless *p*-rosaniline
(leuco-base)

*p*RA-SO2-formaldehyde

The light absorption of the product is measured by a spectrophotometer at 540 to 580 nm. The calibration curve is prepared with the help of Na_2SO_3 or $K_2S_2O_5$ solutions. The method is suitable for determining SO_2 in a concentration range of 0.015 to 15 mg m^{-3}. It is very selective, it is time consuming, however, it can be automated.

The *polarographic determination* is based on a reduction of sulphur dioxide in acid medium to sulphoxylane ions SO_2^{2-}. The height of the polarographic wave is proportional to the sulphur dioxide concentration.

Several types of sulphur dioxide monitors are based on amperometry, in which an electrical current, that is proportional to the SO_2 concentration in a collecting solution, is measured [9]. Commonly, sulphur dioxide reacts with bromine in solution, causing a change in a measuring electrode potential:

$$SO_2 + Br_2 + 2H_2O \quad \rightarrow \quad H_2SO_4 + 2HBr$$

The potential is restored to its original value by regenerating Br_2 electrochemically and measuring the current required for the regeneration.

In the conductometric determination, sulphur dioxide is collected in a hydrogen peroxide solution and the increased conductance of the sulphuric acid solution ($SO_2 + H_2O_2 \rightarrow H_2SO_4$) is measured.

The combination of conductometry with ion chromatography is also used for SO_2 determination. The method consists of bubbling the gas through hydrogen peroxide solution, followed by determination of the sulphate by ion chromatography, a method that separates ions on a chromatography column and detects them by conductivity measurement [14].

Gas chromatography [15], flame photometry [9] and sometimes flame photometry in combination with gas chromatography are used for the detection of sulphur dioxide and other gaseous sulphur compounds. The gas is burned in a hydrogen flame, and the sulphur emission line at 394 nm is measured.

Several direct spectrophotometric methods are used for the sulphur dioxide measurement, including non-dispersive infrared absorption, ultraviolet absorption, molecular resonance fluorescence and second-derivative spectrophotometry.

Cumulative effects of SO_2 (e.g. corrosive effects) are determined by a cylinder with a surface area of 100 cm^2 coated with PbO_2 paste (a sulphur candle method). Lead sulphate is produced by action of SO_2 ($PbO_2 + SO_2 \rightarrow PbSO_4$), which is determined after a 30-day exposure [10, 11].

5.5.3.2 Sulphuric acid mist

Photometric determination. The sulphuric acid aerosol captured on a paper or membrane filter and dissolved in water releases from insoluble barium chloranilate an equivalent amount of red-violet chloranilate ions, which are suitable for a spectrophotometric determination [18].

Nephelometric and turbidimetric determination. The sample is collected in a bubbler containing water and isopropanol, and the sulphate content is determined turbidimetrically or nephelometrically after addition of $BaCl_2$ [13].

A further possibility for determining sulphuric acid is based on the classical method involving titration with sodium hydroxide.

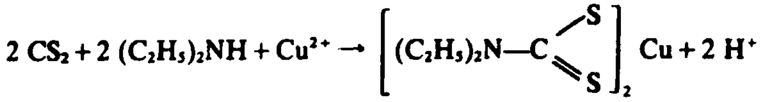
5.5.3.3 Hydrogen sulphide

Spectrophotometric determination. Hydrogen sulphide is captured in a zinc acetate solution with an admixture of N,N-dimethyl-p-phenylenediamine and an iron(III) salt, forming Methylene Blue. This compound is determined by spectrophotometry at 670 nm [20].

Hydrogen sulphide can also be determined by gas chromatography [15].

5.5.3.4 Carbon disulphide

Carbon disulphide reacts with diethylamine to form diethyldithiocarbamate, which yields a yellow-brown colour with copper ions,

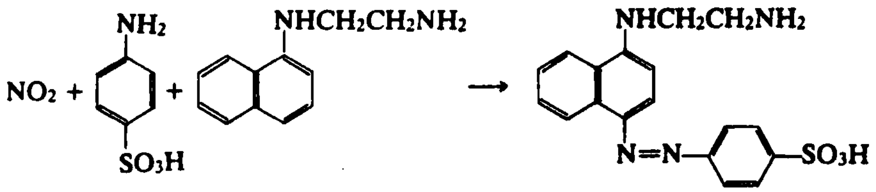


$$2\,CS_2 + 2\,(C_2H_5)_2NH + Cu^{2+} \rightarrow \left[(C_2H_5)_2N{-}C\begin{smallmatrix}\diagup S\\ \diagdown\!\!\!\diagdown S\end{smallmatrix}\right]_2 Cu + 2\,H^+$$

which may be measured by a photometer [18].

5.5.3.5 Nitrogen oxides

The Saltzman method [21, 22]. Nitrogen dioxide, when passing through an acid solution of sulphanilic acid and N-(1-naphthyl)ethylenediamine yields a pink azo dye



The intensity of the colour is proportional to the nitrogen oxide concentration (to be measured at 545 nm). The method may be used over a wide concentration range, from several μg to 10 mg m^{-3}. The method is very selective in the presence of other nitrogen compounds; a fivefold excess of ozone or tenfold excess of SO_2 exert negligible effects. The standardization presents the most serious problem. It was found experimentally that 1 mol of nitrogen dioxide gives the same effect as 0.72 mol of sodium nitride, which is typically used as a standard. Thus, the results based on the calibration with sodium nitrite are multiplied by a correction factor. Teflon tubes are suitable for the calibration procedure.

The determination of mixtures of nitrogen oxides. A mixture of nitrogen oxide and nitrogen dioxide is absorbed in an alkaline hydroxide solution, forming nitrites and nitrates:

$$\begin{aligned} 2NO_2 + 2NaOH &\rightarrow NaNO_2 + NaNO_3 + H_2O \\ N_2O_4 + 2NaOH &\rightarrow NaNO_2 + NaNO_3 + H_2O \\ NO_2 + NO + 2NaOH &\rightarrow 2NaNO_2 + H_2O \end{aligned}$$

Nitrates are reduced with hydrazine, via the catalytic action of a copper salt, to nitrites. The total amount of nitrites is established by a diazotization of the sulphanilic acid and coupling with 1-naphthylamine to red azo dye (to be measured at 530 nm) [12].

Among other methods is that based on the chemiluminescent reaction of nitrogen oxide with ozone:

$$\begin{aligned} NO + O_3 &\rightarrow NO_2^* + O_2 \\ NO_2^* &\rightarrow NO_2 + h\nu \end{aligned}$$

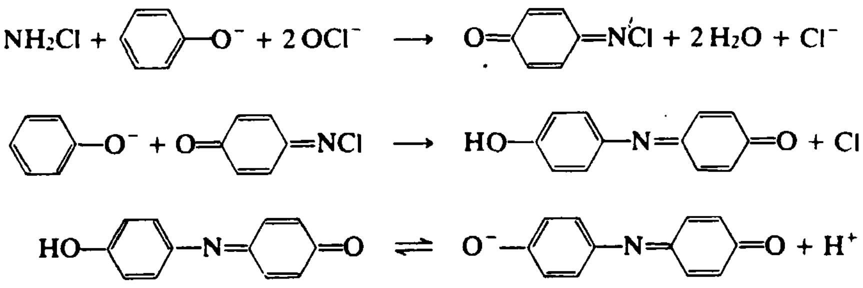
The resulting photoluminescence is detected by a photomultiplier [17]. The reaction is specific for NO. Nitrogen dioxide may be determined in this way after a catalytic conversion to NO. This method allows for a continuous recording of nitrogen oxide concentration. Nitrogen dioxide can also be determined on the basis of molecular fluorescence, involving excitation by a He-Cd laser and measurement of the resulting photon beam. The method is specific for NO_2.

5.5.3.6 Ammonia

Ammonia is absorbed in 0.05 mol l^{-1} H_2SO_4 and the resulting ammonium salt gives a yellow colour after adding Nessler's reagent (for details see p. 304).

Other methods are based on the formation of indophenol dyes from ammonia and phenol with an oxidizing agent in alkaline medium. For example, the formation of blue indophenol (spectrophotometric determination at 630 nm):

$$\begin{aligned} 2NH_3 + H_2SO_4 &\rightarrow 2NH_4^+ + SO_4^{2-} \\ NH_4^+ + HOCl &\rightarrow NH_2Cl + H_2O \end{aligned}$$



5.5.3.7 Chlorine

The *photometric determination* is based on the discoloration of an acid methyl orange solution by the action of chlorine. The decrease of the colour intensity is proportional to the amount of chlorine; the measurement is made at 553 nm [18].

Polarographic determination. Free chlorine oxidizes iodides to iodates in moderately alkaline medium (pH 10), which are determined by a polarographic method.

5.5.3.8 Fluorides

Fluorides and hydrofluoric acid are absorbed in a sodium hydroxide solution and released by distillation from sulphuric acid medium at 135°C. The interfering sulphate ions are removed by a barium salt and the determination itself is performed by a titration with thorium(IV) nitrate and sodium alizarinesulphonate [20].

Further procedures are based on a discoloration of organic dyes with zirconium(IV) salts (zirconium-eriochromcyanine R), leading to the formation of a blue fluoride complex with trivalent lanthane and alizarine complexone, or they depend on the measurement with a fluoride ion selective electrode based on lanthanum fluoride [18].

5.5.3.9 Carbon monoxide

The air to be analysed, at 130 to 140°C, is drawn through a iodine pentaoxide layer, where iodine is released by action of carbon monoxide. It is captured in an arsenite solution and determined by back titration with iodine [18].

Another method is based on the reaction of CO with an alkaline solution of the silver salt of *p*-sulphoaminobenzoic acid [24]. Colloidal silver obtained is evaluated quantitatively by a spectrophotometric method. Interfering substances present in significant amounts, such as acetylene, olefins, H_2S and aldehydes are removed by drawing the air to be analysed through a silica gel filter containing H_2SO_4.

Carbon monoxide may be determined over a wide range of concentration via infrared analysis [25]. Good results are achieved at concentrations as low as 1.25 to 2.5 mg m^{-3}. The main disadvantage of this technique is the non-linear response, as well as possible interference by CO_2, water vapour and hydrocarbons. The use of the gas chromatography for determining CO includes a catalytic reduction system, which converts carbon monoxide quantitatively to methane and a flame ionization detector. For a rapid CO determination, indicator tubes with palladium salt as a catalyst and silicomolybdate complex, which yields a blue colour with carbon monoxide, are used. The CO determination can also be carried out on the basis of its reaction with the radioactive kryptonate of palladium chloride [18, 25].

5.5.3.10 Formaldehyde

Photometric determination. Formaldehyde yields a red-violet colour with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) in concentrated sulphuric acid, its intensity being proportional to the concentration of formaldehyde. The measurement is made at 560 nm [23].

5.5.3.11 Phenols

Photometric determination. The phenols are absorbed in a sodium carbonate solution. A red colour of a relevant azo dye is induced by addition of diazotated *p*-nitraniline, and may be evaluated by photometry [18].

Phenols can also be determined on the basis of their oxidation condensation with aromatic amines to indophenol dyes or by *gas chromatography.*

5.5.3.12 Mineral acids

Solutions of strong mineral acids (H_2SO_4, HCl, HNO_3) change the yellow colour of neutral methyl red solution to a pink colour. The colour intensity is proportional to the concentration of hydrogen ions of mineral acids in the atmosphere. The results are presented in mg m^{-3} H^+ [18].

5.5.3.13 Benzene

Benzene vapours are captured in a nitration mixture ($H_2SO_4 + HNO_3$). On heating, dinitrobenzene is produced, which reacts with methyl ethyl ketone in alkaline medium, yielding a red-violet colour, which is evaluated by *photometry.*

In the determination of benzene, interfering effects of dinitrotoluene and dinitroxylenes originating from toluene and xylenes are removed by oxidation of methyl groups with a chromic acid solution. Dinitrobenzene is stable during this oxidation process. After adding pyridine and alkalization of the diluted nitration mixture, the two layers are separated from each other. Sodium salts of nitrocarbonic acids formed by the oxidation remain in the aqueous layer, whereas *m*-dinitrobenzene passes into the pyridine layer. The pyridine layer is separated, methyl ethyl ketone is added and the red-violet colour is evaluated by *photometry* [18].

After a suitable concentrating procedure, benzene can also be determined by *gas chromatography* [25].

5.5.3.14 Lead

Polarographic determination. The air aerosol is retained on a membrane filter, which is then mineralized with a mixture of sulphuric acid and nitric acid. In the solution, lead is determined by a polarographic reduction of the lead salt on a mercury drop electrode in a medium of alkaline hydroxide and cyanide [18].

Photometric determination. The air aerosol is captured with the use of a membrane filter or in a nitric acid solution. In the case of the membrane filter, the mineralization is performed as in the preceding case. Solutions are evaporated to dryness, the dry residue is eluted with nitric acid and a reaction with dithizone and extraction with chloroform is performed in alkaline medium. The intensity of the red colour obtained is proportional to the lead concentration. The measurement is made at 520 nm [26].

5.5.3.15 Manganese

The airborne aerosol is filtered and after the filter mineralization, manganese is determined in the solution by a *spectrophotometric method* following oxidation with periodate in acid medium to the red-violet MnO_4^- anion

$$2Mn^{2+} + 5IO_4^- + 3H_2O = 2MnO_4^- + 5IO_3^- + 6H^+$$

5.5.3.16 Arsenic

Spectrophotometric determination. The airborne aerosol is filtered and after the filter mineralization, arsenic compounds are reduced with zinc in HCl medium to arsine. Arsine with a solution of silver diethyldithiocarbamate in pyridine yields a red colour, which is suitable for spectrophotometric determination. The measurement is made at 540 nm [26].

5.5.3.17 Soot

The soot is retained on paper or membrane filter. The degree of the filter blackening, which is proportional to the amount of the soot is ascertained by comparing it with a scale prepared from a suspension of pure soot.

Photometric determination. The filter blackening can also be measured by a photometric method. Free carbon is frequently determined for the indication of the soot. Impurities of a biological character, such as pollen grains, are removed by hand or by special procedures.

5.5.3.18 Suspended dust

Suspended dust is retained on a membrane filter and its amount is ascertained from the increase in mass of the filter [27].

5.5.3.19 Sedimenting dust (dust fall-out)

The sedimenting dust is collected over a period of 1 month in glass vessels containing water (in winter, a mixture of water and alcohol) mostly free-standing at the locality of interest. After exposure, the liquid is evaporated and the vessel is weighed.

It is useful to perform a further analysis of the retained sedimenting dust. Even a simple separation of the sample into fractions (water-insoluble, water-soluble and benzene-soluble fractions) yields very useful data about its general character.

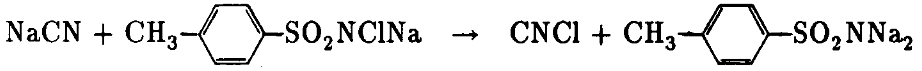
Chemical analysis provides much more precise data about the sample, particularly the determination of metallic elements, mainly lead, cadmium, iron, calcium, sodium as well as anions, chlorides, fluorides, nitrates, carbonates and sulphates. The analyses are performed most frequently by spectrophotometry, atomic absorption spectrometry, or polarography; in recent years radionuclide X-ray fluorescence and activation analysis have been used.

5.5.3.20 Free silicon dioxide in the dust fall-out

Spectrophotometric determination. In the sample of the dust fall-out, silicon dioxide is transformed into a solution by melting with a mixture $NaHCO_3$ + NaCl. The silicic acid formed yields Molybdenum Blue by reaction with ammonium molybdate and the concentration is determined by spectrophotometric measurements. The portion of amorphous silicon dioxide is dissolved by boiling with NaOH solution and the determination is performed in the same way as mentioned above [18].

5.5.3.21 Hydrogen cyanide

Hydrogen cyanide is absorbed in an NaOH solution to form NaCN, which reacts with chloramine-T (*N*-chloro-*p*-toluenesulphonamide), forming chlorocyane



The cyanopyridine cation is obtained by the addition of chlorocyane to pyridine. During its hydrolysis, the pyridine ring is opened, forming glutacone aldehyde $OCH{-}CH{=}CH{-}CH_2{-}CHO$. This reacts with barbituric acid to form a colour whose intensity is proportional to the hydrogen cyanide concentration [18].

5.5.3.22 Ozone and oxidizing agents

Oxidizing agents are frequently determined by *iodometric procedures.* By the action of oxidizing agents on potassium iodide solution at pH 6.8, iodine is released, which is determined by a spectrophotometric measurement at 352 nm [22, 28, 29].

An ozone analyser operates with a high degree of the selectivity, based on a chemiluminescent reaction [15, 30]. Rhodamine B, adsorbed on silica gel is applied onto a disc, which is then exposed to air containing ozone. Radiation emitted is detected by a photomultiplier. Ozone can be determined on the basis of the ozonolysis of 4-4$'$-dimethylstilbene to yield anisaldehyde, which is determined by a spectrophotometric measurement at 510 nm [31].

5.5.3.23 Hydrocarbons

Light hydrocarbons C_1–C_4. Light hydrocarbons are frequently determined in the atmosphere, since some of them contribute to photochemical smog formation. In most cases, data are required about the concentration of particular components and thus, the analysis is performed on *gas chromatographs*, equipped with a flame ionization detector. The light hydrocarbons should be concentrated, usually by a polymer sorbent [32], prior to the analysis.

Chlorinated hydrocarbons. The total amount of chlorinated hydrocarbons in the atmosphere may be determined by a *combustion method* (combustion at 850 to 900°C; Pt catalyst). The combustion products are absorbed in a sodium arsenite solution. The chloride formed is determined by a *polarographic method* and in the case of higher concentration by *argentometric titration.*

In another method, an intense reaction of diphenylsodium in non-polar organic solvent with chlorinated hydrocarbons is used. The amount of the NaCl released is determined by a *photometric measurement* after evaporating the organic solvent. The procedure is suitable for the determination of tetrachloromethane, tetrachloroethylene, chloroform, trichloroethane, hexachlorocyclohexane, *p*-dichlorobenzene and some other chlorinated hydrocarbons [8, 9, 18, 20, 25].

Polychlorinated biphenyls (PCB) are determined by photometric or gas chromatographic methods. In the former method, the polychlorinated biphenyls are determined by spectrophotometry indirectly, via mercury rhodanide after their mineralization with metallic sodium in ethanol. In the latter determination, a flame ionization detector is used [33].

Polycyclic aromatic hydrocarbons (PAH). The PAH determination usually requires the following steps: sampling procedure, PAH concentrating procedure and the determination itself. The choice of methods in these particular steps is affected by the type of the sample and by the purposes of the analysis as well as by the equipment available in the laboratory. Some of these steps may be omitted in certain cases.

The polycyclic aromatic hydrocarbons in the atmosphere are mostly adsorbed on solid particles and thus, the sampling procedure is mainly a matter of retaining these particles on suitable filtration materials (preferably glass fibres). The extraction of the filters with retained particles in a Soxhlet extractor with the use of benzene as the extraction agent is the most frequently used isolation method. In the extract separated from the sample, a number of substances are present besides the PAH, which may interfere with or even render impossible the analysis itself. For removing these substances, liquid-liquid extraction, column chromatography, thin-layer chromatography or gel chromatography are most frequently employed. For the identification and determination of particular PAH in the preliminarily purified extracts, gas chromatography, liquid chromatography, electron spectrometry and mass spectrometry methods may be used. Combinations of chromatographic and spectral methods give the most reliable results [32].

5.5.3.24 Asbestos

The sample is collected with a high-volume sampler on microsorban paper. The paper is dissolved in benzene and the inorganic residue is analysed by X-ray diffraction and optical microscopy [34].

5.5.3.25 Airborne radioactivity

For the analysis of air samples, a number of approaches are possible [35]:

(1) direct emanometric determination with large volume (20 l) differential ionization chambers which permit measurements at activity levels of approximately 10^{-7} Bq cm^{-3},

(2) preconcentration of radioactive emanation by condensation, adsorption on activated charcoal, cooling with liquid air, or by sorption in cooled organic solvents (e.g. toluene, carbon disulphide). After collection, the radioactive gases can be purged from the collectors and transferred to an appropriate ionization chamber,

(3) capture (e.g. filtration) of aerosols and measurement of their activity via scintillation counting or by autoradiography.

The analysis of natural radioactive materials is relatively straightforward, since it usually involves the determination of a small number of well-known radioisotopes of a few elements. The determination of man-made radionuclides in air samples is more complicated, because several radionuclides of a number of elements may be involved: both qualitative and quantitative studies may be needed, and carriers may have to be identified.

The final aim of qualitative analysis is the identification of all radionuclides present in sample. The procedure has two steps:

(1) The characterization of all activities present, e.g. nature and energy of radiation, relative intensities, half-life values.

(2) Identification of the radionuclides responsible for the various activities.

The nature and energy of radiation can be determined by [36]:

(1) Gamma spectrometry with NaI(Tl) crystals or solid state detectors such as Ge/Li or Si/Li systems.

(2) Alpha spectrometry with surface barrier detectors.

(3) Beta spectrometry with silicon semiconductor detectors (surface barriers or Si/Li type).

(4) Absorption measurements.

The aim of quantitative analysis is to measure an amount of radioactivity in either a relative or an absolute sense. Common units are the becquerel (Bq), becquerel per unit mass or becquerel per unit volume. In special cases, the activity is expressed as a mass of the radionuclide.

5.5.4 A simple system for the atmosphere control

Regional, vertical, time and competency aspects are usually considered when categorizing the problems of air pollution. In the case of *local pollution*, the immediate vicinity of the pollution source is considered in general up to the height of the relevant emitting chimney, where significant changes may be observed in several hours, and local authorities are responsible for dealing with the situation.

From the standpoint of the *pollution of cities and smaller industrial agglomeration*, this involves the atmosphere above cities and conurbations up to a height of about 1500 m where essential changes with time may be observed in several days. Authorities of particular regions are competent to act in these cases.

The *pollution of large industrial agglomerations* is related to wider regions up to levels of about 10 km. As regards concentration changes, times of several weeks are important and the regional authorities are responsible for action taken.

Nation-wide pollution is related to the territory of a whole country, and in the vertical direction this is a matter of the whole troposphere. Essential changes occur over periods measured in months and the responsibility is carried by the national authorities.

In the wider sense, *regional pollution* involves problems concerning whole territorial areas or even parts of continents, up to an atmospheric height of about 25 km. Essential changes are measured in terms of years and the competency is attributed to international bodies.

Global pollution is clearly a matter of the whole Earth and of the whole atmosphere. Essential changes are observed over periods as long as decades and in this case again, international bodies also carry the responsibility for action.

Wide international cooperation has developed in recent years in the field of measuring and monitoring the regional and global pollution of the atmosphere. According to the World Meteorological Organization, at least one regional station should operate per 250,000 km^2 of land surface. The minimum programme involves the chemical analysis of monthly precipitations and determination of the attenuation of solar radiation. According to the relevant convention, the regional stations should be situated at least 100 km from the nearest important industrial sources — the regional level of concentrations of pollutant is one order of magnitude lower than that of pollutants in cities and industrial agglomerations.

The *Global Earthwatch Monitoring System* of the UNO was established for following the global pollution of the atmosphere. Very strict criteria are insisted upon for the siting of global measurement stations, so that in central Europe they may be situated only at high mountain localities and, in addition to this, any particular regional effect has to be precluded. Within the GEMS, which serves for the evaluation of global changes of the earth's environment, SO_2, CO, CO_2, NO_x, sulphates, ozone, photochemical oxidants, reactive hydrocarbons, asbestos and other pollutants are followed in the atmosphere.

Effective control of the atmosphere quality requires systematic measurements of long-term character. These measurements are mostly concerned with research studies, control measures and special measurements.

The *research measurements* include particularly the choice and determination of relevant harmful substances, the study of their propagation, determination of the quality and quantity of their detrimental effect to the man, fauna and flora, and the study of their presence in particular components of the biosphere.

The results of *control measurements* serve particularly as a basis for provisions for restricting emissions. Long-term control measurements make it possible to evaluate the course at atmospheric pollution.

The group of *special measurements* include particularly studies using special vehicles, aircraft mapping of atmospheric pollution, measurements accomplished under abnormal conditions, measurements performed for preventing potential accidents, etc.

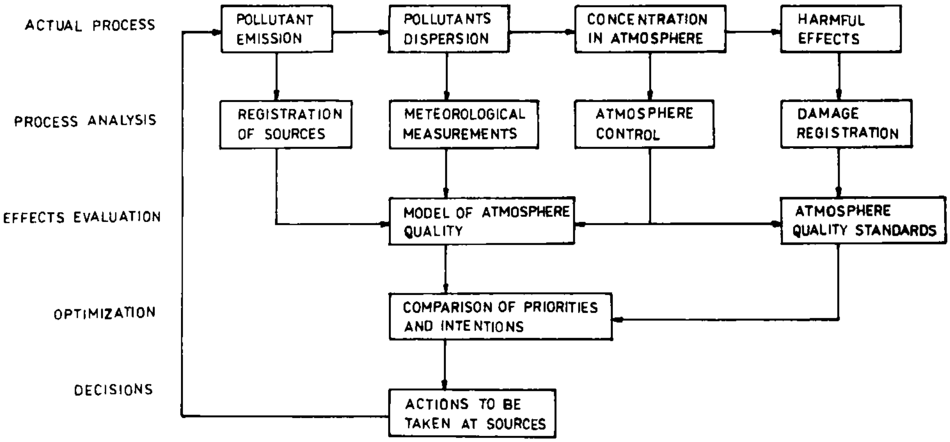


Fig. 5.27. Information flow in atmosphere protection

The proper coordination between the three basic types of measurements remarkably increases the efficiency of using particular results, and it is essential for the construction of a comprehensive data bank.

In addition to this, the use of computing technique makes possible not only the continuous following of air pollution conditions, but also automatic use of correcting and safety procedures. Figure 5.27 is a block diagram of the flow of data in a typical atmosphere protection system.

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6 The biology of the atmosphere

The atmosphere of the Earth contains many minute particles of matter, a large proportion of which is of biological origin. "Most viable airborne particles are spores which are to some extent suited for survival in such an environment for a limited period, but most eventually succumb to the rigours of airborne travel. Not only spores of fungi, myxomycetes, bryophytes, and pteridophytes, but also pollen grains, moss gemmae, propagules of lichens, cells of algae, vegetative cells and spores of bacteria, cysts and protozoa, and virus particles may occur in the air and constitute the air spora. The largest of these particles are the pollens which may range up to 200 μm in diameter, though most are 20–50 μm. Most airborne fungal spores are between 3 and 30 μm in diameter, most bacterial cells about 1 μm in diameter, and viruses 0.1 μm" [1].

In this century, the term *aerobiology* has been introduced to describe the research mainly concerned with microbial life in the atmosphere. Originally the discipline was divided into the so-called *extramural aerobiology*, which had overlapping areas with phytopathology, and *intramural aerobiology*, having overlapping areas with the work of the hygienists.

This chapter deals with the principles of microbiology of the atmosphere and some palynological aspects of the atmosphere.

6.1 Microbiology of the atmosphere

The air serves as a temporary habitat for viruses, vegetative cells and spores of bacteria, small algal and protozoal cysts, spores of lichens, myxomycetes and lichens. Many of these organisms may be involved in the production of infectious diseases of man, animals or plants. Others can elicit allergic responses of man or animals. Spores of toxicogenic fungi are transported by air currents which can cause contamination of plants and agricultural crops thus enabling fungal growth and mycotoxin production. Mycotoxins are considered important environmental pollutants synthesized on seeds, nuts and other plant materials. Acquisition by the host is by ingestion, inhalation or contact and even small amounts of these compounds may involve serious health hazards [2].

Basic methods used in microbiological studies of the atmosphere have been described elsewhere [3, 4].

6.1.1 Sources and dispersion of microorganisms in the atmosphere

The basic sources of airborne microorganisms comprise soil, plants, wastewater, man and animals, and some industrial processes based on growth and activities of microorganisms. Aerosols, produced by wastewater treatment processes, represent a real health risk.

Many microorganisms, including viruses, bacteria, protozoa, yeasts and algae, lack active dispersal mechanism. They rely on external mechanical forces for their liberation into the atmosphere.

Most plant viruses and bacteriophages can enter the air in water droplets or in debris. Mushroom viruses can be transmitted by infected mushroom spores. Some viruses infecting the animal or human respiratory tract are expelled into the air during talking, sneezing or coughing. Fowl-pest viruses may become airborne on dust particles rising by convection from intensive-rearing poultry houses. Industrial processes generating droplets have been associated with outbreaks of virus diseases [3].

Active discharge-mechanisms involving natural processes capable of producing aerosols of bacterial cells are unknown. Endospores are not more easily airborne than are vegetative cells. However, mechanical disturbance of dust, surgical dressing, clothing, etc., carries into the air contaminated particles bearing clumps of bacteria.

The mycelial organization of most of the actinomycetes allows the development of aerial hyphae bearing dry powdery spores which are exposed to the moving layers of the atmosphere. Rain impacts can put some single spores of streptomycetes into the air, but the majority appear to have been attached to soil particles. By contrast, the thermoactinomycetes are shed freely into the air when infested hay is shaken in the dry condition. *Thermoactinomyces vulgaris* is known to cause "farmer's lung disease", its peak incidence being during the winter months following a wet summer [3, 4].

Myxomycetes are adapted to wind dispersal. Some merely expose a dry, powdery mass of spores above the substratum. Others expose small, dry spore masses on stalks. A few species are splash-dispersed or possess an active discharge mechanism.

The frequent abundance of yeasts in the air is unexplained, except for the Sporobolomycetaceae which exhibit the basidiospore (ballistospore) discharge mechanism.

Filamentous fungi are well adapted for the aerial transmission of spores. The discharge can be passive or active. Passive mechanisms have been classified as follows [3]:

(a) Shedding of spores or conidia under gravity; e.g. *Cunninghamella* species, some *Deuteromycetes* including conidia of *Botrytis cinerea, Monilia sitophila* or macroconidia of *Fusarium*;

(b) Shedding in convection currents induced by temperature differences; e.g. *Botrytis cinerea* or *Monilia sitophila*;

(c) Blowing away; e.g. dry-spored fungi, smuts, and the uredospores of rusts;

(d) Mist pick-up; conidia of some fungi are removed from their conidiophores via minute droplets carried by mist-laden air;

(e) Bellows mechanism; certain *Gasteromycetes* have a thin, flexible, waterpoof wall covering the spore mass. Indenting this wall forces out a jet of air laden with spores;

(f) Rain tap and puff; detachment of spores when leaves are vibrated by falling raindrops;

(g) Hygroscopic movements of conidiophores which may result in detachment of conidia during violent twisting.

Active mechanisms for spore liberation are known in many *Phycomycetes, Ascomycetes, Deuteromycetes* and *Basidiomycetes.* Some *Phycomycetes* have various discharge mechanisms for ejecting spores into the air. Some *Ascomycetes* have explosive asci, which typically swell at maturity and finally burst at the tip, propelling the spores into the air. In *Basidiomycetes*, the basidium produces one or more sterigmata, at the end of each of which, one basidiospore is formed. When the spore is mature, a drop of liquid is excreted at the hilum end of the spore and almost immediately the spore moves off.

Some of the simpler types of algal cells get into the air regularly but adaptations facilitating take-off into the air are not known.

Theories explaining horizontal and vertical diffusion and deposition processes of airborne microorganisms have been extensively discussed by Gregory [3]. Bacteria and fungal spores are the most numerous members of airborne microorganisms near ground level. The vertical profile of spore concentration generally shows a decrease in concentration with height. Using meteorological observation rockets, microorganisms have been isolated from the mezosphere at the heights of 48 to 77 km. Bacteria (*Mycobac-*

terium luteum and *Micrococcus albus*) and microscopic fungi with black spores (*Circinella muscae, Aspergillus niger, Papulospora anomala*) and green conidia (*Penicillium notatum*) have been identified [5].

The concentration of microorganisms in the atmosphere decreases rapidly with distance from a source and with time from the moment of release. However, wind dispersal of fungal spores over long distances seems particularly favourable. Some typical results of wind-dispersal processes of fungal spores as described by Gregory [6] may be mentioned here. Records of *Puccinia graminis* uredospores during rust outbreaks in southern Manitoba in the early 1930s are particularly instructive. An ideal pattern of logarithmic decrease with height (up to about 4200 m) was observed. Trapping from aircraft reveals a spore concentration over oceans which is by no means negligible; for example at 2700 m over the northern part of the Atlantic Ocean up to 137 fungus spores per m^3 in an air mass of polar origin and 530 per m^3 in a tropical air mass were recorded.

Long-distance transport of cereal rusts occurs in the northern United States, Canada, India, in the USSR, and in western Europe. There is no theoretical reason why windborne spores should not be carried in small quantities between any two parts of the earth. Far-reaching consequences may ensue when a plant pathogen is introduced in an area previously uninfested. Two remarkable examples, described by Gregory [6], deserve to be mentioned here.

Puccinia polyspora is a rust fungus attacking maize. It has been present in the south-eastern United States at least since 1879, but American host varieties sustain little damage. In 1949 the fungus suddenly appeared in Sierra Leone, causing a severe disease of maize. From there, it spread, evidently by wind, reaching all other parts of western Africa by 1951, Congo and eastern Africa by 1952, Rhodesia and Madagascar by 1953, and the remote islands of the Indian Ocean by 1955.

Perenospora tabacina, the tobacco blue mold, was first described in Australia in 1890. It did not succeed in crossing the dried areas of that continent to reach Western Australia until 1950. However, it appeared in North America in 1921 and in South America in 1938. Its invasion of Europe has been spectacular. It first occurred in England and Holland in 1958, probably introduced by aircraft. By the following year it was well-established in Germany, and by 1960 it had invaded nearly all of Europe including eastern Russia. France, Belgium and Germany lost 60–65% of their tobacco crop. By 1961 the fungus has reached Tunisia, Algeria, and Greece; and in 1962 it reached Turkey, Morocco, Syria, Lebanon, and Iran, its spread averaging approximately 1120 km per year since its first discovery in Europe.

Hirst et al. [7] demonstrated that vast amounts of spores may be carried by wind over the North Sea. *Cladosporium*, pollens and *Ustilago* were used in this study as major representives of the diaspores liberated during the daytime. Maximum numbers of spores were noted at hights between 500 and 1500 m, but relatively high concentrations of *Cladosporium* spores were noted near sea level close to the Danish coast. It is therefore likely that a considerably amount of spores carried by wind across the North Sea is deposited over neighbouring land areas.

The airborne flight of a spore draws to a close when various factors tend to accelerate the downward velocity of spores. Rain is perhaps the most important factor in this process. Another mechanism of deposition is sedimentation in association with boundary layer exchange, a process by which spores from a cloud of particles overhead diffuse into the boundary layer of air in which settling is mainly gravitational. Deposition of spores is also achieved by their impaction against solid objects. The relative importance of these various deposition processes varies with the circumstances [1].

6.1.2 The microbiology of air inside enclosed spaces

Microorganisms normally found in the outside air will also be present inside buildings where they are introduced by air currents, but the main sources of contamination arise from within the buildings [1].

A variety of indoor sources of microorganisms have been observed. The following data were taken from the Gregory's book [3], where references may be found.

In dwelling houses, defective timber attacked by fungi may be an important source of spores. Timber in mines is particularly liable to fungal decay and may also bear superficial mould growth. Extensive growth of *Sporotrichum heurmanni*, pathogenic to man, was found on fresh timber in mines and the fungus was also isolated from the air.

Penicillium dominates the air inside most houses, in contrast to *Cladosporium* outside. Bacteria tend to be more abundant indoors in winter than in summer. In densely populated rooms in schools and mills, the stirring up of dust increased the ratio of bacteria to moulds in the air. Shaking beds, brushing carpets, and repair work increase the mould-spore content of the air up to 17 times, but it rapidly returns to normal when the activity ceases.

Recommendations for the maximum tolerable number of particles carrying bacteria in operating theatres are 700 per cubic metre for minor operations, and down to 70 or even 15 per cubic metre for dressing burns and in neurosurgery. The spread of strains of bacteria resistant to antibiotics has raised interest in the possible role of air in hospital cross-infections [8, 9].

High microbial concentrations often occur in farm buildings, such as cowsheds, where hay is being fed to animals, or in barns where threshing and cleaning is in progress. Moist storage of grain in open-topped silos presents another hazard. Glasshouses may act as spore emitters through open ventilators [3].

Special attention has been given to microorganisms present in the air of underground railways in London and New York in the first quarter of the century [3], and more recently in the Hungarian capital of Budapest [10].

Air in holds and living quarters on board ships was studied as early as in 1886 [3]. The advent of nuclear submarines and space vehicles has introduced a new environment where man is sealed in for prolonged periods in a recycled, artificially replenished atmosphere. The incidence of upper respiratory infections in relation to air contamination of Polaris submarines was reported [4]. During a patrol a crew member could inhale unacceptable levels of staphylococci, coliforms and enterococci.

6.1.3 Airborne microorganisms and health problems

Many human diseases can be transmitted by the aerial route, particularly by droplet infection. Viral infections such as influenza, common cold, measles, smallpox and poliomyelitis can be spread by this route. Bacterial and fungal infections acquired by droplet infection are summarized in Tables 6.1 and 6.2. Similar and other diseases can occur in cattle and poultry.

The importance of the serial route in transmission of antibiotic-resistant staphylococci can be indirectly illustrated by findings in the environment, patients and the nursing personnel of a surgical clinic in Bratislava (Czechoslovakia) [8]. The results were obtained during corroborative studies on the distribution of resistant staphylococci from different environments in Slovakia [11]. The strains of coagulase-positive strains of *Staphylococcus aureus* from the clinic were tested for their sensitivity to six common antibiotics of that time. With staphylococci isolated from the environment, patients and the personnel, the percentages of resistance to benzylpenicillin, streptomycin, chlorotetracycline, erythromycin, chloramphenicol and vancomycin are shown in Fig. 6.1. The percentages of resistance to the individual antibiotics were positively correlated with the consumption of their preparations at the clinic.

Table 6.1. Bacterial infections which may be acquired by inhalation [4]

Disease	Organism
Pulmonary tuberculosis	*Mycobacterium tuberculosis*
Pulmonary anthrax	*Bacillus anthracis*
Staphylococcal respiratory infections	*Staphylococcus* sp.
Streptococcal respiratory infections	*Streptococcus pyogenes*
Pneumococcal pneumonia	*Diplococcus pneumoniae*
Nocardiosis	*Actinomadura asteroides*
Q-fever	*Coxiella burnetii*
Whooping cough	*Bordetella pertussis*
Diphtheria	*Corynebacterium diphtheriae*
Sinusitis, bronchitis	*Haemophilus influenzae*
Primary atypical pneumonia	*Mycoplasma pneumoniae*
Pneumonic plague	*Yersinia pestis*

Microorganisms present in a working environment can represent an occupation hazard. Fungal spores and conidia are usually present in air, but their numbers and types are controlled by a variety of factors (humidity, seasons, time of day, location, etc.); this is particularly true on farms.

Some people can develop allergic reactions to certain types of fungal spores. Allergic reactions to fungal spores or other cell components are possible in industrial fermentations [12]. The spores and fragments of hyphae from fungal species of *Penicillium, Mucor, Rhizopus, Aspergillus, Candida, Fusarium, Helminthosporium, Alternaria* and *Cladosporium* are capable of being allergenic [13].

The occurrence of toxicogenic fungi in an environment can result in their growth and mycotoxin production on or in various agricultural products. At harvest time, grain may be damaged and easily infested by fungal conidia or spores. Factors influencing mould growth and mycotoxin production during shipment, storage, and compounding of agricultural commodities have been reviewed [14]. Mycotoxin-producing fungi and their toxins are broadly distributed in nature and they have been detected in many agricultural crops. In a recent book [15], the production of mycotoxins in various agricultural products has been described. The presence of the following mycotoxins, presenting health hazards for domestic animals or man, has been well documented: aflatoxins, ochratoxins, citrinin, zearalenone and trichothecenes. Further details are given in the above-mentioned book.

Human pathogens are present in wastewaters at all stages of handling, and if aerosols are produced, they may be carried over long distances by

Table 6.2. Fungi and actinomycetes associated with respiratory infection [4]

Disease	Source	Organism
Extrinsic allergic alveolitis		
Farmer's lung	Mouldy hay	*Micropolyspora faeni*
Bagassosis	Mouldy sugar cane	*Thermoactinomyces vulgaris*
New Guinea lung	Mouldy roofing thatch	*Streptomyces olivacecus*
Maple bark pneumonitis	Mouldy maple bark	*Cryptostroma corticale*
Malt worker's lung	Mouldy malt	*Aspergillus fumigatus*
Mushroom worker's lung	Mushroom compost	*M. faeni* *T. vulgaris*
Sequoiosis	Mouldy redwood sawdust	*Graphtum and Pullularia*
Other infections		
Cryptococcosis	Pigeon droppings	*Cryptococcus neoformans*
N. American blastomycosis	Soil, probably restricted distribution	*Blastomyces dermatitidis*
S. American blastomycosis	Saprophyte on vegetation or soil	*Paracoccidiodes brasiliensis*
Coccidioidomycosis	Soil	*Coccidioides immitis*
Histoplasmosis	Chicken or bat droppings	*Histoplasma capsulatum*
Sporotrichosis	Straw, sphagnum moss	*Sporothrix schenckii*
Adiaspiromycosis	Nests of field mice	*Emmonisa crescens*

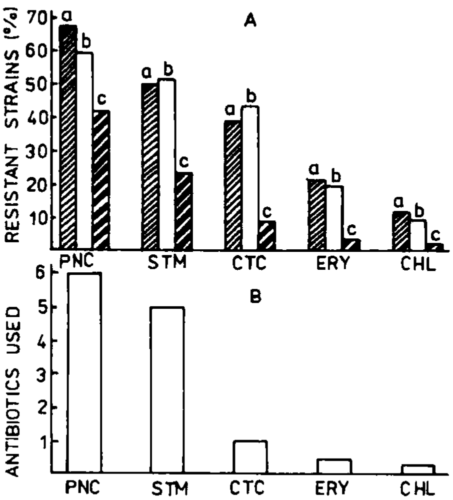

Fig. 6.1. Per cent of resistant strains of staphylococci (A) isolated from patients (a), environement (b), and personnel (c), and monthly uses of antibiotics (B, in hundreds of grams) in a surgical clinic. PNC — benzylpenicillin, STM — streptomycin, CTC — chlorotetracycline, ERY — erythromycin, CHL — chloramphenicol (modified from ref. [8])

wind currents. The literature on airborne organisms arising from the wastewater treatments has been reviewed [4].

6.1.4 Effects of air pollutants on microorganisms

Atmospheric pollution can affect microorganisms. When spores of *Sclerotinia fructicola* were exposed to ozone, half the spores were killed at approximately 50% of the ozone concentration normally required, when the exposure time was doubled [16]. It seems that the exposure of living objects for long time intervals at low pollutant concentration can give equivalent biological responses compared to a short exposure at high concentration, i.e., CT = constant [4]. Similar relationships were observed for growing sclerotia of *Rhizoctonia tuliparum, Sclerotium delphinii* and *Botrytis* sp. when exposed to sulphur dioxide, hydrogen sulphide or ammonia for various concentrations and time exposures [4].

The toxic effect of ozone has been used to purify water, and in the food industry to control the growth of contaminating bacteria and fungi, and to control fungal growth on Cheddar cheese, bread, lemons and apples [4].

Formaldehyde vapour generated from formaldehyde solution is an effective space disinfectant for decontaminating rooms or buildings. It inactivates vegetative bacteria, bacterial spores, and viruses. Formaldehyde vapours have been used for sterilization of medical equipment, wool and blankets.

Sulphur dioxide and metabisulphite is used in wine making, as a general preservative for fruit juices.

Lichens are very sensitive indicators of sulphur dioxide pollution and their absence has been reported in many parts of the world. The primary target for the action of sulphur dioxide seems to be the algal symbiont, but the fungal symbiont is also negatively affected.

Hydrogen fluoride and the volatile fluorides released from aluminium factories also adversely affect the lichen flora [17].

Various methods have been proposed for detoxication of aflatoxin-contaminated food stuffs. One of the most promising practical approaches to the *Aspergillus flavus* or *A. parasiticus*-damaged oil-seed meals is their chemical treatment with ammonia gas at relatively higher temperatures and pressures. The mold growth is inhibited and the aflatoxin is transformed mostly to the non-toxic aflatoxin D_1. The practical application of the method was reviewed [18].

6.1.5 Airborne microorganisms and biological warfare

Microorganisms or their metabolic products can be potentially misused in biological warfare. Pathogenic organisms transmissible by the air route would be the most dangerous candidates for such a misuse.

"Biological warfare is the intentional use of living microorganisms or their toxic products for the purpose of destroying or reducing the military effectiveness of man. It is the exploitation of the inherent potential of infectious disease agents by scientific research and development, resulting in the production of biological warfare weapons systems. Man may also be injured secondarily by damage to his food crops or domestic animals" [19].

An important factor in biological warfare for an aggressor would be to create an aerosol or cloud of the agent over the target area. The importance of particle size in such aerosols has been demonstrated. The defensive features of the upper respiratory tract are capable of separating out larger particles. However, very small particles in the size range 1 to 4 micrometres in diameter are capable of passing these barriers and entering the alveolar bed of the lungs which is highly susceptible to infection. Some agents have been shown to be much more toxic or infectious to experimental animals when exposed to aerosols of optimum particle size. For example, botulotoxin is several thousandfold more toxic by this route than when given per os.

An aggressor would obviously choose an agent that is believed to be highly infectious such as those causing tularemia, brucellosis, Q-fever, coccidiomycosis. Very probably an agent would be used, against which there is a minimal naturally acquired or artificially induced immunity. It is also possible that certain mutational forms may be produced such as antibiotic-resistant or highly toxigenic strains. Genetic engineering might also be misused in this respect.

Another aspect of biological warfare is the possible delivery of biological agents via enemy sabotage or the use of agents for the reduction of agricultural crops and domestic animals. These and other aspects of biological warfare and defence were extensively discussed by Fothergill [19].

Some trichothecene mycotoxins (e.g., T-2 toxin, nivalenol and deoxynivalenol) were suspected to be the toxic ingredients within the "Yellow Rain", an alleged biological warfare agent thought to have been utilized towards the end of the 1970s. According to a recent review [20] there seem to be two divergent opinions regarding the composition of yellow rain. Both have been expressed by eminent scientists. The claim that certain yellow rain samples contained trichothecenes was based upon chemical analyses. On the other hand, from palynological analyses it was concluded that yellow rain consisted of indigenous pollen grains emanating from honey bee feces during mass cleansing flights. It appears that the latter scientists did not analyse their yellow rain samples for the trichothecene mycotoxins and thus their conclusion is unsound in this respect. Both chemical and palynological analyses suggest that yellow rain consists of both trichothecenes and pollen grains. Ascertaining the relationships between these two findings requires further studies.

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6.2 Air palynology

Palynology is concerned with studies of pollen and its occurrence in the environment.

Pollen in the atmosphere can be considered from the following two aspects:

(1) the function of pollen in the fertilization of plants,

(2) the ability of pollen to induce allergic reactions and diseases.

The presence of pollen in the atmosphere is obviously a necessity, since it corresponds to known biological requirements resulting from the existence of plants pollinated by wind. These plants are known as anemophilous, whereas the plants pollened by insects are called entomophilous. Among flowering plants there is approximately a tenfold higher number of entomophilous species than anemophilous, but this is valid only within the system classification. As far as the number of individuals concerns, the facts are usually controversial [1]. Particularly in the Temperate Zone the number of anemophilous individuals in the growths is several times higher than the number of entomophilies (although their species can show a greater variety). The situation in tropical forests with an exceptionally flourishing variety of species and where most of plants are pollinated by insects is quite different. In general, however, it can be said that over the major part of the earth's surface anemophilic vegetation prevails, and also that due to this, such vegetation is noted for quite a high uniformity. Habitats of entomophilous species are more local since entomophilies require a closer specialization because of their dependence on insects, and thus lead to a more distinct territorial restriction of plants. Pollen of the entomophilous plants must be adapted so that it is able to fix to the body of insects. Therefore, it has a very articulated surface with various projections, hooks and other attachment structures. It is often covered by adhesive substances. The pollen is released into the atmosphere in small amounts only. Anemophilous species produce pollen grains with smooth or only slightly rough surface, and the flowers are arranged so that ripe pollen can easily be released by air in amounts as high as possible. It is therefore readily understandable that most of pollen in the atmosphere comes from anemophilous plants.

In spite of the significant variety of the shape of surface structures, there is a generally constant structure of the outside protective layer. Each pollen grain has a double wall and both layers have typical chemical structure: inner wall, termed intima, consists of cellulose and pectin; the external wall, exine, is formed of a highly polymerized carotenoid sporopolenine. The exine is exceptionally resistant to degradation processes. Part of its external side is formed by the already mentioned surface structures which maintain the typical shape of a pollen grain of each species even a long time after their death. The inner space of pollen grains is entirely filled with cytoplasm [2–4].

Because of the high allergenic potential of various types of pollen, its occurrence in the atmosphere is inconvenient. Pollen is thus considered to be one of the most adverse components of the atmospheric pollution [5, 6]. The principle of pollen allergy is ascribed particularly to the chemical structure of pollen grains, but the question of which component is responsible for the end result has not yet been answered [7]. It is supposed that it is a protein-type compound, however, opinion as to whether it is a high molecular polypeptide, denaturated albumin, low-molecular nondialysable protein or one of the protein complexes is diverse. Accurate chemical determination of an allergen is also complicated by the fact that the pollen grain is a motionless organ adapted to transport, but at the same time it is a living system exceptionally labile as far as the chemical aspects are concerned. Protein composition changes with the development of pollen, during maturing and ageing, and particularly during germination of the pollen grain. These physiologically conditioned deviations in the quality and quantity of chemical components of pollen grains concern particularly its inner content and are very distinctive: the total quantity of proteins varies from 5 to 45% of dry residue, and the weight of saccharides, consisting particularly of starch and soluble simple saccharides, makes as much as one third of the weight of the pollen, and significant differences were observed in the content of lipids. Also the content of ash matter varies from 0.9 to 7% and that of water from 2 to 3% depending on the plant and ripeness of pollen [2, 3]. Even with considerable deviations, the content of water in the pollen grains is much lower than that in other parts of plants. Changes in the water content are indicated by changes in the specific weight of pollen grains, which has a direct influence on the distribution and transfer of pollen by air. The transfer of pollen grains by air, similarly to that of any transported fine particles, is determined by three factors:

(a) rate of descent of pollen grains,
(b) prevailing direction of the horizontal air (wind) motion,
(c) intensity of vertical motion and air turbulence.

The fall or sedimentation of pollen can be followed and measured only in still air. Entire immobility of air can be provided artificially, it never occurs in nature. Therefore, the notion of air immobility is mostly extended to such conditions in which the effect of wind, turbulence and molecular activity of air is negligible. Fine particles, such as dust, microorganisms, spores and pollen grains fall in motionless air at a certain constant (final) rate, due to viscosity or molecular activity of air. When a particle is released into the atmosphere initially, its velocity increases due to gravitation, but since the resistance of air is increasing more rapidly, it quickly reaches an equilibrium state in which the rate of fall does not increase and the particle falls at constant final velocity. Table 6.3 shows the specific weight and terminal velocity for pollen grains of various types, determined experimentally [6]. Since most of the pollen grains have approximately spherical shape and their size usually does not exceed 100 μm it is possible to use Stoke's relationship derived for smooth spherical particles of 1–100 μm for the calculation of the final fall rate of a pollen particle:

$$w_s = \frac{2}{g}\frac{\tau\varrho}{\mu}gr^2$$

where w_s is the terminal velocity (sedimentation), τ — the specific weight of the particle, ϱ — the medium density (air = 1.27×10^{-3} kg m^{-3}), g — the acceleration due to gravity, μ — the viscosity of air and r — the particle diameter. For particles larger than the mentioned range an appropriate correction should be made. Smaller particles fall slightly faster and the larger particles more slowly than would correspond to Stokes' equation. In the case of an elongated shape, for example, the approximate relationship by McCubbin can be used:

$$w_s = \frac{\text{length} \times \text{width}}{40}$$

with dimension in μm and final rate in nm s^{-1}.

Table 6.3. Density and terminal velocity of pollens and spores

Species	Density	Terminal velocity
Angiosperms		
Betula alba		2.4
Fagus sylvatica	0.71	5.5
Quercus robur		2.9
Tilia cordata		3.2
Dactylis glomerata	0.98	3.1
Gymnosperms		
Abies pectinata		38.7
Picea excelsa	0.55	8.7
Pinus sylvestris	0.39	2.7
Bryophytes		
Lycopodium sp.	1.175	1.7–2.2
Polytrichum sp.	1.53	0.23

However, a clearly elongated shape occurs rather rarely in the case of pollen, but it occurs frequently, for example, in the conidia of some fungi.

Sedimentation of pollen in quiet air is undisturbed only in closed spaces, and thus in rooms where the air is not in movement, pollen falls at its terminal rate and then sediments. However, in the open, the effects of wind, convection and turbulence of air prevail.

Convection is the term for vertical streams of rising warmer air which are generated by uneven heating of the earth's surface. The convective streams can lift the pollen grains up to a height of 3 km and more, and the differences in their size and terminal rate are also manifested in the vertical distribution of various types of pollen. The turbulent motions of ground air layers cause intensive dispersion of pollen, but this rarely reaches more than 500 m, it is mostly dispersed only to a height of several tens of metres. At these levels and above, the effect of wind is more significant.

Most of the pollen remains close to the earth's surface after being released, the highest density has been observed up to the height of trees. Under these circumstances as much as 90% of released pollen settles within 100 m from the source. However, part of the pollen grains can be transported by air over long distances. The upper limit is considered to be about 100 km, but in some rare cases also very much longer distances have been recorded; a possible explanation is that it was pollen whirling again after sedimentation and thus continuing to be transported in stages. The most advantageous conditions for distant transport are windy days with no rain and with a low relative air humidity. Rain and high humidity accelerate sedimentation of pollen quite significantly [1, 6, 8].

The highest quantities of pollen can be found during mass blossoming plants. In mid-European conditions, for example, this is from April till July when 1 m^3 of air near to the earth's surface can contain up to several thousand pollen grains. However, pollen on the continent is present in the atmosphere practically all the year round, although in winter months only about 1 pollen grain can be found per m^3. In the non-vegetation period there can be a considerable part of pollen additionally whirled after its previous sedimentation [1, 6, 9–11]. Changes in the quantity and structure of pollen in the atmosphere during a year are illustrated in Fig. 6.2, showing

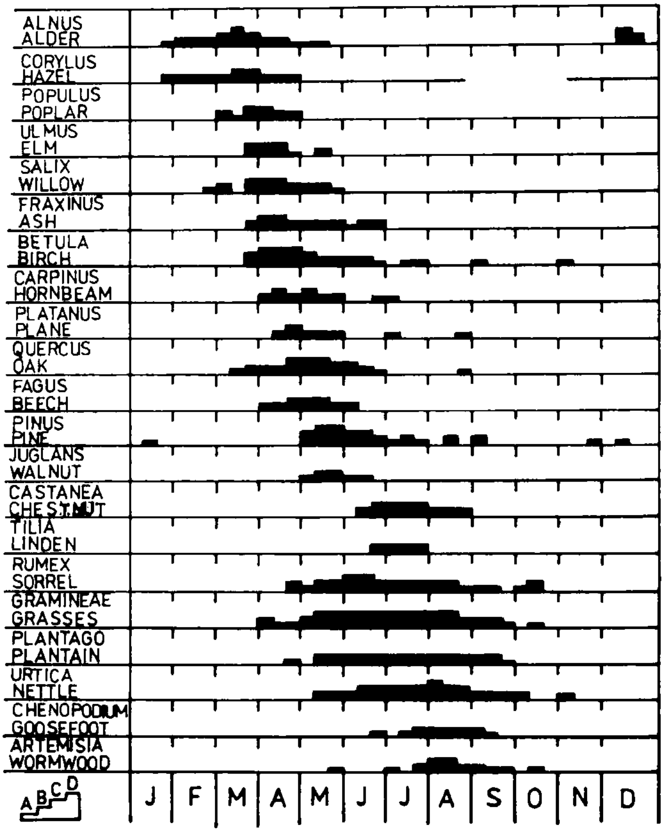

Fig. 6.2. An example of changes in the quantity of pollen in the atmosphere during a year. Samples of air were taken in forest region near the Rhine. The highest 10-day values (i.e. according to decades) from several years' observations are given in the graph.
A — 0.5–0.9, B — 1–9, C — 10–99, D — 100–999 pollen grains in m^3 of air

average results of observations of several years carried out daily at a forest near the Rhine [12].

The air above oceans and in polar regions is noted for a very low content of pollen. At several hundred kilometres from the coastline the quantity of pollen does not exceed several pollen grains per 100 m^3 of air [13].

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7 The chemistry of soil

7.1 Soil structure

From the standpoint of the material composition, the soil may be characterized in general as a heterogeneous polydisperse system, consisting of solid, liquid and gaseous phases. Each phase contains a mineral and an organic portion, the liquid phase is the soil solution and the gaseous phase is soil air. The mineral portion of the soil is a mixture of particles of different sizes, characterized by certain petrographic, mineralogical and chemical compositions. An essential part of the organic portion is formed by soil organisms and humus. The soil solution consists of water, and soluble mineral and organic substances. Soil air is a mixture of gases and vapours, filling void spaces in the soil.

7.1.1 Solid mineral portion of the soil

The mineral portion represents an essential part of the soil material, its abundance in the soild phase being usually as high as 95 to 99%. It is formed by the weathering of different rocks in surface layers of the earth's crust; as regards grain size it is a polydisperse system. With respect to the elementary composition, the mineral portion contains essentially all the natural elements, however, only eight elements are present with abundances exceeding 1% as follows: O 46.6%, Si 27.7%, Al 8.1%, Fe 5.0%, Ca 3.7%, Na 2.8%, K 2.6%, Mg 2.1%. Among the macrobiogenic elements, mineral particles supply plants particularly with Ca, K, Mg and P (in plant tissues, it is possible to find 16 macro- and microbiogenic elements as follows: C, O, H, N, P, K, Ca, Mg, S, Fe, B, Mo, Cl, Mn, Cu, Zn).

The origin of the mineral portion. Rocks covering the earth's surface, which are submitted to intense weathering, may be divided into three main groups, igneous, sedimentary and metamorphic rocks.

The igneous rocks were formed by the solidification of magma. Depending on the site of this solidification, such rocks are divided into those situated at a depth (intrusive) which were formed under the earth's surface, and igneous rocks which solidified on the surface (effusive). From the chemical standpoint, particularly with respect to the SiO_2 content, we can consider acid neutral and basic rocks.

(a) Acid igneous rocks contain 65–80% of SiO_2, of which above 20% is in the form of silica, the remaining portion being formed by different silicates. The proportion of basic and alkaline elements (Ca, Mg, Na, K) in acid igneous rocks is typically 7–12%. The intrusive igneous rocks include, e.g., granite and siliceous diorites. The most common effusive acid igneous rocks are siliceous porphyries and porphyrites.

(b) The neutral igneous rocks contain 52 to 65% of SiO_2, the silica content being below 20%. The content of bases and alkalies ranges between 12 and 18%. Neutral grandiosites, syenites and diorites are the best known neutral intrusive rocks. Non-siliceous porphyries, non-siliceous porphyrites and phonolites are the most common neutral effusive rocks.

(c) The basic igneous rocks contain 35–52% of the total SiO_2, the portion of bases and alkalies is 18–36% or even higher. Silica is not present, however, and they are characterized by a rather high abundance of colouring elements (Fe and Mn 9–15%). In the case of a decrease of SiO_2 below 42% they are considered as ultrabasic. Among the basic and ultrabasic rocks particularly gabbrodiorites, gabbros and hornfels occur most frequently. The most common effusive basic rocks are melaphyres and diabases, and volcanic igneous basaltic rock.

Sedimented rocks were formed from transported products of weathering of igneous and metamorphic rocks. Depending on the origin and mechanism of the formation, the sedimented rocks may be categorized as follows:

(a) Mechanical sediments consisting of fragments of different sizes obtained by a disintegration of igneous and metamorphic rocks, and also older sedimented rocks. The weathering products are transported by action of the wind, water or glaciers. They were sedimented in inundation areas of water flows, in lakes and seas, in areas of the drift by action of the wind, and at sites affected by glaciation.

(b) Chemical sediments formed by a sedimentation of mineral substances precipitated in ground-, surface and seawaters.

(c) Biogenic (organogenic) sediments formed by a sedimentation of mineral and organic debris.

Sedimented rocks are frequently characterized by a remarkably stratified and very heterogeneous (or sometimes, in contrast, rather uniform) grainy structure. Their chemical composition depends on the composition of the original substrates, on climatic conditions and the degree of weathering.

The sedimented rocks form the most frequently occurring group of rocks and thus, they are the most important for soil formation. Loesses belong to the most important sediments forming the soil. These are fine loams drifted by the wind, frequently characterized by a homogeneous, stratified texture. In their mineralogical composition, silica and feldspar are predominant, usually with the presence of certain amounts of limestone, which has been eluted into lower layers in more humid areas. Clays also occur frequently, which may be changed into shales by action of the pressure from the upper layers. They are characterized by high contents of silicates. Argillaceous slates and sandstones are usually formed from clays and from more grainy materials, respectively.

Chemical, biogenic and mixed sediments are categorized depending on their mineralogical and chemical compositions. Carbonate sediments, such as limestones tuffs, dolomites and arenaceous marls, occur most frequently. Limestones were formed by a solidification of shells and other debris of biogenic origin, with their ensuing recrystallization to calcite, and frequently with different abundances of the other carbonates. Dolomites are also of the biogenic origin, however, with a prevalence of magnesium carbonate, in a portion of at least 25%. Calcareous tuffs were precipitated, mostly in the presence of plants, from waters with high concentrations of $Ca(HCO_3)_2$. They are soft and porous, with typical imprints of plants and shells of molluscs. Arenaceous marls are mixed sediments formed by a solidification of different carbonates, silicates and further admixtures. The presence of silicate needles from debris of porifera is typical.

Metamorphic rocks were formed by a secondary conversion of igneous and sedimented rocks, due to certain geological tectonic processes. The pressure, temperature, and chemical effects, particularly effects of gases and thermal solutions were the main factors in these conversions. The texture of metamorphic rocks may be characterized by the presence of layers or scales. Typical metamorphic rocks are gneisses, mica-schists, serpentines, crystalline limestones and crystalline dolomites.

Basic minerals contributing to the soil formation. The rocks consist of minerals, each of them being characterized by a certain chemical composition and arrangement of the crystalline structure. The basic units of the mineral crystalline structure are not molecules, and thus, electrostatic forces, which are not restricted by particular valence bonds, play the most important role in binding relevant ions and their groups. Coordination bonds occur in minerals. The arrangement of basic structural units is governed by the radii of ions, by their situation and numbers of coordination bonds. Each structural unit of the crystal lattice has a certain internal energy, which is a function of the charge and its radius. The total lattice energy and its distribution in the lattice affect essentially the weathering process of the given mineral.

Although a wide variety of minerals occur in different rocks, the major portion of minerals contributing to soil formation are primary and secondary silicates. Carbonates, phosphates, sulphates and sulphides are represented in minor proportions.

Silicates are the most frequently occurring minerals in the earth's crust. Their relative abundance is roughly 75%, however, in soils it may be as high as 92 to 96%. Their internal crystalline structure is based on anions $(SiO_4)^{4-}$ in the shape of a silica tetrahedron (Fig. 7.1). Silicon may be frequently replaced by aluminium, which leads to the formation of aluminosilicates. The remaining free charge of this structure may be balanced by other cations from the external medium. Aluminium can also participate in the formation of octahedral anions, where it is surrounded by six O^{2-}, i.e. $(AlO_6)^{9-}$ (Fig. 7.2) or OH^- $(Al_2(OH)_6)$. Even here, the central atom of

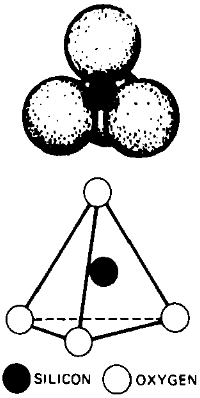

Fig. 7.1. A single silica tetrahedron

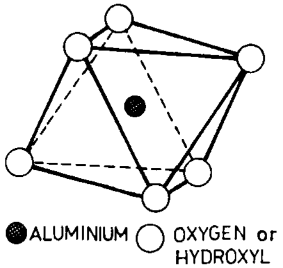

Fig. 7.2. A single alumina octahedron

aluminium may be replaced by another atom, such as iron or magnesium. The whole group of silicate minerals is (similarly as for other minerals) divided into two subgroups — primary and secondary silicates:

(a) Primary silicates are components of magnetic rocks and they remain unaltered even after their metamorphosis. In the course of weathering they are only mechanically disintegrated; their chemical and structural characteristics remain unaltered. Silica SiO_2, is a frequently occurring primary mineral in soils. On account of its extraordinary resistance it is a typical residual material in most weathering processes. Among the primary aluminosilicates, feldspars occur frequently, where cations K^+, Na^+, Ca^{2+} are bound to the negatively charged aluminium tetrahedrons. In this group we can consider:

- potassium feldspars with orthoclase $K(AlSi_3O_8)$ as the main representative,
- sodium feldspars, e.g. albite $Na(AlSi_3O_8)$,
- calcium feldspars, e.g. anorlite $Ca(Al_2Si_2O_8)$ and different isomorphous mixtures of these basic components, such as sodium-calcium plagioclases. Micas are aluminosilicates with a remarkably stratified structure. Depending on the cations bound, there are magnesium-iron micas (e.g. biotite), aluminium micas (muscovite) and lithium micas.

(b) Secondary silicates are different from primary minerals on account of their modified chemical composition. Chemical conversions were brought about by the action of volcanic-hydrothermal processes (zeolites) or surface weathering (clay silicates). Among these substances, clay minerals occur most frequently in soils, forming the main portion of the clay fraction. The clay minerals may be categorized according to the position of tetrahedral and octahedral layers in the crystal lattice. In the soil, clay minerals of the following groups are most frequently present:

- kaolinites have a simple structure, formed by double layers of silicon tetrahedrons and aluminium octahedrons. Here, particular layers are mutually bound by shared anions of octahedrons and vertices of tetrahedrons (Fig. 7.3). A replacement of Si and Al by other cations occurs very seldomly, so that there are no unsaturated valences on the double-layer surface. For a short and constant distance of double layers, water cannot enter into spaces between the layers, so that kaolinites do not swell. Kaolinites were formed in the weathering process in the environment of a humid subtropic and tropic climate and thus, they occur frequently in older Tertiary formations;
- montmorillonites have, in their basic structure, two layers of silicon tetrahedrons with an interstitial layer of aluminium octahedrons. The

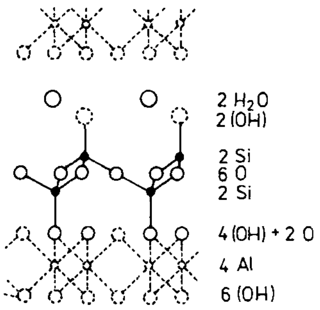

Fig. 7.3. A schematic structure of kaolinite

vertices of tetrahedrons are directed oppositely to the central octahedral layer. Their chemical composition varies widely due to an intense ion exchange. In the space between the layers, large amounts of water may be bound, which is accompanied by a separation of triple layers and expansion of the crystal lattice. Thus, the montmorillonites can be considerably expanded. This feature is remarkably affected by cations participating in the exchange. At the beginning, small cations with larger charges potentiate a more intense expansion, approximately in the following order: $Mg^{2+} > Ca^{2+} > Ba^{2+} > Li^{+} > Na^{+} > K^{+} \ldots$. However, with increasing moisture, this order is altered and in the case of unrestricted moistening, montmorillonites saturated with univalent cations exhibit the most intense expansion. The montmorillonite minerals are formed under conditions of temperate climate and they occur frequently in soils of Temperate Zones;

- illites have a triple-layer basic structure similar to montmorillonites. The main difference is that in their tetrahedral layers, a considerable fraction of silicon (about 1/6) is replaced by aluminium. The negative electric charge is compensated by K^+ ions, whose presence reduces the possibility of the separation of basic triple layers and thus, lower amounts of water which can enter into the triple layers, so that illites expand to a much smaller extent than montmorillonites; those with higher contents of K^+ ions exhibit practically no expansion. In general, illites are similar to micas as regards their structure and chemical composition and thus, they are also referred to as hydromicas. Illites are the most frequently occurring clay minerals in central-European soils;
- allophanes represent the most frequently occurring group of amorphous clay minerals, having no regular structure. Under suitable conditions, they can be recrystallized, e.g., to kaolinite.

The following minerals can also occur in soils in appreciable amounts:

— iron oxides, which may be amorphous, such as limonite, as well as crystalline varieties such as hematite or magnetite,

— aluminium oxides such as corundum (anhydrous) or diaspor (hydrated),

— sulphides, such as pyrite FeS_2, chalcopyrite $CuFeS_2$ or sphalerite ZnS,

— halogenides, e.g. sylvite KCl or halite NaCl,

— nitrates, particularly Na- and K-salpetres,

— carbonates — either anhydrous, e.g. calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$, magnesite $MgCO_3$, siderite $FeCO_3$, or hydrated, such as natrite $Na_2CO_3.10H_2O$ and gypsum $CaSO_4.2H_2O$,

— phosphates, e.g. apatite $Ca_5(PO_4)_3$ (OH, F, Cl).

Out of the elements themselves only carbon (graphite) and sulphur are important in the formation of rocks [1–4].

The granulometric composition of the mineral fraction. The mineral fraction in the soil represents a polydisperse system consisting of particles and fragments of varying size. The polydispersity of this diverse mixture, its granulometric composition and properties may be characterized by the relative abundance of grains in certain selected size intervals. The grains which belong to a certain size interval represent particular fractions. The choice of dimensions and number of fraction when analysing the granulometric composition is in principle a subjective matter, affected particularly by the purpose of the analysis and requirements of the practice. The analysis of soil dispersion composition is among the oldest topics not only in the history of the pedology, however, also that of geology and the building industry, etc. Thus, there are many more or less similar scales and methods of categorizing the granulometric fractions; the choice among these is to some extent governed by the availability of appropriate instruments. A simple classification of dispersion proposed by Pallmann (1938) is used most frequently:

< 0.2 mm — coarsely dispersed (stone, coarse and small gravel or coarse sand); they are characterized by a small total surface area, only their mechanical effects in the soil are manifested,

0.002–0.2 mm — finely dispersed (fine sand, coarse and fine dust; their total surface area is larger and thus, besides the mechanical effects, physico-chemical effects (such as sorption) can also be manifested,

1 nm–2 μm — colloidally dispersed (dispersoides, ultramicrons); in the colloidal dispersion in the soil it is possible to observe dispersoids (ultramicrons), particularly clay minerals, SiO_2, sesquioxides and humus. They have large external as well

as internal surface areas and physico-chemical sorption is their main effect,

> 1 nm — molecularly dispersed (molecules and ions of salts, acids and bases in soil water); they are sources of chemical reactions in the soil.

The particle size affects the value of the active surface, as is clearly shown in Table 7.1. The surface area also depends on the particle's shape — the smallest specific surface is encountered with spherical particles, the largest specific surface being characteristic for particles of plate shapes in the given fraction. In the more coarse fractions, spherical particles are prevalent. In colloidal dispersions flat and needle-shaped particles are predominant, this is connected with the stratified character of the crystal lattice of clay minerals forming the major portion of the colloidal fraction.

Table 7.1. Relationship between particle size and specific surface (according to Kutílek)

Grain-size fraction		Specific surface ($m^2\ g^{-1}$)
Material	Grain-size	
Fine sand	0.05–0.10 mm	$10^{-}1$–10^{0}
Coarse dust	0.01–0.05 mm	10^{0}–10^{1}
Fine dust	0.002–0.01 mm	10^{1}
Clay	0.002	10^{1}–10^{2}

For more precise granulometric analyses, classification scales with larger numbers of fractions are required. Two basic groups are usually considered, referred to as the fine soil and skeleton. The grain diameter of 2 mm is considered as a dividing line between them and for more detailed analyses, fine soil II is also considered with a grain size below 0.25 mm. The fine soil classification, using the scale by Schöne (1865), is one of the oldest scales; it is still used, since it serves a basis for the granulometric analysis of soils based on washout methods. The scale by Schöne includes four categories as follows:

	Grain diameter in mm
I — clay particles	> 0.01
II — dust	0.01–0.05
III — sand power	0.05–0.10
IV — sand	0.10–2.00

In the skeleton category four fractions are also considered as follows:

Name of the fraction	Diameter of grains in mm
Coarse sand	2.0–5.0

Fine gravel	5.0–10.0
Coarse gravel	10.0–50.0
Stones	< 50.0

The relative representation of particular fractions in the fine soil is used for classifying soils and earths based on results of their granulometric analyses. Particular species of soils or earths are classified according to the percentage abundance of one or more grain-size categories.

The granulometric composition is a fundamental aspect of the character of the soil and its importance has been recognized since the very beginning of pedology. The granulometric composition of the soil directly affects the process of soil formation and a number of important soil characteristics. The grain size affects:

- — Weathering of the soil-forming substrate. Substrates with smaller grain sizes are submitted to more intense changes and the soil forming process is more complete. The homogeneity of the granulometric composition has an important effect. Deep, morphologically well-developed soils are formed particularly from homogeneous substrates of an intermediate grain size.
- — The dynamics of soil water, which is connected with the porosity. Sandy soils are readily permeable to water, they are characterized by a small water retention and they can be easily eluted. Heavy soils with many capillary pores are characterized by a low permeability, high retention of water and restricted motion of soluble and dispersed substances.
- — Sorption capacity manifested by binding and exchanging univalent and bivalent cations. Clay soils are characterized by a high sorption capacity.
- — Biogenic activity. In sandy soils, rapid microbial decomposition of organic matter is facilitated up to its mineralization. In clay soils, anaerobic processes are prevalent with humic substances occurring as decomposition products, and under extremely anaerobic conditions, insufficiently decomposed organic matter may be accumulated.
- — Temperature regime. Sandy soils are heated more efficiently than clay soils.
- — Technological characteristics of the soil. Clay soils are more cohesive, sticky, and thus mechanically more difficult to treat as compared to sandy soils [5].

The granulometric composition is also connected with the soil fertility with respect to particular species of both cultured and wild plants.

7.1.2 Liquid soil component — soil solution

The liquid component, with dissolved salts, organic compounds, gases and dispersed substances of different origin is considered as the soil solution. It is a very dynamic component of the soil with its composition varying depending on fluctuations of the soil humidity and on reactions of the soil water with inorganic and organic compounds. Only that portion of the soil water, which is able to dissolve electrolytes, gases and to disperse colloids is considered as a direct part of the soil solution. Thus, water vapour and water bound by adsorption is not considered as a part of the soil solution. Among the inorganic substances, the soil solution contains predominantly soluble salts, such as chlorides, nitrates, carbonates, sulphates and phosphates; as regards organic compounds, different low-molecular substances are present as, e.g., fulvoacids and soluble organomineral acids of the chelate type. A part of the dispersed colloids is usually also of organic origin. The ratio between amounts of mineral and organic substances in the soil solution varies depending on the type of the soil, the soil horizon and also on the season of the year. In podzol and peat soils, organic substances are prevalent in the soil solution. In black soil (chernozem) there are about the same portions of organic and inorganic substances in saline soils. In non-saline soils, the total concentration of soluble substances is usually of the order of several hundredths of a per cent; in non-saline soils it may be increased up to tenths of a per cent, however, it seldomly exceeds 1%.

Among the anions, HCO_3^- and NO_3^- occur most frequently in the soil — they represent as much as 90% out of the total anion content. The remaining portion corresponds, in non-saline soils, particularly to SO_4^{2-} and Cl^-. The content of phosphate ions is very low on account of their low solubility. As regards cations, the soil solution contains particularly H^+, Ca^{2+}, Mg^{2+}, NH_4^+, K^+ and in lower amounts Fe^{3+} and Al^{3+}.

In the soil solution of saline soils, there are enhanced amounts particularly of chloride and sulphate anions, the relative abundance of sodium and magnesium being also enhanced.

The following characteristics of soil solutions are the most important.

The osmotic pressure, which is directly dependent on the concentration of water-soluble substances and on the degree of their dissociation. When its value exceeds the value of the osmotic pressure in cells, then the plants are unable to take up soil water. The highest osmotic pressure is observed in the soil solution in saline soils.

The pH value of the soil solution directly affects the course of most chemical, physico-chemical and biological processes in the soil. It is affected particularly by the presence of dissolved acids and acid or basic salts and it ranges usually between pH 4.0 and 8.5. A neutral reaction of the soil solution, about pH 6.5 to 7.2, is preferable.

The buffering capacity of the soil solution is manifested by its ability to restrict changes in soil pH values. This capacity depends on the presence of weak acids or bases and their salts. The mixture $H_2CO_3 + Ca(HCO_3)_2$ or possibly a mixture of phosphoric acid and phosphates are the most frequently encoutered and effective buffer systems in the soil solution.

The oxidation-reduction potential is a measure of the redox activity of the soil solution and it governs the course of oxidation and reduction reactions. It is denoted by the symbol *Eh* and expressed in mV. Low values of *Eh* (-200 to 200 mV) are characteristic of reduction conditions; high values (of above 550 mV) give rise to strong oxidizing conditions. For most plants, the optimal *Eh* value ranges between 200 and 700 mV.

Soil colloids. In the soil, which is a polydisperse system, there is usually a considerable colloidal fraction, formed by submicroscopic particles. As an upper limit of the colloidal size, the average wavelength of visible light was chosen, i.e. 500 nm, however, the colloidal fraction generally includes particles as large as 2000 to 2500 nm. 1 nm is considered as the lower limit of the size of colloidal particles.

In the colloidal fraction of the soil, there are particles of mineral as well as organic origin. Organic colloids consist particularly of humic acids and fulvoacids, the mineral colloids being formed mainly by weathered particles of secondary minerals with crystalline as well as amorphous structures. Clay minerals are the prevalent components in crystalline colloidal particles; among the primary minerals, only small amounts of dispersed silica and mica particles are present. Amorphous mineral colloids are represented by hydrated aluminosilicate gels and hydrates of iron and aluminium oxides. Organic and mineral colloids are usually not separated in the soil. They mostly form a complicated organo-mineral colloidal complex, consisting of a crystalline core of aluminosilicates and an adsorption layer of hydrated sesquioxides (Fe, Al, Mn) and organic colloids.

The colloidal particles are not electrically neutral, they carry an electric charge on their surface, which is negative in most cases. A negative charge is predominant on the surface of clay minerals and humic substances (due to dissociated carboxy and phenolic groups); a positive charge may be obtained from hydroxides ($Fe(OH)_3$ and $Al(OH)_3$) and it also sometimes occurs at edges and corners of the crystal lattice of clay minerals. Certain organic and mineral colloids are of an amphoteric nature, in an acid medium they release OH^- ions, thus gaining a positive charge; in a basic medium they release H^+ ions, gaining a negative charge. The pH value at which the amphoteric colloids show neutral behaviour is named the isoelectric point. Negatively charged colloids are also referred to acidoids, positively charged are named basoids, and amphoteric colloids are also termed ampholytoids.

A very significant characteristic of colloidally dispersed particles is their large specific surface area, which may be as large as 10^4 to 10^7 cm^2 cm^{-3}. This value increases with decreasing size of colloidal particles. Due to their internal as well as external active surface, the colloidal particles affect many important characteristics of the soil, such as its ability to bind ions, water, gases and its tendency to swelling and adhesion. This results from the fact that the most important chemical, physico-chemical and physical processes occur on phase interfaces formed between the active surface of the colloid and liquid phase, i.e. soil water.

To the surface of a colloidal particle, carrying a certain electric charge, oppositely charged ions are attracted from the liquid phase. In this way, an electric double layer is formed consisting of

(a) a charging layer on the colloid surface, determining the potential and carrying the total charge Q_1,

(b) a compensation layer, having the charge of an opposite sign Q_2.

For these two layers, $Q_1 + Q_2 = 0$. The compensation layer is bound to the colloid particle surface by electrostatic and adsorption forces. The adsorption forces act only at a short distance, whereas the range of the effect of electrostatic forces is fairly large and they decrease only slowly with increasing distance. Thus, the compensation layer is divided into two layers. The first one is a stationary (Stern) layer with a thickness corresponding to the size of one ion, which behaves as a part of the colloid particle. The second part of the compensation layer is a diffuse (Gouy) layer, where the ions are icreasingly influenced by the translational thermal motion in a direction away from the Stern layer and their concentration gradually decreases, so that the potential difference with respect to the liquid phase decreases to zero. The diffuse layer complements the structural unit of the colloidal system, named the colloidal micelle. The structure of typical colloidal micelles are given in Fig. 7.4.

By increasing the electrolyte concentration, the electric double layer is compressed and the compensation ions are situated tightly above the charging layer. In the case of a low electrolyte concentration, or in the absence of ions of a low valency, the thickness of the compensation layer increases, the compensation ions dissociate and they are separate from the charging layer by diffusion. This results in the formation of a micelle charge and increase of the value of the electrokinetic potential. The electrokinetic po-

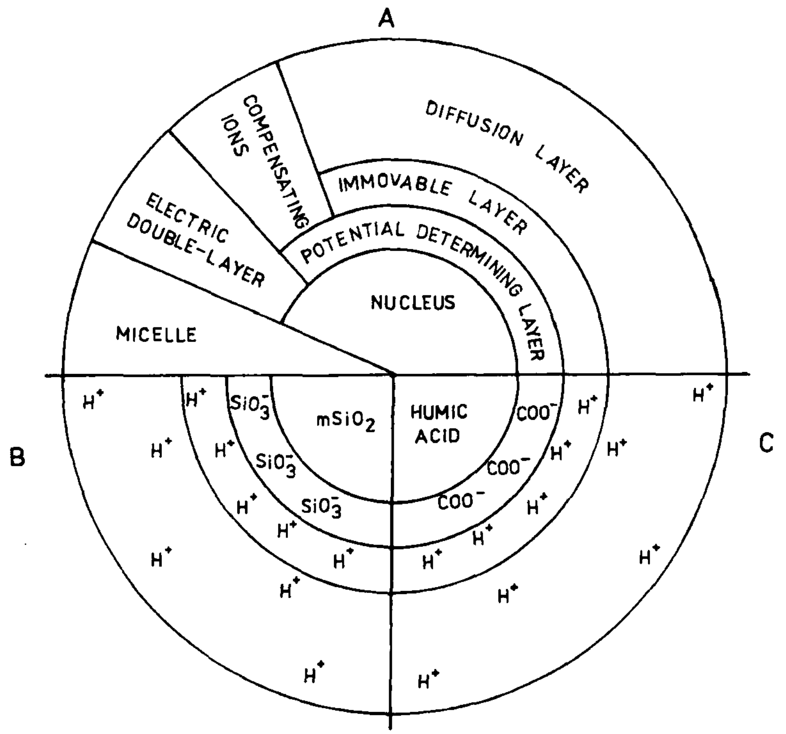

Fig. 7.4. The structure of colloidal micelle. General scheme (A), mineral colloid (B) and humic acids micelle (C)

tential ζ is the potential of the moving boundary of the colloid micelle. The moving boundary is situated in the diffuse layer at a distance from the colloid particle surface, at which the compensating ions can already be detached from the charging layer. The value of the ζ potential is affected by the concentration and character of electrolytes. The increase of the univalenion concentration increases the ζ potential to a maximal value, with a subsequent decrease. The increase of the bivalent ion concentration results in a continuous decrease of the potential. The decrease of polyvalent ion concentration leads to a rapid drop of the ζ potential to zero and then it is increased with an opposite sign to a maximum with a subsequent decrease to zero, again. In this case, the zeta potential exceptionally has the same sign as the charging layer, since at a high concentration of polyvalent ions, the charge of the Stern layer exceeds the charge of the layer determining the potential and $|Q_1| < |Q_2|$. The ions of the diffusion layer have, in this case, the same charge as the charging layer.

The value of the electrokinetic potential is expressed in mV and it may be as high as several tens of millivolts (in calcium-saturated soils 30 to

40 mV, in sodium-saturated soils even above 60 mV). The value of the zeta potential is closely related to the coagulation and peptization of colloids. At a high zeta potential value, the colloidal particles are mutually repelled, at low values (30 mV) or at a zero value of the zeta potential they are not repelled and by the action of adhesive forces they tend to flocculate or to form macroaggregates. The coagulation may be brought about, for instance, by saturating negatively charged colloids with polyvalent cations even at a minimal concentration of electrolytes in the soil solution, and at a high concentration coagulation may also occur by the action of univalent cations. The coagulating ability of cations of the compensation layer increases with their valency, radius and mass, and it decreases with the size of their hydration shell: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Si^{2+} < Ba^{2+}$, etc.

The peptization, i.e. disintegration of the aggregates coagulated is the reverse process. Peptization occurs for colloids saturated with univalent cations after diluting the electrolytes in the dispersion medium or in the case of colloids saturated with polyvalent ions after their displacement and replacement by univalent cations, and after a strong dilution of the soil solution. The colloid particles forming the macroaggregate accumulate a large charge in this way, and after exceeding the coagulation threshold, they start to be mutually repelled and the aggregate is disintegrated. In this process, a low concentration of electrolytes in the dispersion medium is of importance. The coagulation or peptization of colloid particles in soils may occur, for example, by the fluctuation of the moisture content, which also leads to changes of electrolyte concentrations in the soil solution. Colloidal systems undergo considerable changes during fertilization with organic fertilizers, liming, etc. The peptized colloids exhibit a high migration ability and deteriorate the soil characteristics.

Characteristics of the soil water and the water regime

The soil water is the total content of water present in soil pores in the liquid, solid and gaseous states of matter. Liquid water is clearly the usual form of water in soil, and it thus, receives the greatest attention.

The main source of drinking water comes from atmospheric precipitations, surface and ground inflow and capillary elevation of the groundwater. The amount of water taken up, its binding and motion depend on the relationship between the soil and water, which involve the statics and dynamics of the soil water. The statics of the soil water characterizes the content of water in the soil, expressed by the moisture and water capacity of the soil.

The moisture of soil by volume (W_0) is given as a ratio of the volume of soil water (V_w) to the initial volume of intact soil (V_i):

$$W_0 = \frac{V_w}{V_i} 100 \, (\text{vol.\%})$$

The moisture of soil by mass (W_m) is expressed by a ratio of the soil water mass (M_m) and dry soil mass (M_d):

$$W_m = \frac{M_m}{M_d} 100 \, (\text{wt.\%})$$

The dynamics of soil water follows from the action of different forces, either supporting the water motion in the soil or restricting this motion. Water in soil is affected particularly by gravitation, capillary forces, sorption forces, osmotic pressure, and sorption force of roots. The potential energy of soil water is due partly to its level in the earth's gravitational field, and partly to the other force fields in soil. In practice it is unnecessary to separate particular force fields from each other; only their combined effects are considered, as a result of which the water particle in the soil acquires a certain potential energy, characterized by the total potential of soil water. When relating this potential energy to the soil mass, it is expressed in J kg^{-1}. It is, however, frequently related to the soil volume as a pressure or to the gravitational field when the potential is obtained in length units

$$p = \varrho g H$$

where p is the pressure, ϱ is the specific mass of water, g is the acceleration of gravity and H is the head of pressure.

The dominant effects of particular forces give rise to different energy categories of soil water. Thus, there are three main groups; adsorption, capillary and gravitational waters.

Adsorption water accounts for water molecules bound to the soil particle surfaces by electrostatic forces, hydrogen bonds and van der Waals forces.

The capillary water is the result of the action of forces of a molecular character, acting at the soild/liquid phase interface. The capillary forces depend on the water surface tension, on the wettability of solid particles and on the pore size.

The gravitational water is due to increased moisture in non-capillary spaces, and it is mainly under the control of gravitation. It resides in the soil for a short time, since it penetrates rapidly through non-capillary spaces into deeper layers and it is also fairly easily evaporated.

The groundwater is formed above the impermeable layer (aquifer) so that it fills all the capillary as well as non-capillary spaces, thus forming a continuous water layer bounded by its upper level.

For the moisture distribution in the soil profile from the soil surface down to the groundwater level, it is possible to consider three forms of moisture:

(1) Water suspended by capillary forces, which is not connected with the groundwater ("hanging water").

(2) Water supported by gravitational forces, i.e. groundwater accumulated above the impermeable soil layer serving as its support.

(3) Elevated water is transported above the groundwater level in capillary spaces, thus forming a capillary shell above the groundwater. The height of the elevating column depends on the capillary pore diameter.

A schematic diagram of divisions of the soil water is given in Fig. 7.5. Between the zone of the water suspended by capillary forces and zone of the

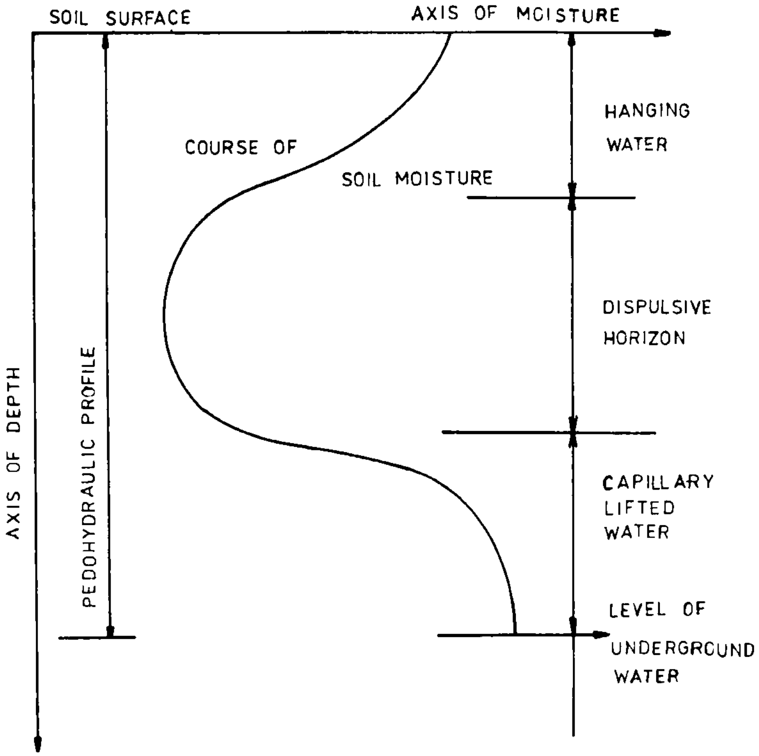

Fig. 7.5. Types of soil water

elevated water, there is usually a zone with a low moisture content named a dispulsive horizon.

The gravitational water can move most easily and most rapidly, the slowest motion is observed for the water bound by sorption, and the capillary water exhibits an intermediate mobility.

The effect of all the various phenomena connected with the water circulation between the atmosphere, biosphere and hydrosphere is reflected in general in the water regime of the soil. The water regime includes the water penetration into the soil, its motion and retention in the soil, and its escape from the soil. It is characterized quantitatively by the soil water balance, which may be expressed by the relationship:

$$R_1 + P + K = E + O_1 + O_2 + R_2$$

where R_1 is the water reserve in the soil at the beginning of the period balanced, P the amount of precipitations in the period of interest, K the water increment in the soil from the groundwater, E the water evaporation and transpiration, O_1 the surface outflow, O_2 the ground outflow and R_2 the water reserve in the soil at the end of the period balanced. All measurements are in mm [1–5].

7.1.3 Gaseous component of the soil — the soil air

Besides water, air is also present in soil pores, and it forms a significant part of the soil. The air penetrates into the soil from the atmosphere, however, the soil air is rather different from the atmospheric air as regards its composition. The soil air is characterized by a higher carbon dioxide and water vapour content and a lower oxygen content. The following components of the soil air are important:

Carbon dioxide (CO_2) occurs in the soil air in a concentration of 0.1 to 1.0% in the topsoil, and below the topsoil the concentration may be as high as 5%. The increased content results particularly from the decomposition of organic matter and respiration of soil organisms, including plant roots. Carbon dioxide is an important regulator of the soil pH, and it exerts toxic effects when present in concentrations exceeding 10%.

Oxygen (O_2) is present in the soil air to the extent of 10 to 20%. The decrease of its concentration below 15% results in a decrease and deterioration in the crop yield and in an intensification of reduction processes.

Nitrogen (N_2) occurs in the soil air in about the same proportion as in the atmosphere; it is also present as ammonia. It is the initial as well as final product in the formation and conversion of organic and mineral nitrogen compounds.

Water vapour saturates the soil air, the relative humidity being frequently above 98%. The air humidity is important in the soil for the formation of the adsorption water and for providing suitable conditions for the life of soil organisms.

Due to the decomposition of organic substances, the air is enriched in H_2S, H_2, CH_4, SO_2 and other gases, which negatively affect the soil air quality from the standpoint of the plant growth.

The ability of the soil to bind the gaseous phase is expressed by the soil air capacity and it affects the soil air statics. The soil air dynamics includes the motion of the gaseous phase in the soil and its exchange with the atmospheric air. The binding of air or of its particular components, generally referred to as the air sorption in the soil includes three different phenomena as follows:

— the physical adsorption, which binds the air on the solid particle surfaces,
— the dissolving of gases in soil water, which is important particularly in the case of carbon dioxide and oxygen,
— the adhesion of the air in capillary pores in the form of bubbles in the capillary water.

Similarly as in the case of the bound water, there are also certain important values as regards the air capacity:

— the soil aeration is the instantaneous content of the air in pores, i.e. volume of pores filled with the air. It is given by the difference between the total porosity and humidity ($A = P - H$),
— the air capacity in the strict sense is the air content in the soil, which is saturated with capillary water. It equals the difference between the porosity and capillary water capacity ($C_a = P - C_w$),
— the optimal and minimal air capacities are respectively the most favourable and the lowest contents of the air in the soil as regards desirable conditions for plant respiration.

The soil air is in a state of permanent motion, which is facilitated by changes of temperature, barometric pressure, wind and soil water motion. The motion of the air in the soil, the escape of CO_2 into the atmosphere and the penetration of oxygen into the soil are accomplished mainly via diffusion.

Changes in the content and composition of the soil air characterize the air regime [1–5].

7.1.4 Organic components in the soil

Although amounts of organic components in the soil are low, they are of great importance. The content of organic components seldomly exceeds 10%, but they can affect the course of physical and chemical processes and the general quality of the soil even in trace amounts. The organic components in the soil can be readily divided into two groups:

- living matter, including all the organisms living in the soil,
- non-living matter, formed by the debris of organisms at all the stages of their decomposition.

The living component of organic matter is made up mainly of soil microorganisms, roots of plants and animals living in the soil. The non-living matter of organic origin represents different low- and high-molecular-mass substances of a protein, saccharide or lipidic nature (together with the other compounds released from organic matter), particularly the soil humus. The living and the non-living matter of the organic substances interact in many respects. The organisms are a natural source of substances forming the non-living organic matter which, on the other hand, provides suitable living conditions for the organisms and for many of them it represents an essential source of nutrients and energy. The organic matter affects all the processes occurring in the soil and it is a governing factor in the soil development. The amount and composition of the organic matter are different in various soils and they may be remarkably diverse even within a restricted locality. In common soils, the living and non-living organic matter is represented particularly in humus horizons, which are characterized by an intense biological activity with the formation and decomposition of the organic matter, with the thorough mixing of the mineral substances. Figure 7.6 shows an approximate composition of organic matter in the soil covered by the grass.

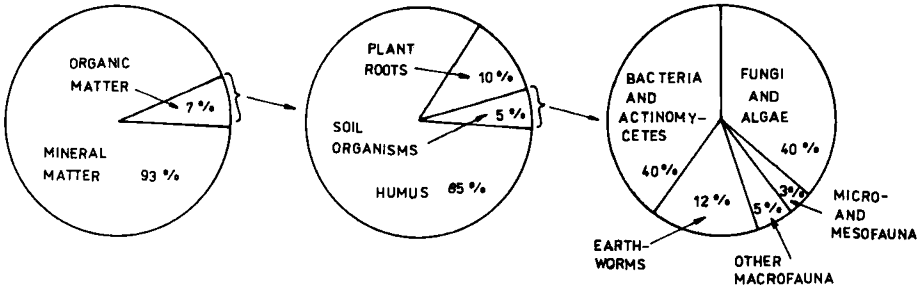

Fig. 7.6. Approximate composition of the organic part of meadow soil

Non-living organic matter in the soil — humus. Humus forms the main and most important part of the non-living component of organic matter in the soil, but it is very difficult to define humus exactly. In pedology, the humus is most frequently characterized as a system of organic substances accumulated on the soil or in the soil, mixed or non-mixed with mineral substances, produced from decayed plants, animals and microorganisms and being at different stages of decomposition. More concisely the humus may be defined as a complex system of organic substances at different stages of the conversion of the plant and animal debris. The main point is that humus is formed by a partial decomposition of the organic debris, during which the original plant or animal character is lost.

Conversions of organic substances in the soil may result in mineralization, humification and peat formation (and possibly carbonization). The mineralization represents a complete decomposition of organic matter and it is accomplished particularly under the conditions of intense activity of aerobic microorganisms. The peat formation and carbonization occur under conditions of a very limited microbial activity with the accumulation of decayed debris, which exhibit very slow decomposition. Humification is a particular form of microbial decomposition, which, however, may also involve condensation and polymerization of decay products. To a considerable extent this is an oxidative process, resulting in the formation of high-molecular-mass nitrogen compounds with a remarkable abundance of aromatic components. This conversion is of a biochemical nature; it occurs in the presence of oxygen and oxidases of organisms. A preliminary portion of nitrogen substances comes from proteins, the particular source of aromatic components of the humus formed being lignin. One of possible mechanisms of humification is shown in the schematic diagram, Fig. 7.7.

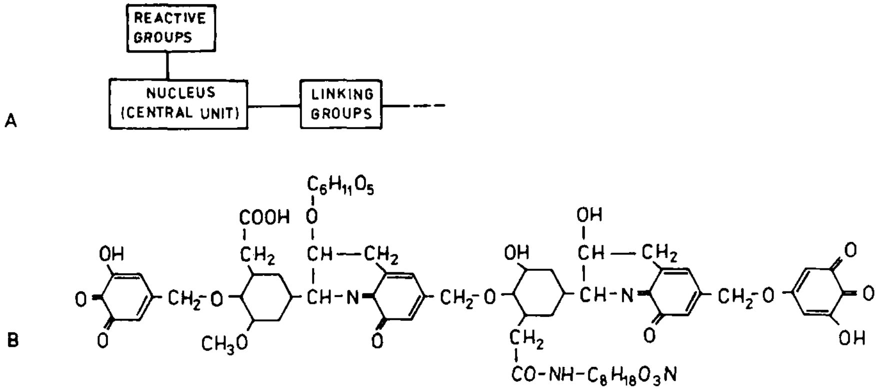

Fig. 7.7. A schematic structure of humic acids (A) and a possible example of the chemical arrangement (B)

From the chemical standpoint, the humus is a very heterogeneous material, from which two groups of substances may be separated as follows: humic substances themselves; and a second group which includes non-specific substances, also referred to as non-humic substances.

Humic substances are typical products of the humification process. They are the basic component of the humus, occurring in the humus material to the extent of 80 to 90%. They consist of a group of acid, yellow to dark brown polymeric substances of a heterogeneous aromatic and polydisperse character. Their acid nature allows them to react with mineral substances to form stable organomineral complexes sometimes referred to as humines. They differ from the remaining organic material in the soil by various typical features as follows:

- in their elementary composition, having a higher oxygen content,
- by the presence of a low number of carboxy and phenolic groups,
- by a high content of nitrogen, incorporated into central heterocycles and peripheral chains.

Due to a high content of acid carboxy and phenolic groups, the humic substances may be dissolved in alkaline solutions. In the soil, the humic substances behave as natural ion exchangers, molecular sieves and as material able to accumulate mineral substances, particularly cations. At the present time it is assumed that macromolecules of humic substances, in spite of being a chemically very heterogeneous mixture, have in common a certain general molecular structure. The basic scheme and approximate molecular structure of humic substances are shown in Fig. 7.8.

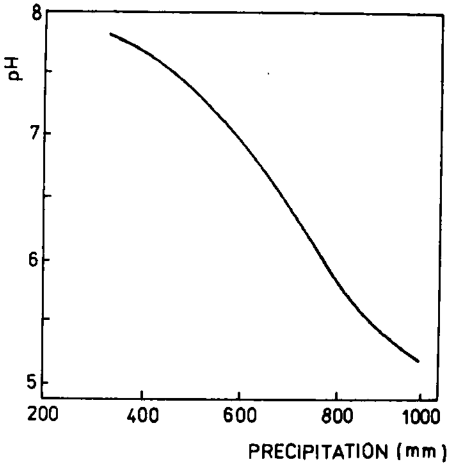

Fig. 7.8. Effects of humidity on soil reaction

The essential part of the macromolecule is a ring given by aromatic compounds derived from different derivatives of benzene, quinone, pyridine, furane, thiophene, etc. To the ring, side chains and functional groups are connected. The rings are interconnected by side chains or simple bonds, particularly via oxygen, nitrogen and sulphur, so that they can polymerize to form larger molecules. The rings are formed in the humification process from lignin substances, which are oxidized in the presence of nitrogen compounds and oxygen with a conversion to some of the above-mentioned aromates. These reactions are catalysed mostly by microbial enzymes, such as phenol oxidases. As a result of this, very stable polymers of a complicated structure are obtained, with a relative formula mass ranging from several hundreds to 100,000.

In spite of the heterogeneity, the humic substances can be grouped into three different types on the basis of certain characteristics as follows:

Humic acids are soluble in weak alkaline solutions and are essentially insoluble in water and mineral acids. They may be precipitated from solution by the action of mineral acids and bivalent or trivalent cations, however, they are fairly resistant to the acid hydrolysis. They are dark spherocolloids with a cross-linked structure which plays a part in their high sorption capacity. They exhibit different degrees of a tendency to aggregation and very different degrees of dispersion. In comparison with other types of natural organic substances, the humic acids are characterized by their extraordinary stability in the soil. This stability is due to their ability to form organomineral complexes, particularly with clay minerals and with aluminium and iron hydroxides.

Fulvic acids are lightly coloured substances, which remain in the solution after precipitating humic acids by acidification and which retain their solubility even in a moderately acid medium. Fulvic acids have not been studied as much as humic acids. It is assumed that in their macromolecules, there is a lower representation of aromatic rings with a predominance of peripheral chains with larger numbers of functional groups, particularly $-COOH$, $-OH$ and $-C=O$. The rings are more frequently connected by aliphatic bonds. A higher content of functional groups increases their acid character and results in an enhanced aggressivity of fulvic acids to mineral substances and in an increased participation in exchange reactions. As a result of a high acidity and good solubility in water, in contrast to humic acids, they are not stabilized by mineral substances, however, they cause their decomposition and they are very mobile in the soil. They form fulvates soluble in water together with products of the mineral decomposition, frequently of the chelate type, which also easily migrate in the soil profile. Fulvic acids predominate in acid podzol and peat soils, their destructive activity being restricted in the presence of higher concentrations of humic acids.

Humins (humus coal) are soluble neither in alkalies nor in acids. This group in humic substances have been very little investigated. They are characterized as an insoluble form of humic acids. Humins are considered as the oldest, and ultimate products of the humification process. They are assumed to be strongly carbonized substances, where the high stability is increased by a strong bond to the mineral fraction. Due to their high chemical stability or even inert character, humins do not participate in the soil formation process and they do not fulfil the function of the true humus.

All the types of humin substances occur in the soil in the free form as well as bound to mineral components, enveloping them with a fine film. They are fairly resistant to the microbial decomposition, however, in spite of this, they are gradually degraded in the soil. Thus, in each soil type, a certain dynamic equilibrium is established between the production and degradation of the humus; this is disturbed by cultivation, which supports the degradation. The mineralization occurs slowly; under conditions of optimal aeration and moisture, about 10% of the total humus amount is decomposed annually. The most rapid mineralization occurs in the case of fulvic acids, whose total amount may be decreased even by one third during a year. The course of the mineralization is also considerably affected by the granulometric composition of the mineral substances; the mineralization in sandy soils is much more rapid than that in clay soils. The decrease of the amount of humus in cultivated soil should be compensated by using organic fertilizers.

Non-specific humic substances (non-humic, non-humified) are also products of the decomposition of organic debris, however, they have not undergone severe chemical changes as in case of specific humic substances and they generally preserve their original character. They include a great variety of organic substances, mostly readily degradable, which can be arranged as follows in order increasing resistance to the decomposition: low-molecular substances (simple saccharides, fatty acids, alcohols, esters, etc.), starch, proteins < complex proteins < pectins, hemicelluloses < celluloses < lignin < waxes, tannin materials, bitumens. In the soil humus, their abundance does not usually exceed 10 to 15%, however, under less favourable conditions for the humification, e.g. in peat and forest soils, the portion of non-specific humic substances may be as high as 50 to 80%. There is a lack of data for a more precise estimation of the function of non-specific components of the humus, however, their importance cannot be considered as negligible in spite of their lower abundance. Many of them represent a form of organic nutrients, which may be utilized; acid components support the decomposition of minerals and may participate actively in the soil formation process [1–3, 5–8].

Living components in the soil

The living components of organic matter in the soil are formed by roots of plants and edaphon, which forms a complex biocenosis of organisms living in the soil layer. Edaphon consists of different groups of organisms, i.e. plants (fytoedaphon) and animals (zooedaphon), particular groups being dependent on each other particularly via nutritional relationships. Depending on the size of the organisms it is possible to differentiate the micro-, meso- and macroedaphon.

Table 7.2. Approximate numbers of specimens of main groups of the edaphon in 1 g of earth and their mass in a 15-cm soil layer, per ha

Group	Number	Weight
Bacteria	600,000,000 in 1 g	10,000 kg
Fungi	400,000 in 1 g	10,000 kg
Algae	100,000 in 1 g	140 kg
Protozoa	1,500,000,000 in 1 l	370 kg
Nemathelminthes	50,000 in 1 l	50 kg
Collembola	200 in 1 l	6 kg
Mites	150 in 1 l	4 kg
Enchytraeus	20 in 1 l	15 kg
Chilopoda	14 in 1 l	50 kg
Insects, Araneidea	6 in 1 l	17 kg
Molluscs	5 in 1 l	40 kg
Earthworms	2 in 1 l	4 000 kg

The microedaphon is formed by all the soil microorganisms of plant origin (microflora) and animal origin (microfauna). The main representatives of the microflora are *Actinomycetes* and the other groups of bacteria, further *Cyanobacteria, Algae* and *Fungi.* The microfauna consists mainly of *Protozoa*, however it also includes further microscopic animals, such as *Rotatoria, Rhabditoidea*, etc. The mesoedaphon includes larger worms, different stages of the development of insects, molluscs, etc., and the macroedaphon includes particularly small vertebrata.

The organisms included in the edaphon may be grouped according to the stage of their life in which they reside in the soil as follows:

— geobionts — living entirely in the soil for their whole life,

— geophils — living partially in the soil and partially beyond the soil,
— geoxens — occurring only temporarily or randomly in the soil.

A summary of the abundance of main groups of the edaphon in the top soil of an intermediate fertility soil is given in Table 7.2 [5–7].

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7.2 The main characteristics of the soil

7.2.1 Basic physical characteristics of the soil

The basic physical characteristics of the soil are as follows:

The *specific mass*, expressed as a ratio of the mass of the solid phase of the soil to the mass of the same volume of water at 4°C. It can also be expressed as a mass of one cm^3 of non-porous soil material in g ($g\ cm^{-3}$). The soil specific mass depends on specific masses of the main mineral components and on the amount of the humus. The specific mass of a soil poor in humus is thus close to that of silica, feldspar and clay minerals and its value is about 2.6 to 2.7 $g\ cm^{-3}$. Increased humus contents result in a decrease of the soil specific mass to about 2.4 to 2.5 $g\ cm^{-3}$; the presence of minerals containing iron can increase the specific mass above 2.7 $g\ cm^{-3}$.

The *bulk density* is a mass of a unit volume of soil (1 cm^3) in the natural spatial arrangement of the soil, expressed in $g\ cm^{-3}$. It depends on the specific mass and on the porosity, i.e. on the air and water content in the soil. Thus, it is possible to consider the non-reduced bulk density, corresponding to a certain soil volume including its actual moisture and reduced bulk density, which is determined after drying the soil sample at 105°C.

The bulk density varies in the course of a year and during the vegetation season as a result, for example of swelling, drying of the soil or cultivation interventions. The value of the bulk density usually ranges between 0.2 g cm^{-3} (peats) and 1.8 g cm^{-3} (solidified earths). Most typically it is, however, between 1.20 and 1.60 g cm^{-3}. The bulk density usually increases with increasing depth of the profile.

The *porosity* is a measure of the total number of pores contained in a certain soil volume and it is expressed as a percentage. It is considered as the most important characteristic among the basic physical quantities. It is calculated from the formula

$$P = \frac{S - S_1}{S} 100 \text{ (vol.\%)}$$

where S is the specific mass and S_1 is the reduced bulk density.

The porosity value is also very variable, in medium-heavy structural soils it is between 40 and 50%, in lighter sandy and dense solidified soils it decreases to 25–30%; in soils rich in humus and in peat soils it may be as high as 90%. The porosity value depends on the mutual arrangement of soil particles and aggregates affecting the total volume of pores, and their shape, size and situation.

In structural soils, the pores are present between the aggregates and inside of the aggregates and the porosity is given by the sum of the two. Good structural top soil should show a total porosity of at least 50% with at least 1/3 of pores between the aggregates. The shape, size and arrangement of pores are the decisive factors for the water and air regime in the soil, playing an important role of communication between pores, and between pores and soil surface.

The *pores* may be categorized in various ways. Capillary, non-capillary and semi-capillary pores are frequently considered.

Capillary pores are those characterized by capillary forces, so that in them, water moves in the direction of elevation forces and not of gravitational forces. The capillary pore volume determines the soil water retention capacity. The motion of air in capillary pores is strongly restricted.

Non-capillary pores do not restrict the gravitational action, water is free to move downward and air enters into the emptied spaces. The volume of non-capillary pores is a measure of the soil aeration, i.e. its minimal air capacity (during the saturation of the soil capillaries with water).

Semi-capillary pores represent a bridge between the two above-mentioned types of pores and they are characterized by effects of both capillary and gravitational forces.

The pores can also be classified by size, from coarse with a pore diameter exceeding 30 μm, to medium-sized with diameters of 3 to 30 μm, and lastly fine with a diameter below 3 μm. In general it holds that in the case of a good soil porosity fine, medium-sized and coarse pores are present in approximately the same abundances.

The *structure* expresses the ability of the soil to form larger or smaller aggregates. The soil aggregates may occur at different stages of their development. For example, weakly developed aggregates are separated only during the action of a strong pressure or impact, medium-developed ones separate during a moderate pressure or impact, and well-developed aggregates may be separated from each other easily and they may be identified macroscopically according to their shape and size. According to the size, the structural aggregates are grouped as follows:

(a) microaggregates (smaller than 0.25 mm in diameter),
(b) macroaggregates (0.25 to 50 mm in diameter),
(c) megaaggregates (above 50 mm in diameter).

Aggregates may occur in the shape of spheres, cubes, prisms and plates. Besides natural effects, cultivation effects also contribute to the formation of structural aggregates in cultured soils. There is a particularly important role played by the irreversible coagulation of mineral and organic colloids, which occurs by the action of exchangeable calcium ions. Via the irreversible coagulation of colloids, water-resistant aggregates with favourable characteristics are formed. Larger aggregates are formed by the adhesion of microaggregates, which represent the basic structural unit in the formation of the soil structure. During microaggregation, physical, chemical as well as biological effects are active. Among the various mineral substances, particularly sesquioxides (R_2O_3) are of importance, which are sorbed on the surface of soil particles and hydrolysed. Organic substances are also an efficient adhesive factor, frequently reacting with Al^{3+} and Fe^{3+} ions which are absorbed on mineral particles after preceding hydrolysis. By enriching the soil in organic matter, the biological factor will also participate on the aggregation process by supporting the adhesion through the production of mucous substances and through the disintegration of compact soil material. Macroaggregates are formed from microaggregate material by volume changes during the soil drying (formation of small cracks), by the action of freezing, and by dehydration and cultivation. The cohesion of macroaggregates depends on the nature of their formation, on the stability of the macroaggregates and on their mutual adhesion. The aggregate cohesion is sometimes strengthened by an organic membrane on the aggregate surface or by fine roots on their surface [1–5].

7.2.2 Physico-mechanical characteristics of the soil

The physico-mechanical characteristics of the soil determine directly its technological properties. They depend particularly on the grain-size, moisture, structure, and also on the human content and cationic composition of the soil colloidal complex. The most important technological characteristics of the soil are as follows:

Cohesion, which is due to attractive forces between mechanical particles. It is manifested by the ability of the soil to resist external pressure, to resist the disintegration of aggregates and to resist the penetration of objects into the soil. The degree of cohesion and the strength are connected with the structural state of the soil. In soil with a good structure, there is a sufficient cohesion between particles forming aggregates, whereas between particular aggregates the cohesion is lower, so that the soil is loose. The cohesion is increased by drying of the soil and it is reduced by the action of increased moisture.

The *adhesion* is manifested by the soil sticking to the surface of working tools and it is due to attractive forces between soil particles and surfaces of such tools. It depends on the grain size and soil moisture. In loamy to clay soils it increases with increasing moisture; after exceeding the lower limit of plasticity it again decreases.

The *consistency* is a general term for soil quality including its cohesion, adhesion and resistance to the deformation at a certain soil moisture. For the same moisture, different soils exhibit different consistencies; on the other hand, they can have different moisture values for the same consistency. Soils with small grain-size can have several degrees of consistency with increasing water content, referred to as the hardness, plasticity, sticking quality and paste consistency. Sandy soils are loose in the dry state, on increasing the moisture content, they acquire a certain plasticity, and when saturated with water they completely lose their cohesion and they then behave as flowing sands. Loamy-sand and clay soils tend to disintegrate after reducing the moisture, and after drying they are hard.

There are other technological characteristics, among which the following should be mentioned: the compactness, carrying capacity, swelling, clodding tendency, scattering tendency, and resistance during ploughing.

7.2.3 The sorption capacity of the soil

Depending on the mechanism of binding substances, several types of the sorption in the soil may be considered as follows:

— the mechanical sorption involves a mechanical retention of coarsely dispersed particles in soil pores,

— physical sorption (adsorption) is conditioned by surface phenomena on the interface of phases, leading to changes of concentration of gases, liquids, electrolytes and non-electrolytes,

— physico-chemical sorption (exchange) is accomplished through an ion exchange between the soil colloidal complex and soil solution in equivalent ratios. It is most important for the chemistry of soil and for its typical dynamics,

— chemical sorption (absorption) is based on irreversible binding, particularly of anions able to form sparingly soluble or insoluble substances, which can also be retained mechanically after their precipitation,

— biological sorption results from the taking up of biogenic elements by plant roots and microorganisms. This type of sorption is characterized by its selectivity.

The sorption mechanism includes diffusion motion, facilitating the penetration of molecules and ions to the active surface of colloids, their release into the medium and mutual exchanges. The diffusion is manifested during the motion of ions in the electric double layer of colloids as well as during the motion of ions and molecules to the surface of plant and microbial cells.

The sorption of ions is geverned by exchange and non-exchange reactions between soil colloids and soil solution. The reactions are mainly of a physico-chemical character and they tend to establish a dynamic equilibrium between the two reacting components. The assembly of colloids participating in exchange reactions is named the *soil colloidal complex*. It is formed by colloids of mineral as well as organic origin with different degrees of dispersion and activity. These heterogeneous particles are characterized by different capacities for binding and releasing substances present in the dispersion medium which means that they have different sorption capacities. Ions in the compensation (diffuse) layer of colloidal micelles, which are able to participate in exchange reactions, may be considered as exchangeable cations or exchangeable anions. Acidic colloids, which are strongly predominant in the colloidal complex, exhibit the sorption of cations. This may be shown schematically as follows (scc — soil colloidal complex):

$$\text{scc}\left]\begin{array}{l}\text{Ca}\\ \\ \text{Mg}\\ \\ \text{H}\end{array}\right. + 5\text{KCl} \rightleftharpoons \text{scc}\left]\begin{array}{l}\text{K}\\ \text{K}\\ \text{K}\\ \text{K}\\ \text{K}\end{array}\right. + \text{CaCl}_2 + \text{MgCl}_2 + \text{HCl}$$

Basoids with a positive charge are able to bind anions, for example

$$\text{scc}\ ]\ H_2PO_4^- + NaOH \rightleftharpoons \text{scc}\ ]\ OH^- + NaH_2PO_4$$

Equivalent amounts are exchanged. A non-exchanging sorption can also occur in the soil, e.g. in the charging layer of colloids or by binding ions in layers between lattices of clay minerals.

In the exchange sorption, particularly cations participate, however, their degrees of sorption are different. The ability of cations to be sorbed increases with their valency, relative atomic mass and radius. Cations with a higher adsorption degree, such as Ca^{2+} may be displaced by cations with a lower adsorption degree, such as, e.g., Na^+, only when the displacing cations are present in great excess in the soil solution. The sorption ability of cations is limited by the hydration shell and thus, univalent cations with a larger hydration shell exert a lower degree of sorption. Hydrogen ions are an exception, since in an aqueous solution they form hydroxonium ions H_3O^+ with water molecules, which are sorbed very intensively.

The exchange sorption capacity (T) of the soil is expressed in mEq of cations exchanged per 100 g of dry soil. Besides the exchange sorption capacity, the representation of groups of basic and alkaline cations (Ca^{2+}, Mg^{2+}, K^+, NH_4^+) is of importance; it is also expressed in mEq 100 g^{-1} of soil and it is denoted by S. The ratio of the abundance of basic and alkali substances to the total sorption capacity is determined by the degree of the sorption saturation with bases V, which is expressed as a percentage as follows:

$$V = \frac{S}{T} 100\%$$

Soils which have sorbed in their sorption complex almost exclusively basic and alkaline cations are considered as sorption-saturated, those also containing higher proportions of exchangeable hydrogen and aluminium are considered as unsaturated.

A high sorption exchange capacity is characteristic, e.g., for humic acids (T = 250 to 450 mEq 100 g^{-1}) or montmorillonite (80 to 150 mEq 100 g^{-1}), a very low exchange sorption capacity is shown, for example, by kaolinite (3 to 10 mEq 100 g^{-1}).

The sorption capacity of the soil depends on its mineralogical composition, dispersion humus content and pH of the medium. In an acid medium, the negative charge of acidoids is decreased, which results in decreasing the total exchange capacity. A very acid medium can induce a change of the sign of the colloid charge and hence a transition from cation sorption to the anion sorption.

The sorption capacity of soils may be classified as follows (Kutílek 1978):

Very high	40 mEq 100 g^{-1},
High	25 to 40 mEq 100 g^{-1},
Intermediate	12 to 25 mEq 100 g^{-1},
Low	8 to 12 mEq 100 g^{-1},
Very low	8 mEq 100 g^{-1}.

Depending on the degree of the sorption saturation, the soils can be categorized as follows (Kutílek 1978):

Soil	Value (%)
Completely saturated	90–100
Saturated	75–90
Weakly saturated	50–75
Unsaturated	> 50

The saturated soils exhibit more advantageous physiological and technological properties, they are characterized by a water-resistant small-clod structure, good aeration and water retention. Unsaturated soils show a weak penetration for both water and air, and they are sticky with an unfavourable prismatic structure.

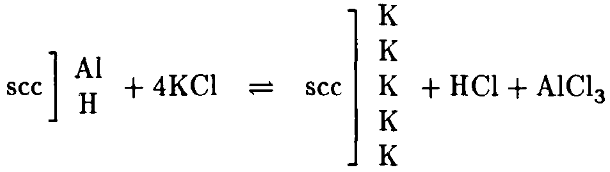
7.2.4 The pH of soil

The soil pH considerably affects soil characteristics. It is important for many soil-forming processes and it also affects the biological activity of soil organisms. The soil pH directly affects particularly the solubility of many substances, ion adsorption and desorption, coagulation and peptization of colloids and chemical reactions. By its action on the soil structure it also affects most of the physical properties of the soil. Thus, the soil pH is an important parameter of the soil fertility.

Owing to the very complicated character of relationships in the soil, it is useful to consider the active acidity and potential (exchange and hydrolytic) acidity.

The active soil acidity is determined by H^+ (or more precisely H_3O^+) and OH^- ions, present in the free state in the soil solution. It is mostly evaluated on the basis of the soil filtrate. The active soil acidity may be manifested only when having hydrogen ions non-associated with bases, basic salts or basic groups of colloids and in the absence of their exchange with basic cations during exchange reactions. This is the case particularly in sorption-unsaturated soils. The potential acidity is governed by ions H^+ and Al^{3+} adsorbed by the soil complex, which may be released into the soil solution by an exchange for basic ions of a salt. Depending on the method of determination the potential acidity may be established as:

— an exchange acidity, which is defined as the ability of the soil to acidify solutions of neutral salts. It is measured by displacement of hydrogen and aluminium ions with a neutral salt solution (KCl):



$$\mathrm{scc}\left]\begin{matrix}\mathrm{Al}\\ \mathrm{H}\end{matrix}\right. + 4\mathrm{KCl} \rightleftharpoons \mathrm{scc}\left]\begin{matrix}\mathrm{K}\\ \mathrm{K}\\ \mathrm{K}\\ \mathrm{K}\\ \mathrm{K}\end{matrix}\right. + \mathrm{HCl} + \mathrm{AlCl_3}$$

— hydrolytic acidity is defined as the ability of a soil to acidify solutions of basic salts. A sodium acetate solution is typically used for displacing hydrogen and aluminium salts:

$$\mathrm{scc}\;]\;\mathrm{H} + \mathrm{CH_3COONa} \rightarrow \mathrm{scc}\;]\;\mathrm{Na} + \mathrm{CH_3COOH}$$

The hydrolytic acidity is generally higher than the exchange acidity, since the reversibility of the ion exchange is strongly restricted by a lower CH_3COOH dissociation. The potential acidity is higher (lower pH) than the active acidity. The difference between the two values is shifted when determining the sorption saturation of the soil. The soil acidity is usually evaluated according to the following scale:

Type of soil	Active pH	Exchange pH
Strongly acid	4.9	4.5
Acid	5.0–5.9	4.5–5.5
Weakly acid	6.0–6.9	5.5–6.5
Neutral	7.0	6.5–7.2
Weakly alkaline	7.1–8.0	7.2–8.5
Alkaline	8.1–9.4	8.5
Strongly alkaline	9.4	8.5

The soil acidity results from mutual effects of several factors, particularly the soil composition, moisture and biological activity. The soil reaction is strongly reduced by action of excess moisture (Fig. 7.8), and also by the fertilization with acid industrial fertilizers or by an unfavourably high production of fulvic acids during the humification process.

The presence of large amounts of basic salts can considerable shift the soil reaction into the alkaline region. Soil alkalinity is mostly caused by exchangeable sodium cations in soil colloids.

Plants usually require weakly acid to neutral soils, in which most biogenic elements occur in utilizable forms. Soil bacteria prefer neutral soils, and weakly acid soils are advantageous for fungi. The soil acidity is usually adjusted by soil liming, which should be accompanied by the application of organic fertilizers and suitable industrial fertilizers [3–6].

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7.3 Inorganic substances in the soil

7.3.1 The chemical composition of the soil — the elemental composition

The chemical composition of the soil is mostly determined by its predominant mineral portion. In the soil, there are almost all the known chemical elements; however, approximately 90% is made up of O, Si, Al and Fe. A further 9% includes Ca, Na, K and Mg, and after these, Ti, Mn, P and other elements are present in lower amounts. The average content of elements in the soil and in the lithosphere is given in Table 7.3.

The main elements occur in the soil in the form of different compounds as follows:

— Oxygen is present in the form of oxides and hydroxides, in hydrated minerals and together with carbon and hydrogen also in organic substances.

— Silicon is present mostly in the form of SiO_2 and silicates.

Table 7.3. Mean contents of elements in the lithosphere and soils in %

Element		Lithosphere	Soil
Oxygen	(O)	47.2	49.0
Silicon	(Si)	27.6	33.0
Aluminium	(Al)	8.8	7.13
Iron	(Fe)	5.1	3.8
Calcium	(Ca)	3.6	1.37
Sodium	(Na)	2.64	0.63
Potassium	(K)	2.6	1.36
Magnesium	(Mg)	2.1	0.6
Titanium	(Ti)	0.6	0.46
Hydrogen	(H)	(0.15)	—
Carbon	(C)	(0.1)	2.0
Sulphur	(S)	0.06	0.085
Manganese	(Mn)	0.09	0.085
Phosphorus	(P)	0.12	0.08
Nitrogen	(N)	0.01	0.1
Copper	(Cu)	0.01	0.002
Zinc	(Zn)	0.005	0.005
Cobalt	(Co)	0.003	0.0008
Boron	(B)	0.0003	0.001
Molybdenum	(Mo)	0.0003	0.0003

— Aluminium is a component of primary and secondary minerals, organo-mineral complexes, and in acid soils it is also converted to exchangeable or even water-soluble forms (hydroxide).

— Iron occurs in soils in the form of Fe-silicates, oxides, hydroxides and in simple as well as complex salts. Iron is of importance with respect to its variable valency. Similarly as for aluminium, in acid medium, and under reducing conditions it is free in solution, since it is converted into its soluble bivalent form.

— Calcium and magnesium may be bound in carbonates or in other compounds. They participate in exchange reactions and they serve as cations supporting the coagulation of colloids.

— Potassium and sodium occur in crystal lattices of minerals; in the form of salts they are present in the soil solution and their cations are active in exchange processes of the soil colloidal complex. Potassium is important in plant nutrition. Sodium unfavourably affects the chemical and physical characteristics of soils because it plays a part in the destruction of structural aggregates.

- Phosphorus in mineral form is bound in phosphates (Ca, Mg, Fe, Al) or in the soil colloidal complex in the form of phosphoric acid amides. Phosphorus bound to organic substances is also of importance.
- Manganese is characterized by its variable valency and its mobility in the soil is comparable with that of iron.
- Nitrogen enters the soil first of all by means of the biological accumulation of atmospheric nitrogen, since rocks contain essentially no nitrogen. From organic (proteins) forms, it may be converted by the mineralization to ammonia, nitrate and nitrite forms. The ammonium cation is sorbed more easily by the soil and thus, it is more firmly fixed than the nitrate anion. Nitrite anion is toxic; in the soil it is rapidly converted to nitrate by the action of nitrifying bacteria.
- Sulphur occurs in the soil in the form of sulphates and sulphides, and also as organic substances. At the present time, large amounts of sulphur are entering the soil with atmospheric precipitations in the form of SO_2.

It is of interest that the quantitative elemental composition of living organisms is remarkably different from that of the lithosphere as well as the pedosphere. Most of 99 elements of the earth's crust have been found in organisms, however, more than 99% of the body weight includes only 11 elements. These are the macroelements, H, C, N, O, Na, Mg, P, S, Cl, K, Ca. The remaining elements are microelements.

Microelements are present in soils only in very low concentrations, mostly up to 0.001%. In the life of plants and animals, including man, they play a very important role, since they are components of vitamins, enzymes, hormones and other biological substances with a high physiological activity. Their insufficiency can lead to different diseases and disturbances and thus, they are a focus of agricultural and nutritional interest.

7.3.2 The soil radioactivity

The soil radioactivity is due to the occurrence of a high number of radioactive isotopes in the natural environment, which come from different natural as well as artificial sources. They may be categorized into four groups as follows:

- radioactive intermediate products of the decay of a known decay series of radioactive elements with a high atomic mass, such as uranium, actinium and thorium,
- radioactive isotopes of elements with a lower atomic mass, but with long half-lives and low natural activity such as ^{40}K, ^{87}Rb, ^{147}Sm, ^{48}Ca, ^{96}Zr,

- radioactive isotopes formed from stable isotopes in the atmosphere by the action of cosmic rays, e.g. ^{3}H, ^{7}Be, ^{10}Be, ^{14}C, and
- radioactive isotopes formed during nuclear explosions, in the operation and accidents of nuclear facilities, during irradiation of stable isotopes by neutrons in reactors and charged particles in accelerators, etc.

The origin of radiation sources leads to either natural or artificial radioactivity.

The natural radioactivity of soils depends particularly on the origin and composition of the parent rock, on the degree of weathering, and on the prevalent types of the soil formation process (particularly leaching). For example, the soils obtained by weathering of acid rocks contain higher amounts of radioactive elements as compared to those produced from basic rocks. Heavy soils contain higher amounts of radioactive elements than sandy soils. The distribution of radioactive isotopes in the soil profile is usually fairly uniform, and only in certain soils is it possible to observe an increased accumulation in illuvial horizons.

Natural radioactivity is formed particularly by long-lived isotopes, i.e. by those with half-lives of 10^{8} to 10^{16} years. These isotopes are usually widely scattered in the soil. The activity level depends particularly on contents of uranium, thorium, radium and potassium; the radiation energy of these elements represents as much as 98% of the total energy of radiation of all the natural radioactive elements in the soil.

By the action of the cosmic radiation, nitrogen in the atmosphere is converted to radioactive carbon ^{14}C and tritium ^{3}H. The radioactive carbon with a half-life of 5770 years and tritium with a half-life of 12.26 years enter the soil with precipitation, and together with radioactive potassium they are included into the biological circulation of elements. The principles of the formation and decay of radioactive carbon are used when determining the age of organic compounds in the organic debris and soils.

Artificial radioactive elements are all the isotopes formed by fission and other nuclear reactions carried out intentionally by man. In the form of radioactive fallout they enter the air, water and soil. These are particularly the radioisotopes ^{137}Cs, ^{90}Sr, ^{95}Zr, ^{95}Nb, ^{106}Ru, ^{141}Ce, ^{144}Cs and ^{131}I. Except for ^{90}Sr and ^{137}Cs, they have short half-lives and thus, they disappear fairly rapidly from the soil. From an environmental viewpoint strontium and caesium are the most dangerous on account of their long half-lives (28 and 30 years, respectively), high radiation energies and ability to be included in the biological circulation of substances and to be accumulated in organisms of plants, animals and man, this last being the result of a chemical similarity with certain biogenic elements. Radioactive strontium has characteristics similar to calcium, and radioactive caesium is similar to potassium. Thus, their accumulation in organisms depends on the chemical form of the isotope and on characteristics of soils. A high proportion of both elements occurs in the form of exchangeable ions. Strontium can be easily displaced; in contrast to this, caesium is strongly sorbed. From the soil, strontium is taken up mainly by plants requiring calcium (calcophilic), and plants with higher requirements for potassium take up larger amounts of caesium. Lighter soils, poor in humus, facilitate a larger amounts of caesium. Lighter soils, poor in humus, facilitate a larger utilization of radioactive isotopes as compared with heavy soils, characterized by a higher content of organic substances, particularly of humic acids. The ^{90}Sr intake is lower in cultivated soils well supplied with calcium and nutrients, particularly phosphorus and potassium. Potassium fertilizers can also restrict the ^{137}Cs intake. Nitrogen-containing fertilizers can moderately support the utilization of radioactive isotopes. The content of radioisotopes in plants is also affected by the temperature, moisture and composition of mineral soil colloids, particularly by their size and sorption capacity [1–5].

7.3.3 Important exchangeable cations

In soils of temperate zones, Ca^{2+}, Mg^{2+}, H^+, Al^{3+} are the main exchangeable cations, to a lesser extent accompanied by ions of K, Na, Mn, Fe, etc., which occur in trace amounts.

In the topsoil, calcium predominates, representing in some cases, more than one half of all the exchangeable cations. Magnesium concentrations are usually lower by a factor of 4, but during a strong leaching of the soil, the calcium content decreases more rapidly, so that the magnesium concentration may then become dominant. In acid forest soils, the situation is different. Such soils contain lower concentrations of calcium, even less than 10% of the exchangeable cations, H^+ and Al^{3+} being the main exchangeable cations here.

In countries with an arid climate, sodium also becomes one of the main exchangeable cations and it can even become prevalent. A sodium content exceeding by 5% that of all the other exchangeable cations indicates salination of the soil.

The exchangeable cations in the soil colloidal complex considerably affect not only chemical processes and biological ratios, but also the physical condition and technological characteristics of the soil.

Soils containing mainly Ca^{2+} and Mg^{2+} ions (calcareous soils) are usually most suitable for the cultivation in the Temperate Zone. They show a good chemical exchange dynamics, and thanks to a good buffering ability, their pH is close to the neutral region. They are resistant to sudden changes of acidity due to neutralization effects of free calcium carbonate or exchange of adorbed Ca^{2+} ion for free H^+ (i.e. H_3O^+) ions in the soil solution. The humus formed is also saturated with calcium ions and it maintains its neutrality. The topsoil at these sites has a suitable structure and it is resistant to mechanical effects and to water, so that it may be readily cultivated in a wide range of moisture conditions. Soils permeable to water, able to accept large amounts of water, do not change their volume to any great extent during drying and repeated moistening, so that they neither swell nor crack and they show little tendency to become sticky.

Soils with a predominance of H^+ and Al^{3+} ions (acid soils) are produced in humid regions on well-permeable substrates, most frequently in forests. They are sorption-unsaturated, the humus formed being acid, with a high content of fulvic acids and other organic acids. During intense elution with water from precipitations, basic cations are lost due to an increased adsorption of hydrogen ions. The soils thus become acid and their buffering capacity is insufficient. The structure of the topsoil is instable, the soils are easily fused together, which increases their permeability for water and air. Their fertility is lower, since they are not very suitable for most of the cultivated plants. In the case of strong acidity, the soil microflora is also damaged, and toxic effects of released ions of aluminium, bivalent manganese and iron are also manifested.

Soils with a prevalence of Na^+ ions (alkaline soils), which are formed in arid regions, have very unsuitable characteristics. Soil colloids of organic as well as inorganic character are easily peptized by action of the Na^+ ion adsorption, and the soils lose their structure. On moistening, they swell and become impermeable. After drying, the colloids reduce their volume and the soils tend to hardening and cracking. These soils are very unsuitable for cultivated plants and can hardly be cultivated or improved [1, 5–7].

7.3.4 Important anions

Anions participate in chemical conversions and in the total exchange dynamics in the soil to an essentially lesser extent than cations. The reason for this is that they are less adsorbed on the colloidal complex, since the soil adsorbents are negative rather than positive on their surfaces. The soil exchange capacity increases with the acidity for anions, which is connected with an increase of the positive charge of soil colloids, particularly of hydrated oxides. In cultivated soils of the Temperate Zone, with a pH usually in the neutral region, the anions are essentially non-adsorbed. An exception are the phosphates, which are, however, also bound chemically, yielding insoluble compounds; thus, they are not exchangeable.

The sorption of the ions $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} occurs via different mechanisms. At pH below 6.7 the $H_2PO_4^-$ ion is prevalent, above this value HPO_4^{2-} is prevalent and the abundance of the ion PO_4^{3-} in the soil is low even at pH exceeding 7.

In the case of an acid soil, non-exchangeable (constitutional) basic groups adsorb hydrogen ions, which can thus support the formation of hydrogen bonds

$$\mathrm{R{-}OH + H^+{-}OH \rightarrow R{-}OH_2^+{-}OH^-}$$

and the hydroxyl is exchanged for a phosphate ion

$$\mathrm{R{-}OH_2{-}OH + H_2PO_4^- \rightarrow R{-}OH_2{-}H_2PO_4 + OH^-}$$

This initial stage of the sorption occurs very rapidly in contrast to the following steps. The phosphate ion is bound as a compensating anion and it is still exchangeable.

The phosphate anion can also be exchanged for structural hydroxyls of basoid colloids

$$\mathrm{R{-}OH + H_2PO_4^- \rightarrow R{-}H_2PO_4 + OH^-}$$

In this case, it is bound colloidally as a constitutional, charging ion and it can be released from this bond only with difficulty.

The anion forms a tetrahedron of approximately the same size as SiO_4^{4-} and thus, it may be attached to SiO_4^{4-} along the edges of crystal lattices of stratified aluminosilicates (clay minerals). This irreversible sorption has no exchange character.

Phosphate ions cause a release of silicic acid from aluminosilicates, thus causing their desilication. In this way insoluble alumino- and ferri-phosphosilicates are formed, with irreversibly-bound phosphate ions. Insoluble forms of phosphorus are also obtained by the reaction of phosphate ions with hydrated Al and Fe sesquioxides and hydroxylated aluminium ions or with products of the hydrolysis of clay minerals.

This mechanism of binding phosphate ions into insoluble forms with aluminium or iron leads to considerable losses of phosphate fertilizers in the soil, since in this case, only a fraction of the phosphorus supplied may be utilized by the plants.

In neutral and basic soils, rich in $Ca(OH)_2$, $Ca(HCO_3)_2$ and $CaCO_3$, the phosphate ions are precipitated in the form of sparingly soluble or even insoluble calcium phosphates of different compositions depending on pH and Ca^{2+} concentration. The lowest solubility is manifested at a pH of about 7.5. At this pH value, calcium dihydrogen phosphate is easily converted to bicalcium hydrogen phosphate, which is then the main precipitation product [1, 5–9].

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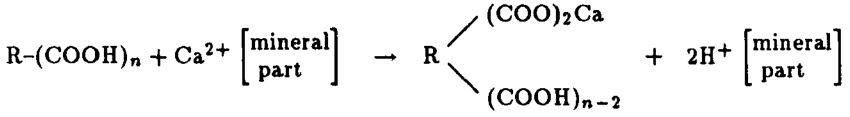
7.4 Organomineral compounds in the soil

Humus and certain other products of the decomposition of organic matter may form, together with mineral substances, organomineral compounds of various kinds. They are generally classified in terms of the principle type of bonding in the structure. In recent classifications the following three basic types are considered:

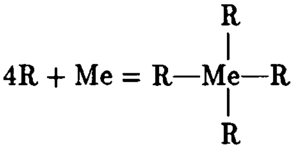
(1) Heteropolar salts — these are formed through the exchange of hydrogen cations of functional groups of humic acids with basic and alkaline cations of mineral particles:



$$R\text{-}(COOH)_n + Ca^{2+}\begin{bmatrix}\text{mineral}\\ \text{part}\end{bmatrix} \rightarrow R\begin{matrix}\nearrow (COO)_2Ca\\ \\ \searrow (COOH)_{n-2}\end{matrix} + 2H^+\begin{bmatrix}\text{mineral}\\ \text{part}\end{bmatrix}$$

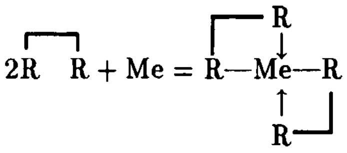
The solubility of heteropolar salts depends on the nature of the organic component and valency of exchangeable cations. Salts of humic acids with univalent cations (K^+, Na^+, NH_4^+) and salts of fulvic acids with univalent as well as polyvalent cations are soluble in water. Salts of humic acids with cations of a higher valency (Ca^{2+}, Mg^{2+}) are insoluble. Thus, particularly fulvates are able to migrate in the soil profile.

(2) Complex heteropolar salts — these are formed by the reaction of humic acids with metallic complexing ions (Fe, Al, Cu, Zn, etc.). Simple metallic complexes



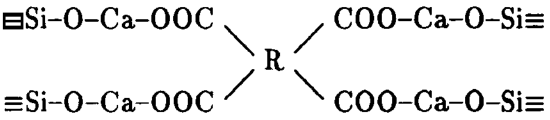
$$4R + Me = R\text{—}\overset{\displaystyle R}{\underset{\displaystyle R}{Me}}\text{—}R$$

or internally complex compounds of the chelate type are obtained.

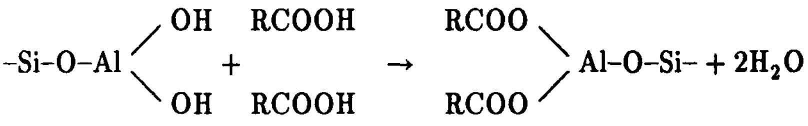


The complexing ion becomes a part of the anionic component of the humus macromolecule and it thus does not behave as a cation. A portion of the carboxylic and hydroxylic groups in humic acids participates in exchange reactions with other cations and thus, the resulting substance is a complex heteropolar salt of the type $(R\text{-}Me)COO^-Me_2^+$.

(3) Adsorption complexes — these are formed by a reaction of humic acids and their salts with the surface of mineral particles, thus yielding complex microaggregates of different degrees of dispersion. They are most frequently formed by coagulation, involving precipitation of humus substances on the surface of clay minerals by means of exchangeable cations:



Chemical bonds can also participate, for example, between hydrated sesquioxides (R_2O_3) and humus substances, with simultaneous dehydration



The adsorption complexes are also formed by a penetration of humus substances into interstitial lattice spaces of clay minerals, however, the mechanism of these processes is still unclear.

The adsorption complexes play an important role in forming the soil colloidal complex and in the formation of structural soil aggregates [1–3].

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7.5 The categorization and systematics of soils

The purpose of the soil categorization and systematics is to differentiate taxonomic units characterized by the same development and characteristics of the soil. The systematics define higher units (above the soil type), the categorization corresponds to the typology and includes a knowledge of soil types and lower classification units. The soil type is the basic taxonomic unit, representing a generalized summary of essential properties and characters of a certain group of particular soils. The following basic characters are considered when differentiating a given soil type:

(a) identical moisture and temperature regime;

(b) identical processes for the accumulation, conversion and transport of substances, identical character of weathering and synthesis;

(c) similar character of plant cover and organic portion;

(d) identical structure of the profile depending on morphological characters and genetic horizons;

(e) approximately the same degree of natural fertility and the same approaches to agrotechnical interventions.

The subtype is a lower unit, including a transient group of soils with a character mainly of a certain type but with some characteristics which belong to another type. Each soil type is characterized by a certain typical stratigraphy of the soil profile, i.e. by a sequence, thickness and development of particular horizons. The horizons may be differentiated from each other on the basis of morphologic features and results of analyses, such as the dispersion composition, mineralogical and chemical composition, etc. The most important morphological characteristics are as follows: the colour, structure, granulometric composition, moisture, consistency, new formations, porosity, edaphon and transition into neighbouring horizons.

The total number of horizons which may occur in different soils is large. Certain symbols are used for denoting particular horizons when describing the stratification of soil profiles, the symbols are listed in Table 7.4.

Table 7.4. Names of basic soil horizons

Horizons	Symbol
1 Overlying organic horizons	
1.1 humous without admixtures of mineral portions	O or Ao
1.2 peat type	
peat type hydromorphic	T
2 Surface horizons (epipedons) with humus accumulation	A
2.1 black soils (chernozem)	Am
2.2 humous soils of remaining types	Ah, Au
2.3 topsoil	Ap
3 Internal horizons	
3.1 eluvial, deprivated, leached	E or A_2
3.2 illuvial, enriched	B
3.2.1 alcali soil (solonetz)	Btna
3.2.2 sesquioxide type	Bs
3.2.3 humous-sesquioxide type	Bhs
3.3 metamorphous	
3.3.1 yellow with clay formation	Bv
3.3.2 structural, less marked browning with clay formation	Bvr
3.4 hydromorphous, oxidation-reduction	
3.4.1 surface gleying	g
3.4.2 gleyish	G
— oxidation subhorizon	
— reduction subhorizon	
4 Underlying horizon	
4.1 soil forming substrates	C
4.2 underlying rock different from C	D or R
4.3 firm, non-weathered rock	M

In the review below we will characterize briefly certain important soil types. More extensive accounts can be found in the pedologic literature (e.g. [2]).

Black soil (chernozem) — this occurs in lowlands under conditions of a dry and warm climate with a mean annual temperature of about 9°C and mean annual sum of precipitations of 450 to 600 mm, at levels up to 300 m. The black soils were formed in regions of former steppes and forest-steppe areas. They belong to the oldest cultivated soils. The water regime of black soils is characterized by the absence of washing through or by partial periodic washing through. The main diagnostic horizons:

A — dark, sorption-saturated humus horizon, clodded structure,

C — carbonate soil forming substrate with the accumulation of eluted $CaCO_3$.

Humus content 2.2 to 7%, the ratio C:N = 8:1 to 9:1. A neutral soil solution.

Brown forest soils — these occur in loess hilly countries and lowlands in marginal zones of chernozem areas. The basic morphology of the profile is as follows:

A_p — light to dark humus horizon, clodded structure,

B — dark, textural horizon, sometimes with bright colloidal coatings.

Illimerized soils are developed in flat areas of hilly countries, in valleys at a level of 300 to 600 m. The mean annual temperature is 6 to 8°C, mean annual sum of precipitations 600 to 900 mm. The main horizons:

A_p — light grey, clodded structure,

E — distinctly greyish-white with transitions in the form of prominences,

B — dark brown, polyhedric to cubic structure.

The aqueous regime is characterized by washing through.

Rendzinae — these are formed at different altitudes and climatic conditions on carbonate and ultrabasic rocks. The main diagnostic horizons:

A — pale humus horizon, sorption-saturated, containing carbonates,

Ah — grey to brown, with gravel,

C — carbonate substrate.

The water and air regime depends on the type of parent rock and climate.

Brown soils occur

(a) at lower altitudes (300 to 600 m) with a mean annual temperature of 6 to 9°C and mean amount of annual precipitations 500 to 800 mm;

(b) in mountain regions at an altitude of 500 m, mean annual temperature of 4 to 7°C, mean amount of annual precipitations 600 to 1200 mm. The characteristic process is the formation of a brown colour resulting from the release of R_2O_3 (particularly Fe_2O_3) during the mineral weathering. The main horizons in the profile are as follows:

O — greyish-brown humus horizon, topsoil, small clodded structure,

Bv — brown to dark brown, indistinct structure,

C — greyish, partially weathered rock.

The water regime is mostly characterized by periodic washing through.

Podzol soils occur in mountain and submountain areas with a mean annual temperature below 5°C and with total annual precipitations exceeding 900 mm. The main horizons are as follows:

O — a pale humus horizon with a weakly developed structure,

E — ash-grey, non-structural horizon,

Bhs, Bs — ferruginously coloured, humus-sesquioxide or sesquioxide illuvial horizon with an indistinct structure.

The prevalent phenomenon is the podzol formation, which is due to a translocation of R_2O_3 in the complex fulvic acids in the downward direction without an essential migration of clay minerals. As a result of this, a depreciated elluvial horizon and an illuvial horizon enriched in humus and sesquioxides are obtained.

Meadow soils occur in recent meadows of rivers by action of floods occurring from time to time. They belong to the group of young soils from the development standpoint, their profile is indistinct:

Ah, O — pale humus horizon, crumb structure,

C — alluvial, brown soil-forming substrate.

They are invariably situated along water flows.

Undeveloped soils are formed on substrates with an extremely granular composition. They are of sandy or skeleton type, with manifestations of initiating stages of the development. They occur at all altitudes except for lowlands. Products of weathering and humification occur frequently without forming an independent horizon.

Anthropogenic soils are formed by the recultivation of exploited earth minerals or devastated soils. Their characteristics depend on properties and characters of substrates and on the recultivation method [1–3].

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7.6 The pollution of soil by non-natural substances

Soil pollution mostly results from the intensification of agricultural production and from a general invasion of chemical products in all the fields of human activity. With some generalization, it is possible to consider two large groups of pollutants. The first group includes substances used intentionally during soil or vegetation treatment, which are directly produced for agriculture. The second group includes chemical substances which enter the environmental mainly unintentionally, in the form of exhalates, different wastes, etc. The effect of the two groups is important from the standpoint of soil pollution as well as of the general protection of the environment.

7.6.1 Substances which enter the environment unintentionally

These are in general exhalates and wastes of different origins and types. Many of them exert adverse effects on the quality of the environment, deteriorating the characteristics of the soil and the condition of the plant cover and, as a final consequence, they also affect the amount and quality of agricultural products.

Industrial exhalates and wastes. The pollutants in the atmosphere may be gaseous, solid and (in the form of aerosols) also liquid. There are also natural exhalates in the atmosphere, e.g. from the volcanic activity. Thus, the purity of the atmosphere has been at risk ever since the development of industry, which releases many different waste substances into the atmosphere, due to imperfect technological procedures. Energy production, metallurgy, the silicate industry and of course also chemical industry are the most important producers of exhalates.

The contributions from energy production to the exhalate formation are particularly due to the fact that fossil fuels of a generally poor quality are used as the main energy source. From the ecological standpoint, especially coal containing high contents of sulphur and ash is unsuitable. Its combustion yields large amounts of sulphur dioxide, nitrogen oxides and fly ash. In the flue dust, the large portion corresponds to particles smaller than 60 μm (more than 95%). Of these, there are of about 65% of particles smaller than 10 μm, 15% smaller than 2 μm and of about 4% smaller than 1 μm. The fly ash is characterized by a moderate acidity (active pH of about 6.4, exchange pH of 6.0). In terms of chemical composition, the oxides Fe_2O_3, Al_2O_3, CaO, SiO_2, Mn_3O_4, MgO, etc. are prevalent. The portion of sulphates is also fairly high [1, 2].

Metallurgy produces gaseous as well as solid exhalates depending on the type of the production and technology used. Fluorine exhalates from aluminium works are very harmful, as also are tars and arsenic compounds. Iron and steel works produce fly ash, its main components being similar to those in the fly ash from coal, only with different abundances (a high portion of Fe_2O_3). The sulphate content is lower, and fly ash is moderately basic (active as well as exchange pH of 7.5).

In the field of the silicate industry, cement and magnesite works are the most important emission sources. CaO, MgO and other oxides are the main components of the fly ash. The pH is considerably alkaline; the active as well as exchange pH from the emissions of cement works is approximately 8.2, which is obviously connected with the high CaO content.

The chemical industry causes air pollution with different chemical substances, particularly sulphur oxides, H_2S, CS_2, nitrogen oxides and various light as well as heavy hydrocarbons.

All types of exhalates also contain trace amounts of heavy metals and carcinogenic substances. Although the proportion of these is low, they represent a potential hazard from the direct contact of man with the atmosphere as well as through the contamination of foodstuffs. Harmful effects of exhalates from combustion engines containing lead, cadmium, carbon monoxide, nitrogen oxides and organic carcinogens in fairly high concentrations, are of particular importance.

Chemical substances which are released from industrial works in insufficiently purified wastewaters, and which enter surface or even groundwaters also exert very important harmful influences. Improper methods of the disposal of chemical wastes, which can pass through penetrable layers of the soil, are also dangerous to the soil and water. These substances can transfer from the soil and surface waters (e.g. during irrigation) even into agricultural products [1–5].

Agricultural wastes. The problem of the environmental pollution by wastes is also complicated by agriculture itself. It is not only exposed to wastes as a part of the whole ecosystem, it also contributes to the pollution of the environment with wastes of the agricultural origin. From the qualitative standpoint, they are not different in character from traditional and essentially useful organic wastes, which have always participated in the agricultural production. The problem is in their quantity.

In general it is desirable to return the wastes from plant and animal production back into the soil. They are well degradable, and they enrich the soil in nutrients in a readily utilizable organic form. From the ecological standpoint they are helpful in the natural circulation of substances in the environment. On the other hand, improperly maintained dung or silage units are traditional sources of environmental pollution, particularly of water pollution. In smaller farms, these pollution sources are of only limited, local importance, however, they can present difficulties due to their scattered distribution and problems in control. The solution of this problem is, however, not technically difficult. It is sufficient to adhere to hygienic guidelines with an appropriate technology and working discipline.

Essentially more serious problems result from the concentration of animal production into large units, which offer a growth in productivity, but which also leads to basic changes in the relationship of agriculture to the environment. The scattered and minor pollution given by the application of dung onto fields is replaced by large point sources, whose polluting power is of the same order of magnitude as cities or industrial plants.

This industrialization development was first observed in the breeding of pigs, which represent an extraordinary problem from the standpoint of the environment protection at the present time. One of assumptions of a high productivity of such an operation is stabling without litter. Thus, each big farm produces large amounts of the mixture of excrements, urine and residues of the forage and service water. If the set limits are adhered to, then the amount of this mixture should not exceed the acceptable range of 10 to 12 litres per animal per day. Serious problems arise when this amount increases above 20 l. These amounts can hardly be destroyed and, as a result of this, a considerable pollution of surface or groundwaters occurs.

The negative effects from these big farms exert impacts on all the basic components of the environment: air, water and soil. The air pollution with the smell is of relatively minor importance. The degradation of soil (e.g. by salting) is more dangerous; the soil structure and moisture conditions are deteriorated. This is a fairly frequent consequence of violating agrotechnical principles of fertilization so that the soil suffers permanent damage. The damage to the hydrosphere is most dangerous. It usually occurs after a long delay, but once established, it is of a long-term nature. From the standpoint of water protection, it would be the best if the big farms produced no waste water. But this is manifestly a counsel of perfection.

The efficient utilization of the liquid organic wastes has not yet been solved anywhere. Under the geographic conditions in central Europe and at a given population density they cannot be destroyed indirectly. Disposal of excrements into the sea, large rivers and empty mines, etc. has been practiced. The trend may be towards the production of so-called biogas (with a high content of methane) during a controlled decomposition to less degradable residues. Up to the present time the only method for the utilization of liquid excrements is their direct application to fields as organic fertilizers. In practice, however, it has been shown that, as an example, for a capacity of 10,000 pigs this distribution is not feasible in 90% of cases with present techniques. Furthermore, it is also impossible to adhere to all the principles of hygiene, efficient agrotechniques and environmental protection. Possible strategies for the recovery of the polluted areas are too expensive or even impossible [6, 7].

Thus, the intensification of agriculture is accompanied by an unusual deterioration of a relationship, which was formerly very simple. The destruction and utilization of traditional agricultural wastes has become a serious ecological problem.

7.6.2 Pollution by substances used intentionally in agriculture

Pesticides and industrial fertilizers are the chief chemical substances used intentionally in the agriculture. Both are important sources of soil pollution.

Pesticides as pollutants. By pesticides we mean substances for the suppression and destruction of harmful organisms. Pesticides are used particularly in plant production. Originally, mainly inorganic substances were used. Most of them are also used currently, particularly in the form of salts or oxides. However, advances in organic chemistry led to the industrial production of ever more relatively inexpensive synthetic organic substances characterized by their extraordinary efficiency. The first of these was dichlorodiphenyltrichloroethane (DDT), which became commercially available as an insecticide in 1942. At the present time, organic pesticides are in wide-spread use.

Depending on their function or purpose, the pesticides may be categorized as follows:

Type	Target organism
Insecticides	Harmful insects
Fungicides	Fungal diseases
Herbicides	Weeds
Rodenticides	Rodents
Molluscicides	Molluscs
Acaricides	Mites
Nematocides	Nematoda

Some preparations may exert combined effects from the standpoint of this classification.

Insecticides may be further divided into those which act: by contact — penetrating through the chitin cuticula of insects, in feeding — penetrating through the digesting tract, and via respiratory routes — penetrating through the respiratory system. The systematic effect of certain pesticides is also of importance. They are transported through relevant tissues into different parts after their penetration into a certain part of the plant treated.

All these substances eventually enter the soil to a greater or lesser extent, where they affect particularly the edaphon, depending on the character of their biological effects. Fungicides damage filamentous fungi and possibly also yeasts, herbicides can essentially affect the development of soil algae, however, the effects of insecticides are the most remarkable. The insecticides exhibit a low selectivity and high intensity of effects, and in the soil they can damage larger as well as smaller metazoa such as worms, insects at different development stages, small rodents, etc. Some of these substances are decomposed rather slowly in the soil, so that they exert long-term effects. The best known of them are chlorinated hydrocarbons, which are currently not in use on account of this slow degradation; however, it is still possible to encounter them in residual amounts [7–12].

The pesticides are produced as application preparations marketed in the form which facilitates the application on the area treated in the dose necessary. For spraying the treated area, they are in the form of liquid emulsifiable or powdered suspended concentrates. In this way, certain amounts of solvents and filling agents are also transported into the environment. These are particularly different mineral oils, tensides and in small aerosol products also freons. In some countries experiments are also aimed at the possibility of using certain antibiotics as pesticides.

Industrial fertilizers. These were the first products of the chemical industry to be used in agriculture in large amounts. They complement nutrients in the soil. Depending on the contents of the main nutrients, they may be divided into single-component and combined fertilizers. The single-component fertilizers may be classified into the following groups:

— nitrogen fertilizers, containing nitrogen in the form of nitrates (salpeters), ammonia (ammonium salts or ammonia itself), amides (urea) or cyanamide (calcium cyanamide),

— phosphate fertilizers, containing phosphorus mostly in the form of dihydrogen phosphates ($H_2PO_4^-$), less frequently hydrogen phosphates (HPO_4^{2-}) or phosphates (PO_4^{3-}). Calcium and less frequently magnesium, aluminium, iron, etc., may be used as cations in these salts. They often contain larger fractions of sulphates,

— potassium fertilizers, these are chlorides or sulphates of potassium.

In recent times, combined fertilizers containing two to three main nutrients in a suitable ratio have been developed. Beside the main nutrients, the industrial fertilizers also contain trace elements such as boron, manganese, copper, etc. They are applied in a solid (powderized or granulated), liquid or suspension form.

The industrial fertilizers are frequently applied in amounts which can affect adversely the quality of agricultural products as well as the quality of the surface and groundwater. This is particularly true of nitrates, which are sometimes used in excess amounts. Due to a weak sorption, they are very mobile in the soil and they are readily accumulated in plant products, particularly in vegetables, and a portion of nitrates penetrates from the soil into water sources. Soil pollution by nitrates is sometimes very considerable, so that it represents a serious hygiene and ecological problem. Some granulate fertilizers are modified on the granule surface by the addition of anti-sintering agents. These are intended to keep the granules apart, preventing sticking even in the presence of moisture. For this purpose different oils, polymers or other organic substances are used. Their amounts in the fertilizers are, however, very low, so that they cannot substantially affect the quality of the soil and the environment [13–15].

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7.7 The effect of irrigation, improvement techniques and cultivation on the soil

In soils suffering from insufficient moisture, the fertility should be increased by irrigation; this is to provide sufficient water for plant cultures at the most appropriate time and thus, to achieve essential increases in the crop yield. Irrigation can, however, also exert detrimental effects on the soil. These are most frequently damage to the soil structure, mud formation, and leaching or salting of the soil. When using polluted water, then the pollution or even intoxication of the soil may occur, and in the case of excess irrigation soil erosion may occur.

This danger is present particularly in fields where irrigation has been in use for several years. The initial adverse effect of irrigation is the formation of local mud areas around hydrants or channels. When excess moisture acts for a longer time, then air is displaced from the moist soil and aerobic conditions are changed to anaerobic ones. Aerobic organisms are suppressed, reduction process prevail in the soil and the character of the decomposition of organic matter is modified as well as the character of the humification, so that the soil may be even converted to peat. Salination of soil can occur even during irrigation with water containing low salt concentrations. This can also occur when using water containing minerals releasing sodium for irrigation over a longer period.

The reverse of irrigation is the drainage of wet soils which can, however, lead to the opposite extreme situation, i.e. over-dry soils. Other soil improvement techniques can involve liming of acid soils, deep loosening of heavy soils, etc. All these interventions, when performed properly, i.e. to an appropriate extent and on suitable soil at suitable time increase the soil fertility. When, however, performed in an unplanned manner and by non-qualified personnel and in unsuitable areas, they can result in a devastation of the soil.

Compression of the soil by tractor wheels and other machines used for cultivation also exerts adverse effects. The compression of heavy soils in the presence of excess moisture is particularly harmful. During this, deep tracks are impressed into the soil, whereby the soil becomes solidified, losing its structure, which is then manifested by a deteriorated vegetation growth. When using such improper cultivation techniques on sloping areas, then the erosion is also enhanced, particularly in the case where the machines move in the direction of the slope. Thus, sloping areas should also be cultivated along contour lines or possibly on terraces landscaped onto sloping areas. These erosion-threatened fields should in any case be protected by a suitable vegetation cover, including forage plants, such as clover and lucerne as much as possible. When at least 30 to 35% of the area is covered by these plants, then, it is possible to work fields with angles of slope as high as 15 to 17° [1–4].

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7.8 The motion and conversions of chemical substances in the soil

After their entrance into the soil, chemical substances are immediately exposed to many effects of the medium. As a result, substances of different origin and composition participate particularly in two main types of processes, i.e. degradation processes, and the motion of original substances and of their degradation products in the soil.

The degradation processes may be categorized as follows:

(1) The biological decomposition, occurring by action of living organisms;

(2) Chemical degradation, via purely chemical processes without contributions from living organisms;

(3) Photodecomposition, i.e. chemical decomposition brought about by the effects of the solar radiation energy.

The motion of substances in the soil includes mainly the following processes:

- — the absorption, accumulation, decomposition and excretion of substances by plants, animals and particularly microorganisms,
- — the transport of accumulated pollutants in agricultural products and in other organic matter,
- — the adsoprtion of substances on soil particles, where liquid or gaseous components are retained on the solid particle surfaces,

- the exchange of substances betweeen the soil and atmosphere. This is not only a transport of emissions from the atmosphere into the soil, it includes also processes involving the evaporation of certain solid or liquid substances from top layers of the soil into the atmosphere,
- the motion of substances in surface layers of the lithosphere by action of water. The substances may be either dissolved and suspended directly in water or adsorbed on soil particles separated by erosion and transported into water flows. From there, they may be transported by irrigation to other localities, or they are carried into seas and oceans,
- the motion of substances in soil layers in the horizontal (in liquid or gaseous form) or vertical direction (by action of capillary effects),
- chemical and photolytic conversions of substances on the surface and inside of the soil medium.

All these processes may be combined in different ways. The total motion and conversions of substances in the soil will be then dependent on particular conditions, such as the water, air and temperature regime of the soil, pH, presence of soil organisms, method of cultivation, etc. [1-3].

7.8.1 The absorption and excretion of substances by organisms

Plants make a remarkable contribution to the vertical motion of pesticides and certain atmospheric pollutants in the top layers of the soil. As members of nutritional chains they also contribute to the transport of xenobiotics into animal organisms. The animals represent a factor participating in the motion of chemical substances absorbed, in the vertical as well as in horizontal directions. Relatively undegradable substances are transported to surprising distances by animals. This has been demonstrated by cases of the occurrence of chlorinated hydrocarbons in bodies of animals living either permanently or transiently in polar regions. Although this is not a matter of large amounts, these effects should not be underestimated, since they can seriously affect the characteristics of the environment and disturb the normal development of the ecosystem [4-6].

7.8.2 The adsorption of substances on soil particles

Both organic and inorganic soil components participate in adsorption processes. Among the organic parts of the soil, such components are particularly humus, dung, peat and similar organic matter, the inorganic components are mainly clay minerals and hydrated iron and aluminium oxides. These types of organic and inorganic particles occur in the soil under normal conditions, however, their relative proportions are different in particular types of soils, thus causing differences in the adsorption capacities of different soils. The adsorption is also affected by the chemical and physical characteristics of substances adsorbed. Adsorption is further affected either directly or indirectly by other factors, such as the moisture, temperature and pH of the soil. The direct effect of the various factors is manifested by changes of the evaporation and solubility of substances. Indirect effects are connected with the intensity of physiological processes in plants and microorganisms participating in the degradation of substances.

The overall effect of this complex of factors is particularly important in the case of pesticides, since their mobility in the environment and their biological effects are connected with their adsorption. The general principles involved in the study of pesticide adsorption are, however, valid in general and they are also relevant to the remaining types of chemical substances.

The low or high adsorption of substances is governed by their chemical and physical characteristics. They are dependent on the molecular structure and on derived characteristics, such as the formula, weight, possibility of ionization, solubility in water, lipophilic character, polarity and volatility. The effects of particular characteristics are now discussed in more detail.

Ionic character. A substance having a positive charge behaves in different way in the soil than a negatively charged substance or a non-ionized one. Soil colloids are able to bind mainly substances of cationic character, such as paraquat or diquat. When these substances are present in soils in doses below the soil exchange capacity, then they are completely bound and thus, they are rendered immobile and hence ineffective for plants and microorganisms. The mobility and thus also the biological activity of basic substances, such as *s*-triazines and triazols are strongly affected by the pH of the soil system. With decreasing pH, their adsorption increases and bioactivity decreases. Acid substances are usually slightly adsorbed due to their negative charge; examples are 2,4-D, MCPA, DNOC, dinoseb, and cycloheximide. They may be bound by organic components of the soil and partially also by hydrated oxides of iron and aluminium. Organic substances of arsenic are an exception, since they are well adsorbed by soil colloids and are thus fairly immobile.

A high mobility is also characteristic of substances which are non-ionized in aqueous solutions, since they are not adsorbed on soil particles. These include most chlorinated hydrocarbons, organophosphates, carbamates, as well as derivatives of urea, phenylamides, different esters, etc. A reasonable solubility in water is the only condition for their good mobility.

Solubility in water. Even some non-ionized substances are fairly soluble in water, e.g. dimetoate can yield a solution of a concentration up to 2%. Other non-ionized substances, such as DDT, are only sparingly soluble. Substances with a solubility of the order of 1 ppm can be considered as sparingly soluble and thus also very slightly mobile. From the standpoint of the mobility, substances whose concentration in aqueous solution exceeds 500 ppm can be considered as sufficiently soluble to give rise to a fair degree of mobility.

It should be noted that although the relative solubility in water can determine to a remarkable extent the mobility and bioactivity of the various substances, comparisons should be restricted to chemical substances with similar properties. Take, for example, paraquat, which can yield even a 70% solution, whereas the concentration of 2,4-D cannot exceed 650 ppm. The mobility of these two substances in the soil cannot, however, be estimated correctly from these data since paraquat is also present in its cationic form in water and it is strongly adsorbed by the soil, whereas 2,4-D exhibits anionic characteristics and it is only slightly adsorbed. In contrast to this, it is possible to compare the adsorption of chemically similar substances, such as phenurone and diurone. Those are both derivatives of phenylurea. Phenurone solubility in water is as large as 2900 ppm and it is much more mobile in water than diurone, which has a solubility of only 42 ppm.

Polarity. Polar substances are more strongly bound by soil particles than non-polar ones. Once again, only substances with similar chemical characteristics can be compared. For example γ-BHC (lindane), with a dipole of $p = 0.95 \times 10^{-29}$ cm (i.e. 2.84 Debye units) is adsorbed more strongly than its isomer β-BHC with a dipole $p = 0$.

Volatility. The vapour tension of a given substance is a value which can be used for estimating its relative tendency to evaporate from the solid or liquid state of matter to form vapour. Since, at a given temperature, the volatility is proportional to the vapour tension, this value is also immediately related to the substance's mobility in the medium. Substances with a vapour tension at 25°C below 10^{-5} Pa are considered non-volatile. Those with a vapour tension between 10^{-2} to 10^{-4} Pa at this temperature exhibit an intermediate volatility. Substances with a vapour tension of above 10^{-2} Pa at 25°C are strongly volatile and are readily mobile in the medium in the form of vapours.

Among the pesticides, intermediate or strong volatility is characteristic for certain thiocarbamates, acetamides, benzonitriles and esters. For example, EPTC (*s*-ethyldipropyl thiocarbamate) has a vapour tension of 2.5 Pa at 20°C and it is rapidly released into the atmosphere unless bound to a suitable additive. Triazine derivatives show a low volatility. Simazine has a vapour tension of about 10^{-6} Pa at 20°C and it is essentially not evaporated from the soil [3–5].

The effect of soil properties on the adsorption of substances. Physical and chemical characteristics of adsorbing components in the soil also affect the binding capacity and stability of chemical substances in the soil. The particle size is a further important factor. Colloidal particles exhibit the largest sorption capacity, with a diameter of 10^{-6} to 10^{-3} mm. The sorption capacity decreases with increasing size, and particles larger than 2 mm in diameter essentially do not affect the soil sorption capacity. From the chemical standpoint the soil sorbents may be divided into two groups:

(a) soil particles with an acidic character,

(b) particles with amphoteric properties; depending on the reaction of the soil solution they can behave either as acids or as bases.

Clay minerals and, of organic components, particularly humic and other high-molecular acids show an unambiguously acid character. Clay minerals are rather complex materials with a high abundance of silicic acid and aluminium, which are frequently combined with Mg^{2+}, Fe^{2+} or K^{+} exchangeable ions. Depending on their submicroscopic structure, it is possible to consider so-called expanding and non-expanding minerals.

Montmorillonite and some minerals of the vermiculite group are the main representatives of expanding minerals. Montmorillonite has a stratified lattice structure and its composition may be approximately expressed by the formula $Al_2O_3.4SiO_2.nH_2O$. Particular submicroscopic layers are negatively charged in these minerals. Their charge is balanced by Ca^{2+}, Na^{+} and other cations. The charge of the layers and characteristics of these ions make possible an easy penetration of water into spaces between the layers. Thus, water molecules surround these cations. The minerals are considered as expanding, since the number of water molecules between the layers is variable and the weight of the dry mineral may be increased even by a factor of six due to the presence of this water. Organic molecules can also enter these spaces and thereby cause an expansion of the whole structure.

Kaolinite $Al_2Si_2O_5(OH)_4$ and illite, which is structurally similar to montmorillonite, belong to the most important non-expanding minerals. The bonds between the layers with K^{+} are much stronger, so that they do not allow expansion.

In the case of non-expanded minerals, the adsorption occurs only on the external surface of colloidal particles; in the case of expanding ones, it also occurs between the layers. The specific surface of expanding minerals can thus vary between 500 and 750 $m^2\ g^{-1}$, that of non-expanding ones only between 25 and 125 $m^2\ g^{-1}$.

Humic acids are very complex high-molecular substances, with a structure which is difficult to define. They are components of humus. In their molecules they have many aromatic rings, with the groups $-COOH$ and $-OH$ providing their acid character.

The acidoid minerals as well as humic acids are very abundant particularly in neutral to moderately alkaline soils with high humus contents.

Amphoteric characteristics are typical particularly for amorphous or crystalline colloids of hydrated iron and aluminium oxides, referred to as sesquioxides. Limonite ($Fe_2O_3.nH_2O$), hematite (Fe_2O_3), gothite ($Fe_2O_3.H_2O$), diaspor ($Al_2O_3.H_2O$) and gibbite ($Al_2O_3.3H_2O$) are the most important minerals in this group. In an acid medium, hydrates of oxides behave as bases, and in basic medium as acids. Among the organic components, proteins are amphoteric, because the side chains of their molecules contain carboxylic groups and amino groups. The carboxylic group can dissociate in solution to H^+ ions, the amino group can accept these ions ($-COOH \rightarrow -COO^- + H^+$, $-NH_2 + H^+ \rightarrow -NH_3^+$). In acid medium the excess H^+ ions are bound to negative groups of preteins, in basic medium they are split off from amino groups to yield water together with OH^-. Different proteins have different proportions of carboxylic and amino groups, so that they show different degrees of acidity.

The soil contains different colloids with opposite electrical charges. They can thus be combined on contact, forming new complex colloidal particles, the so-called ampholytoids, covering a wide range of diversity. In most cases, acidoid colloids are, however, prevalent over the basic ones, so that all the basic particles and only a minor portion of acidoids go to form ampholytes, the remaining portion of acidoids remaining free. Thus, the total electric charge of the soil is usually negative and the physico-chemical exchange mechanism leads to a predominant sorption of cationic substances. The sorption of anions is usually low (this is responsible for the weak sorption of nitrate fertilizers and other substances of anionic character) [1, 3, 7, 8].

7.8.3 The transport of substances by water

Different substances are transported by water in the soil in both horizontal and vertical directions. The mobility of pesticides, fertilizers or other pollutants was discussed in the previous section dealing with the adsorption of substances on the soil. An important point is that the transport by water is easier for less adsorbed and more polar substances. Among the polar substances, anions show the lowest adsorption and thus, they are readily mobile in the medium. Persisting synthetic substances can be very dangerous, residing for long times in both surface and groundwaters. A serious problem is also caused by substances which, although easily degradable by biological processes, occur in excess amounts at certain localities. Those are particularly fertilizers and different waste substances of biological origin, which can burden the environment by an excess amount of nutrients. A portion of these nutrients eventually finds its way into surface or even groundwater. The excess amounts of nutrients enter into water in three main ways as follows:

(a) leaching out of soluble and mobile substances from the soil,
(b) rinsing of substances adsorbed on soil particles, caused by erosion,
(c) rinsing of different biological wastes of animal and plant origin.

Nitrates, chlorides and sodium, potassium, magnesium and calcium sulphates are quite soluble. Ammonium salts, carbonates and hydrogen carbonates can also move easily in solutions. Coarse as well as fine products of the soil erosion are transported in the form of dispersions. These are mainly small particles of the clay fraction, fine clay and colloidal particles of oxides and hydroxides. Organic substances are transported, depending on their nature, either in the dissolved state or as finely dispersed as well as coarse particles of organic matter. Polyphenols, polysaccharides, organic acids, fulvic acids, humic acids, etc., are examples of soluble organic substances. Some organic substances behave as ligands (chelating agents) which may form well soluble metallo-organic complexes — chelates with cations of sparingly soluble substances:

$$\underset{\text{immobile}}{\text{Fe-phosphate}} + \text{ligands} \rightarrow \underset{\text{mobile}}{\text{Fe-chelate}} + \underset{\text{mobile}}{\text{phosphate}}$$

The chelates formed are characterized by a considerable solubility over a wide interval of pH values and thus, they are very mobile in the soil.

Substances which are either soluble or suspended in water are transported from their original sites by rinsing with flowing water or they are washed out and transported by water soaking into deeper layers. The intensity of this transport is affected mainly by the extent of precipitation, soil quality, slope and, to a lesser extent, by the type and density of the plant cover.

Surface transport by water occurs when the amount of water is larger than that which can be soaked into the soil in a given time interval. Soil has good filtration characteristics and it is able to retain many substances which threaten the water quality (phosphates, heavy metals, organic substances, ammonia, etc.). During surface flow, however, the soil does not filter and purify the water. Thus, the danger of losing nutrients and at the same time polluting water is increased. Erosion by water is simultaneously intensified, which leads to losses of cultivated soil. The hazard of the surface removal of nutrients and soil increases with increasing slope and with decreasing ability of the soil to soak up water. Erosion outflows contain many organic substances and fine soil particles with high contents of nutrients. A portion of the removed material is deposited on the slope, however, a large portion accumulates at the foot. Thus, at the foot the depth of cultivated soil horizons is larger than that at higher levels of the slope. A portion of the material formed by the erosion is, however, transported into surface waters.

The soaking capacity is strongly deteriorated when the soil is both moist and compacted, e.g. by cattle or agricultural machines and when the soil is frozen. This soil is rapidly saturated with water in its top layer, and the excess water runs off, carrying with it particles separated by erosion, and nutrients. Losses of nutrients are high in rich soils and rather lower in poor soils. In acid soils, it is possible to observe a remarkably increased removal of phosphates.

It should also be remembered that inappropriate fertilization with organic substrate can result in a large increase of the amount of nutrients removed by the transport with water. Improper application of liquid manure is most dangerous. It contains much water, so that its distribution leads to similar effects as intense water precipitations on soil without plant cover. The application of liquid manure leads to the disintegration of the clodded structure, the soil is sintered and thus, its soaking capacity is reduced. The soil is then unable to retain liquid manure applied in excess doses and thus, it flows down sloping areas with a considerable transportation of dead organic matter and pathogenic microorganisms into surface waters. In soils without plant cover, the limit of the soaking capacity of the soil is already attained at a dose of 10 to 20 m^3 of liquid manure per ha. A dense plant cover and suitable topographic and atmospheric conditions can strongly restrict the negative effects of using the liquid manure. Under favourable conditions, it is possible to apply even doses exceeding 60 m^3 ha^{-1} without damaging the soil and polluting surface waters.

In the soil, different substances are also transported by the soaking water. In Temperate Zones, the amount of water supplied by atmospheric precipitations is frequently larger than that evaporated directly from the soil surface and by the transpiration of plants. Thus a proportion of water is percolated through the soil and it may penetrate down to ground or dammed water. The amount of percolating water increases with increasing non-uniformity of precipitations, decreasing evaporation and transpiration and with greater penetrability of the soil. A part of the water is first retained in top layers by action of adsorption, hydration and cohesion forces and only after exceeding the water capacity of the soil, does the water penetrate into lower layers. The water retention capacity of the soil depends on the following factors:

- the grain size: the finer the soil, the higher the fraction of water adsorbed,
- the structure: the finer the pores, the higher the fraction of capillary water,
- the presence of organic substances: higher contents of porous organic matter increase the amount of bound water,
- the soil colloids: humus colloids bind larger amounts of water than clay colloids, and
- cations sorbed: the proportion of hydration water decreases in the order Na^+, K^+, Mg^{2+}, Ca^{2+}.

The soaking rates are different in different types of soils. Soils with coarser particles and with lower proportions of fine capillary pores are more permeable than heavy soils containing prevalently fine pores. Common types of soils may be listed as follows in order of decreasing permeability: sand–loam–loamy mud–clay. Under conditions of complete saturation with water, the penetrability of sands and clays is about 5 and 0.5 cm h^{-1}, respectively. The rate of the penetration decreases rapidly with increasing water content.

The transport of nutrients by infiltrating water is different from the transport by eroding water as regards both the direction of motion and the character of the substances transported. During the surface flow, larger organic as well as inorganic particles are transported in addition to the water-soluble substances. The amount and size of particles depends on the intensity of the erosion, the soil adsorption capacity being not the limiting factor. With infiltrating water, only those substances are washed out which are not firmly bound to the soil; they are transported into deeper layers.

We have already discussed the fact that the soil adsorption capacity depends on its general physico-chemical characteristics. Soils with the highest adsorption capacity are represented mainly by loamy soils with a sufficient content of humus. They act as an efficient filter for the soaking water. The soil, however, does not retain all the substances to the same extent. Phosphates and heavy metals such as Cd, Cu, Zn, Ni, Pb, Cr, Co, are bound particularly firmly. A fairly good retention can also be observed for K^+ and

NH_4^+ ions. In contrast to this, the anions NO_3^-, Cl^-, SO_4^{2-} are essentially not retained.

The low mobility of phosphorus in the soil is due to the fact that this element occurs mostly in the form of phosphates, which are frequently converted to sparingly soluble or insoluble compounds. In acid soils, these are particularly compounds of phosphorus with iron and aluminium sesquioxides.

For the reasons mentioned, negligible amounts of phosphorus are washed out from the soil by the infiltrating water. The annual amounts lost are typically 100 to 300 g per ha and even increased doses of fertilizers do not increase the amount of phosphorus washed out. An exception is that of silica sands (they show practically no adsorption) or acid peat soils, where insoluble forms of calcium phosphate cannot be formed. In these, phosphorus may be bound to sesquioxides and, in addition to this, these soils are not fertilized.

In contrast to phosphorus, nitrogen is very mobile in the soil. The soil is able to bind the ammonia form of nitrogen but not as firmly as phosphorus, however, the nitrate anion is essentially completely free. It is also necessary to consider that by action of nitrifying bacteria the ammonia nitrogen is converted to the nitrate form. Thus, a great portion of nitrogen present is washed with the soaking water into deeper layers and it frequently penetrates down into the groundwater. Roots of plants are the most efficient factor for reducing nitrogen losses, since they are able to take up rapidly nitrogen from the soil. Simultaneously with this, the amount of the plant mass increases and thus, the amount of nitrogen washed out is further reduced. The transport of nitrogen is directly related to the intensity of precipitations and thus, it is not surprising that the extent of nitrogen washing-out strongly depends on the season of the year. The total distribution of water precipitations is of importance, however, as a general rule about two thirds of nitrogen is transported in the winter, which is rich in precipitation and when large areas of the soil are uncovered. The remaining one third of losses occurs in the summer.

The nitrogen percolation is also affected by the method of working and fertilizing the soil. In an arable soil, the amount of nitrogen percolated is higher by a factor of about ten than that in soils with a permanent vegetation cover (meadows and pastures). For soils richly fertilized with organic and nitrogen fertilizers, having a high portion of humus, the content of nitrogen in the soaking water is higher as compared to that in poor soils.

In general, the effects of different factors on the nitrogen percolation through the soil may be listed in the following order of decreasing importance: cover > soil type > soil penetrability > nitrogen reserves in the soil humus content > soil sorption capacity > method of fertilization [1, 3, 9, 10].

7.8.4 Chemical and photolytic decomposition

The decomposition or transformation of natural and synthetic substances in the environment can occur in an abiotic manner, but from the standpoint of the degradation and circulation of substances, purely chemical reactions are much less important in comparison with biologically facilitated changes. This is shown by the lower level of interest in detailed studies of abiotic chemical conversions in the soil and water. It is, however, obvious that certain chemical changes of substances in the environment occur independently of the biological activity. Mainly oxidation, reduction and hydrolysis reactions are concerned. It is also significant that in the environment, there are generally appropriate conditions for accomplishing these reactions, at least to a limited extent. These include particularly the availability of water, oxygen, suitable temperatures, and organic as well as inorganic materials of different heterogeneity and reactivity. Ions and radicals are also present in the environment in smaller amounts, formed either by photochemical or catalytic reactions, e.g. by the action of metals present.

The abiotic chemical processes, however, do not include reactions catalysed with enzymes, which occur in certain amounts in the free soil, outside of cells. These enzymes, mostly bound to soil particles, are excreted actively by metabolizing cells or released during the decay of dead organisms. Reactions catalysed in this way should, however, be considered as processes dependent on biological activity.

Even in purely chemical reactions, toxic substances may be converted to less harmful ones, which can then more readily undergo further, possibly biological conversions. Certain substances are chemically degraded more easily when being adsorbed on soil particles.

In the case of photochemical reactions, photodecomposition is characteristic for certain complex organic molecules which are exposed to solar radiation. Besides those which are directly suspended in the atmosphere, there are also substances attached to the surface of plants, soil, etc.

Many pesticides, such as 2,4-D, chloramben, picloram, bromoxynil, amitrol, triflualin and paraquat also tend to participate in photochemical reactions.

In the case of water-soluble substances, the extent of photodecomposition is restricted to a certain extent, since they are easily washed out from the plant or soil surface by water from precipitations. The washing-out or soaking of the substances into the soil thus renders them unavailable for photochemical decomposition [1, 2, 4].

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7.9 Soil analysis

Properties of the soil are affected by various processes occurring in the soil, by the chemical composition of the soil-forming substrate and by human interventions. Chemical techniques in agriculture and forestry (the use of large doses of mineral fertilizers, pesticides, etc.), lead to changes not only in the soil chemistry, since after a transport of these substances through the soil medium, surface and groundwater sources may also be polluted. Soil pollution by different wastes may increase the contents of certain elements in cultivated plants. For example, concentrations of heavy metals are increased by several orders of magnitude in the soil as well as in cultivated plants in the vicinity of industrial centres and dense traffic.

Soil analysis is usually aimed at evaluating its agricultural characteristics. The soil chemical composition is very diverse and the definition of pollutants in soil, natural as well as anthropogenic, depends on the soil type, locality and also on the composition assumed to be "normal". The comparison with assumed "normal" levels of particular components is achieved by using standard samples of soils, or of similar soils from a different region. Standard soil samples are not commonly available and thus, the second alternative is mostly used in environmental soil research, with a possible comparison of results with values presented in the literature [1].

Macro- and microcomponents of inorganic character in the soil are frequently directly related to the composition of underlying rocks. The determination of macro- or microcomponents of the soil serves as a basis of one method among the various approaches to a biochemical survey; for the investigation of pollutants, microelements in the soil are of the main importance, being important for the nutrition and health of plants as well as animals. The character of the main elements is determined by their occurrence in the soil profile as whole, whereas their distribution inside of the soil profile is governed by their mobility together with other factors, such as the climate [2].

It is hard to define soil pollutants precisely, since the soil serves as a natural recipient of wastes. According to Hangos-Mahr et al. [3] the following criteria may be employed to consider certain admixtures in the soil as pollutants:

(1) When a certain component (admixture) in the soil restricts the suitability of the soil for the plant growth, reduces the applicability of the plant product obtained from the soil or decreases substantially the variety of plants that may be grown on the soil, then it may be considered as a soil pollutant (this is true for both short-term as well as long-term effects).

(2) When a component (admixture) in the soil does not directly affect the production potential of the soil, but can exert a negative effect on the purity of water soaking through this soil and reaching the water system, then it can be considered as a pollutant.

By means of plants (used as food) and water, the soil pollutants threaten human and animal organisms and disturb natural cycles. Concentrations of heavy metals (Hg, Cu, Cd, Pb) and also other toxic metals, such as Zn, Se and As in soils are continually increasing by the action of intense human activity (civilization, industrialization, road transport). Frequently used pesticides and industrial fertilizers also make considerable contributions to the soil pollution.

Inorganic components (including pollutants) in the soil may be present in different forms, which should be taken into account when analysing the soil. From this standpoint, particularly analyses are of interest, which provide data on those trace elements which are chemically available for the biosphere. The total content of trace elements in soils [1] is of less importance from the chemical standpoint.

Among the hazardous inorganic components, lead occupies the first position, since it pollutes the soil in cities and areas adjacent to highways and roads. In arable soils the fluorine content is ever increasing; it enters the soil together with high doses of natural phosphates. Other metals, such as mercury and cadmium, enter the soil either as a part of preparations used or as microcomponents of fertilizers. Local pollution may occur in the vicinity of industrial and municipal waste disposal areas.

In the case of harmful organic substances, mainly insecticides and herbicides occur in the soil. These substances have been applied in agriculture to a considerable extent, so that their presence can be detected almost universally. Among the various local contaminations petroleum products, which enter the soil in failures of oil pipelines and tanks, are important. In certain cases, dibenzodioxins and dibenzofurans have caused ecological catastrophes [4].

7.9.1 The sampling procedure

The site of the soil sampling depends on the character of the terrain and purpose of the analysis. The choice of sampling sites in the locality investigated should include all the elements of the relief, i.e. valleys, lowlands, middle and top parts of the slope, terrain waves, etc. The sampling point should be situated at a typical site, at a sufficient distance from pollution sources (waste disposal areas, roads, industrial centres, etc.).

The average soil sample is always taken from an area characterized by uniform cultivation (the same plant, fertilization, etc.). Smaller localities with considerably different soil characteristics are eliminated from sampling. The average area for taking one representative soil sample should be in the range 1 to 10 ha. Exceptions to this rule are areas contaminated during accidents. Surface and subsurface [5] sampling can be considered.

The untreated sample represents the basic sample. In the case of agricultural soils, an amount of 0.5 to 1 kg of the sample is taken. The soil (earth), where the mineral portion is well mixed with organic matter (humus) is named the topsoil. When sampling the topsoil, it is necessary to consider the local conditions, i.e. characteristics of the environment of the sampling point, weather, vegetation, etc.

When examining agricultural topsoils, a superficial layer (of about 5 cm) with residual amounts of the vegetation, etc. is removed by a shovel and under this layer, samples are taken from depths of 5 to 10 or 10 to 15 cm in the case of shallow or deeper topsoils, respectively. For meadow and pasture soils, tussocks are removed and the soil situated immediately under them is taken.

When determining pollutants in the soil, the depth profile of the soil can be taken into account, depending on whether the pollutants are expected to be on the surface or in deeper soil layers.

Soil samples are frequently taken by probing rods down to a depth of 20 cm, and during this, one average sample is obtained from at least 30 stabs. Particular stabs are performed in the depth of the topsoil. In meadows and pastures the sampling depth is down to 15 cm, the top layer (5 cm) being eliminated. When sampling the soil, admixtures from deeper layers (particularly layers under the topsoil) should be eliminated. When investigating the surface contamination of water, superficial layers (down to 5 cm) [1, 5–7] are taken.

7.9.2 Preparation of samples for analysis

From air-dried soil samples, coarser pieces of the skeleton and possible residual plant materials are removed. The sample is then ground, to disintegrate agglomerated clods but not skeleton particles. The disintegrated earth is screened through a sieve (usually with a mesh size of about 2 mm). The sample prepared in this way is poured to form a conical pile. The pile is then quartered with the help of a suitable tool. The two opposite portions are taken as a sample. The quartering procedure is repeated to reach the sample amount required for the chemical analysis.

The soil analysis is then frequently performed without further sample treatment. In certain cases, however, it is necessary to obtain a solution from the sample, i.e. to make an extract.

Usually only a small portion of the sample is water-soluble (chlorides, nitrates, nitrites, sulphates, alkali metals — when unbound in silicates, glycides, fatty acids, humic substances). The extract for the determination of nutrients (nitrogen, phosphorus, potassium, trace elements) is prepared with the use of leaching solutions: 1% citric acid, 1% potassium sulphate, 1% hydrochloric acid, calcium lactate, etc.

Sample decomposition is frequently necessary, depending on the purpose of the analysis and character of the component to be determined. The most frequently adopted procedures are as follows:

- decomposition of the sample by melting with Na_2CO_3,
- the decomposition of the sample mineral portion containing silicates by the action of a mixture $H_2SO_4 + HF$,
- sample decomposition by ashing (550°C) or by a wet procedure with H_2SO_4, HNO_3 and $HClO_4$.

During the separation of pollutants from the soil (most frequently by extraction) these materials are released to a certain extent from the soil and they pass into the fraction containing the pollutant. In practically all cases, it is necessary not only to concentrate the pollutants, but also to purify the fraction obtained. In comparison with the analysis of the atmosphere and water, the determination of contaminants in soils is essentially more complicated [1, 4, 5].

7.9.3 The determination of certain characteristics, components and pollutants in soils [1–18]

7.9.3.1 The grain size

The solid phase of soil contains particles of different sizes, and it has different textures. The granulometric analysis of the soil presents data about the relative (percentage) abundance of particles of a certain size and it serves as a basis for soil categorization.

This categorization of soils for pedological purposes is performed with the help of water, in which the soil sample is suspended. During this, the differing velocities of falling grains of different sizes are used in sedimentation methods of the analysis, or the resistance of grains to the driving force of water streams of different velocities in the course of elutriation (washing out) methods is observed.

7.9.3.2 The skeleton

The skeleton is formed by particles larger than 2 mm in diameter. The total skeleton content is determined, which may be possibly further graded, by using a set of sieves, into particular fractions. The determination of the skeleton content is expressed as a percentage, either by weight or by volume. In both cases it is ascertained by a wet method.

7.9.3.3 The hygroscopic water

The hygroscopic water is water contained in air-dried soils. The content of this water varies depending on the relative humidity and on the soil properties; particularly the granulometric composition and humus content of the soil affect its amount.

The content of the hygroscopic water in air-dried soils is determined by a gravimetric method, similarly as the moisture in fresh soils, by drying at 105°C to constant weight.

7.9.3.4 The bulk weight

The non-reduced bulk weight is the weight of 1 cm^3 of intact soil containing its natural moisture. Stainless steel cylinders, sharpened at one end, are used for sampling; they are stabbed into the ground. The non-reduced bulk mass equals the fresh soil mass divided by the cylinder volume. The reduced bulk mass is related to absolutely dry soil.

7.9.3.5 The specific mass

The specific mass is the mass of unit volume of the solid components of the soil (without pores). It is determined with the use of a pycnometer.

7.9.3.6 The porosity

The soil porosity is the total volume of pores in the soil mass expressed as a percentage of the total intact earth volume. The pores in the soil have different shapes and sizes and they are filled either with water or with air. The determination of the total porosity P is calculated from the ratio of the specific (S) and reduced (S_R) bulk weight, using formula

$$P = \frac{S - S_\mathrm{R}}{S} 100\ (\%)$$

7.9.3.7 The soil moisture

The soil moisture is the water content present in the soil under given conditions. It is expressed in percentage by weight or by volume. Drying at 105°C is the most reliable method for determining the soil moisture. Nuclear methods (thermalization of neutrons) and conductometric methods are also frequently used.

7.9.3.8 The soil acidity

The soil acidity is one of the most important soil characteristics. The acid, neutral or alkaline pH of the soil considerably affect factors such as the solubility of various substances, strength of bonds of exchangeable ions, activity of various microorganisms.

The active acidity is the instantaneous condition of free hydrogen ions in the soil solution. It results most frequently from dissociated free acids or dissociated acid salts occurring in the soil. It is expressed by the pH value, and determined by colorimetric or potentiometric methods. It should be determined in fresh samples as far as possible, preferably in the field or as soon as possible after transporting the sample into the laboratory, to obtain the actual acidity under natural conditions.

The exchange acidity is defined as the ability of the soil to change the pH value of solutions of neutral salts (electrolytes). This is the acidity resulting from hydrogen ions displaced from the soil into the solution by the action of neutral salts according to the scheme

$$(\text{soil})\text{H} + \text{KCl} \longrightarrow (\text{soil})\text{K} + \text{HCl}$$

The amount of hydrochloric acid formed equals the exchange acidity. It is ascertained either by titration, as the concentration $H^+/100$ g of the earth, or by a potentiometric method as a value pH/KCl.

The hydrolytic acidity is the ability of the soil to change the pH of salts split by hydrolysis. This represents the ability of the soil to bind a strong base and to release an equivalent amount of a weak acid. For determining the hydrolytic acidity, a salt of weak acid and strong base is used (sodium acetate or calcium acetate); the following reaction occurs:

$$(\text{soil})^{\text{H}}_{\text{H}} + 2\text{CH}_3\text{COONa} \longrightarrow (\text{soil})^{\text{Na}}_{\text{Na}} + 2\text{CH}_3\text{COOH}$$

The amount of the acetic acid released is determined by titration with sodium hydroxide, which makes it possible to determine the amount of hydrogen ions taking part in the hydrolytic reaction.

7.9.3.9 The buffering capacity

The buffering capacity is the ability of the soil to maintain its acidity (pH) on adding acid or base solutions. The buffering capacity is most typically determined from titration curves and it may be used to determine requirements for liming. In soils with a high buffering capacity it is necessary to be careful when considering the use of physiologically acid or basic fertilizers.

During the determination of the buffering capacity, two series of weighed amounts of the soil are used; HCl and NaOH are stepwise added to the first and second series of the samples, respectively. The measured pH values in particular samples are plotted against the volumes of NaOH or HCl added, in ml. The same procedure is employed with a sample of pure sand as a standard. The area between the pH curves of the soil and sand samples represents the value of the soil buffering capacity (in cm^2).

7.9.3.10 Carbonates

Carbonates in soil occur mainly in the form of $CaCO_3$ with a smaller portion of $MgCO_3$. The remaining forms are determined only in special cases. Their determination is based on their easy decomposition with diluted acids:

$$CaCO_3 + MgCO_3 + 4HCl \longrightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2$$

The amount of CO_2 released serves as a measure for determining the carbonate content on the basis of visible estimation, or of a gravimetric or volumetric method.

The visual estimation is performed under field conditions by dropping 10% HCl onto a soil clod and observing its decomposition. Depending on the intensity of the gas release the $CaCO_3$ is estimated as follows:

hardly observable, short-term effervescence	$> 0.3\%$ $CaCO_3$
weak, short-term effervescence	0.3–1% $CaCO_3$
distinct effervescence	1–5% $CaCO_3$
violent effervescence with long-term decomposition	$< 5\%$ $CaCO_3$

For the volumetric determination the volume of CO_2 obtained is measured

- by instruments based on pressure changes (barocalciometers); these are sealed vessels in which the soil sample is exposed to the action of hydrochloric acid, connected to a precise manometer,
- by instruments measuring the gas volume (volumetric instruments); in a vessel for the gas evolution, a soil sample is exposed to hydrochloric acid, the CO_2 released is allowed to pass into a eudiometric tube, which is calibrated on the basis of CO_2 volume obtained at barometric pressure, as a percentage of carbonates.

The gravimetric method is, however, the most precise. It is based on measuring the decrease of the sample weight after decomposing carbonates with acids with simultaneous heating of the sample.

7.9.3.11 The salinity

The salinity (content of salts) of the soil and a high degree of saturation of the sorption complex by sodium may greatly affect physico-chemical, chemical and biological characteristics of the soil and can thus considerably reduce its fertility.

A high soil salinity, or higher amounts of soluble salts, represents an enhanced content of the inorganic portion soluble in water. A saline soil is one in which the saturated aqueous extract has a specific electric conductivity greater than 4 mS cm^{-1} at 25°C, where the Na^+ content is less than one half of the sum of cations of soluble salts and the pH is below 8.5. When the Na^+ content increases, the other factors remaining constant, then we consider the soil to exhibit so-called alkaline salinity.

The salinity may be determined directly as a total content of water-soluble salts, or as a sum of contents of particular ions. The measurement of the specific electric resistance of the soil is a very rough, but simple and rapid method. It is used for soil surveys on a wide scale. For achieving more precise results, it is possible to use a method standardized by measuring the resistance in saturated soil paste (the soil paste is prepared by mixing a soil sample with distilled water to obtain a moderately liquefied paste) and the results are corrected with respect to a temperature of 16°C. Tables are used to convert the measured electrical resistance values to the soil concentration. For more precise data, it is possible to separate the solution from the saturated soil paste and to measure the specific electric conductivity. The solution separated from the soil paste is called the saturated soil extract.

The salinity is determined as a sum of contributions of particular ions (most frequently Ca^{2+}, Mg^{2+}, K^{2+}, Na^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}).

7.9.3.12 The humus

The humus is taken to represent all the decayed organic substances of plant and animal origin. It is determined by the oxidation of carbon from soil organic substances by using a dry or wet process and by relating the amount of carbon to the humus content. The dry processes usually allow for a complete oxidation, whereas during wet processes the results are rather lower; the differences are negligible for common purposes. The oxidation of organic carbon is accomplished either directly in a soil sample or in extracts obtained with the help of different agents.

The dry process determination is based on determining losses of weight after heating a soil sample to constant weight, or on elementary analysis. For the elementary analysis, organic carbon is oxidized in an oxygen stream with simultaneous heating of the sample to be analysed, in a combustion tube. The amount of CO_2 formed is obtained by gravimetric titration or conductometric methods and the amount of carbon is calculated (1 mg CO_2 corresponds to 0.2729 mg C); the proportion of carbon is expressed as a percentage with respect to dry matter. The humus content in percentage is then obtained from this value by multiplying it by a coefficient of 1.724, which is based on an average carbon content in the humus (58%).

The determination by a wet process is performed by oxidizing organic carbon with an oxidizing agent (with Mn(VII), Cr(VI), Ce(IV)) in the presence of sulphuric acid. The amount of carbon oxidized is ascertained either from the amount of CO_2 obtained (as for the elementary analysis) or from the amount of the oxidizing agent consumed during the analysis.

7.9.3.13 Iron

The total iron content may be determined directly in the soil by the X-ray fluorescence analysis or by a spectrographic method. In the case of classic methods, the soil sample should be first decomposed either by melting with Na_2CO_3 or by the action of hydrofluoric acid. The melting procedure is more advantageous, since in this case further elements can also be determined simultaneously with iron. When it is only necessary to determine iron, it is advantageous to use the decomposition with hydrofluoric acid, which does not need the separation of silicic acid. In solution, iron is determined most frequently by the photometry, AAS or polarography.

7.9.3.14 Aluminium

The total aluminium content is obtained in order to characterize the soil with respect to the soil-forming substrate, weathering, etc. Together with analyses of other components of clay minerals, it may be used for calculating values which may be employed in the identification of clay minerals. To obtain the aluminium solution, the sample is melted with sodium carbonate and the melt is dissolved in concentrated hydrochloric acid.

The total aluminium in the solution may be determined by a photometric method with aluminon (ammonium salt of 4-hydroxy-5,5′-dimethylfuchsone-3,3′-dicarboxylic-2′-sulphonic acid), by a gravimetric method, by atomic absorption spectrometry, X-ray fluorescence, etc.

Table 7.5. The natural concentration of toxic elements in the soil and plants [10, 15, 16]

Element	The whole soil		Soil solution ($mg\ l^{-1}$)	Plants range (ppm)
	Characteristic value in ppm	Range (ppm)		
Cd	0.06	0.01–7	0.001	0.2–0.8
Co	8	1–40	0.01	0.05–0.5
Cu	20	2–100	0.03–0.3	4–15
Pb	10	2–200	0.001	0.1–10
Mn	850	100–4000	0.1–10	15–100
Ni	40	10–1000	0.05	1
Zn	50	10–300	0.005	8–15
As	5	1–50	0.1	–
Be	1	0.2–10	0.001	–
Cr	20	5–1000	0.001	–
Se	0.5	0.1–2.0	0.001–0.01	–
Hg	0.05	0.02–0.2	0.001	–

7.9.3.15 Trace and toxic elements

The soil contains elements of biogenic as well as toxic character. The toxicity is usually manifested at relatively higher concentrations. The natural, safe concentrations of certain elements in the soil and plants are given in Table 7.5. Instrumental analytical methods are usually used for their determination, such as emission spectral analysis, atomic absorption spectrometry, photometry, X-ray fluorescence analysis, and polarography.

The emission spectral analysis is a very important technique for the rapid simultaneous determination of several trace elements; it has the advantages of low detection limits, low consumption of samples and speed of the determination. For most elements, the detection limit is $10^{-4}\%$ and below. The reproducibility of the determination expressed in relative percentage is approximately 10%. Table 7.6 gives the detection limits for determining trace elements in soils by emission spectral analysis in the cathodic layer of the arc [17].

For the determination of trace elements in the soil, atomic absorption spectrophotometry is also very suitable. A solution should be obtained from the sample to be analysed, most frequently by a decomposition with hydrofluoric acid; extracts can also be prepared from the samples to be analysed. The detection limits and sensitivities for this technique are shown in Table 7.7.

Table 7.6. Detection limits for determining trace elements in soils by the emission spectral analysis

Type elements	Detection limit			
	< 5 ppm	5–50 ppm	50–500 ppm	> 500 ppm
Non-volatile		ZR	Th	
	Sc	La, Y, Ti	U	Ce
	Ca, Sr, Mg	Ba		
	Al, V	Si		
	Co, Ni, Cr	Mn, Fe		
	Rb, Li, Na, K, Cs	Pb, Rh	Pt, Ir, Os	
	Cu, Mo	W, Nb		
Volatile	Ag, Be	Au		
	In, Ga	Sn, Ge	P, Te	
		Sb	Bi	As
	B, Tl	Cd	Zn	Hg

Table 7.7. Atomic absorption detection limits and sensitivities with a conventional flame atomizer

Element	Wavelength (nm)	Flame gases[a]	Detection limit (ppm)	Sensitivity (ppm)
Al	309.3	N-Ac	0.100	1.90
Ba	553.6	N-Ac	0.100	0.40
Ca	422.7	A-Ac	0.010	0.03
Cd	228.8	A-Ac	0.050	0.20
Co	240.7	A-Ac	0.050	0.15
Cr	357.9	A-Ac	0.010	0.15
Cu	324.7	A-Ac	0.010	0.15
Fe	248.3	A-Ac	0.020	0.15
K	766.5	A-Ac	0.005	0.10
Li	670.8	A-Ac	0.005	0.07
Mg	285.2	A-Ac	0.003	0.01
Mn	279.5	A-Ac	0.005	0.10
Mo	313.3	N-Ac	0.050	0.40
Na	589.0	A-Ac	0.005	0.04
Ni	232.0	A-Ac	0.003	0.20
Ti	365.3	N-Ac	0.200	2.00
Zn	213.9	A-Ac	0.005	0.04

[a] A-Ac — air-acetylene; N-Ac — nitrous oxide-acetylene.

Flame photometry is applied particularly in determining alkali metals and alkali-earth metals. Using suitable fuel gases, it is possible to determine as many as 50 elements, but most of them can also be determined by

Table 7.8. Flame photometric analysis; concentration ranges and detection limits [18]

Element	Optimum concentration range (ppm)	Detection limit (ppm)
Na	3–1000	0.01
K	10–1000	0.05
Li	10–1000	0.05
Mg	500–1000	25.00
Ca	200–1000	2.00
Sr	200–1000	2.00
Ba	500–1000	20.00
Cr	200–1000	20.00
Mn	500–1000	20.00

the atomic absorption spectrophotometry. The sensitivity and concentration ranges for determining certain elements by the flame photometry are presented in Table 7.8.

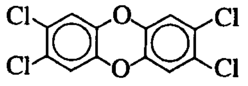
Among other methods for determining trace and toxic elements in the soil, there are also electro-chemical analytical methods, mainly polarography; and in the case of nuclear analytical methods, activation analysis and radionuclide X-ray fluorescence analysis are employed. Mass spectrometry, laser emission spectral microanalysis and other instrumental methods can also be used.

7.9.3.16 Herbicides

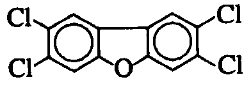
When present in soils, the herbicides are typically below the determination limits of most analytical methods. An additional problem is that the methods are not sufficiently selective, so that they cannot be used for a direct determination of particular herbicides in the wide variety in use. Thus, the determination procedure consists of the separation of herbicides from the soil, concentration procedure, purification of the concentrate and the determination itself, most typically by gas chromatography.

7.9.3.17 Chlorinated dibenzodioxines and dibenzofurans

Chlorinated dibenzo-*p*-dioxines and dibenzofurans are tricyclic aromatic compounds [4], characterized by a high chemical resistance and an ability to be accumulated in the nutritional chain. Some of them are extremely toxic, teratogenic, mutagenic and probably also carcinogenic. The most studied substances in this group are 2,3,7,8-tetrachloro-dibenzodioxine (TCDD) and 2,3,7,8-tetrachloro-dibenzofuran (TCDF), which are among the most toxic substances



2,3,7,8-TCDD



2,3,7,8-TCDF

These substances have already caused a number of ecological catastrophes. In 1968 more than 1200 people were poisoned in Japan, by consuming rice oil polluted with 0.1% of commercial polychlorodiphenyl Kanechlor 400. On heating the rice oil, the heating medium (Kanechlor) penetrated through a crack in a heat exchanger into the product. The rice oil became contaminated with 5 ppm of tetra- and pentachloro-dibenzofurans and it was shown that the main component was 2,3,7,8-TCDF in a concentration of 0.45 ppm.

The other prominent case occurred in Sevesa in Italy in 1976. In a factory producing 2,4,5-trichlorophenol by the hydrolysis of 1,2,4,5-tetrachlorobenzene, the reactor content escaped through the safety valve into the atmosphere during an accident. A cloud containing the above-mentioned components and, in addition, a certain amount of 2,3,7,8-TCDD was formed above the factory. It was estimated that approximately 2 to 3 kg of 2,3,7,8-TCDD was spread over an area with a population of several thousand inhabitants.

The basic steps in determining TCDD and TCDF involve their separation, purification and further separation connected with the identification. During the separation of TCDD and TCDF from the soils, a procedure with hexane or with a mixture of hexane–acetone 1:1 is employed. The purification is performed in two columns filled with alumina or on a column filled with silica gel and after that, on a column filled with alumina. The purification using gel permeation chromatography is very efficient. For further separation and identification, gas chromatography is used in association with mass spectrometry (GC-MS). Cheaper devices are based on the gas chromatograph with a detector of the electron capture, however, the identification is not quite unambiguous with respect to the number of isomers. In addition, appropriate standards are necessary for this procedure. Siliconized elastomers are suitable as a stationary phase, and may be used at temperatures of 250 to 300°C. With the use of GC-MS, it is possible to employ two approaches, using either fragmentography or mass spectrometry with a negative chemical ionization (MS-NCI).

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8 Soil biology

8.1 Soil microorganisms

The establishment of the cardinal roles that microorganisms play in the biologically important cycles of matter on our planet (the cycles of carbon, nitrogen, and sulphur) was largely the pioneering work of S. Winogradsky and M. W. Beijerinck in the late 19th century. Microorganisms show an extraordinarily wide range of physiological diversity in the biosphere in general and in the soil in particular.

One of the most striking examples of microbial physiological specialization is provided by the autotrophic bacteria discovered by Winogradsky. Another discovery, to which both Winogradsky and Beijerinck contributed, was the role that microorganisms play in the fixation of atmosphere nitrogen, which cannot be directly used as a nitrogen source by most organisms. They showed that certain bacteria and cyanobacteria, some free-living, others symbiotic in higher plants, can use molecular nitrogen for the synthesis of their cell constituents. A wide variety of the chemical changes taking part in the soil and related to soil fertility are provided by soil bacteria.

It was not until several decades later that comparable interest began to be shown in the soil fungi and their activities. The soil protozoa were comparatively neglected and only in recent times has interest in the soil algae increased.

Although it is not possible to assess accurately the concentration of soil microorganisms, the data in Table 8.1 give some idea of the numbers of major groups of microorganisms together with an estimate of the biomass of each of the groups in the top 15 cm of agricultural soil. Bacteria are more numerous than any other group but the biomass of the fungi is larger than that of bacteria.

The spatial distribution of microorganisms in the soil is complex. Generally there is a decrease in numbers with depth (Table 8.2) which is a reflexion of decreasing organic matter content in the soil. However, lo-

Table 8.1. Numbers and biomass of some organisms in the top 15 cm of agricultural soil [1]

	Number of organisms per gram	Biomass (g m^{-2})
Bacteria	9.8×10^7	160
Actinomycetes	2.0×10^6	160
Fungi	1.2×10^5	200
Algae	2.5×10^4	32
Protozoa	3.0×10^4	38
Nematodes	1.5	12
Earthworms	0.001	80

Table 8.2. Numbers of microorganisms of the major groups present in various horizons, determined by the dilution plate method [1]

Horizon	Humus (%)	Depth (cm)	Organisms per gram of soil $\times 10^3$				
			Aerobic bacteria	Actinomycetes	Anaerobic bacteria	Fungi	Algae
A_1	3.00	3–8	7800	2080	1950	119	25
A_2	1.28	20–25	1804	245	379	50	5
A_2–B_1	0.91	35–40	472	49	98	14	0.5
B_1	0.37	65–75	10	0.5	1	6	0.1
B_2	0.41	135–145	1	—	0.4	3	—

cal variations due to a number of factors are superimposed on the general distribution.

In the following sections, the major groups of soil microorganisms — bacteria, algae, fungi, and protozoa — are characterized. The most important aspects of interactions of soil microorganisms, and cycles of the most important elements are discussed.

8.1.1 Bacteria

As shown in Table 8.1, bacteria constitute the most numerous group of microorganisms in the soil. However, the number of bacteria per gram of the soil varies greatly and the population curve can go up and down over a period of a few days or even hours. Uncropped soils are likely to contain 10 to 100 million colony-forming units per gram as determined by plate counts. After addition of abundant supplies of organic matter it is possible to find as many as one or more thousand million bacteria (colony-forming units) per gram [2].

Although most bacterial types could probably be isolated from the soils this does not mean that all the bacteria are soil inhabitants. "This description can be applied only to relatively few species which are fairly well categorized. These show considerable diversity in their morphology, most morphological types being represented. Physiologically, they range from aerobes to obligate anaerobes, from heterotrophs to autotrophs, and from saprophytes to symbionts and parasites" [1].

The genera *Pseudomonas, Achromobacter*, and *Bacillus* are represented in most aerobic soils; in anaerobic conditions members of the anaerobic *Clostridium* occur. When suitable substrates are added to the soil, the numbers of such organisms will increase very strikingly. Favourable alterations to the soil will cause a multiplication of autotrophic organisms such as the members of the nitrifying genera *Nitrosomonas* and *Nitrobacter* and the sulphur oxidizers of the genus *Thiobacillus.*

The most numerous soil bacteria are those belonging to the genus *Arthrobacter.* In anyone situation their numbers remain relatively constant. *Agrobacterium* species are also members of this group of organisms.

Soil bacteria belong to the heterotrophs and chemoautotrophs; the photosynthetic bacteria are not an important factor in the soil.

The great majority of soil bacteria are heterotrophs. Essentially every naturally occurring organic compound that is present in the soil is subject to attack of bacteria. These include readily decomposable starches, sugars, fats and proteins; less readily decomposable celluloses and chemicelluloses; and more resistant lignin, waxes and aromatic compounds. These carbon-containing materials are used primarily as sources of energy but may also serve as sources of growth factors.

The heterotrophic soil bacteria include nitrogen-fixing bacteria and the denitrifying bacteria that will be discussed later.

Most autotrophic bacteria seem to grow best in soils that are well supplied with humus, which serves as a source of carbon dioxide, mineral nutrients, and acts as buffer against acids and alkalies. The most studied autotrophic genera are *Nitrosomonas* which oxidizes ammonia to nitrite, and *Nitrobacter* that converts the nitrite to nitrate.

Other autotrophic organisms include *Thiobacillus* and *Ferrobacillus* which are both acidophilic. The acidophilic *Thiobacillus thiooxidans* was first described in 1922 and has been studied for many years. It is able to oxidize elementary sulphur with the production of sulphuric acid, pH values down to 1.0 or less being reported. *T. thiooxidans* can metabolize at pH values below 1.0 and can even survive values close to O, although the pH optimum for its growth is near 3.5. A closely related species, *T. fer-*

rooxidans, has the ability to oxidize ferrous oxide to ferric oxide as well as to oxidize sulphur. A third species, *Ferrobacillus ferrooxidans*, oxidizes iron but not sulphur. Both these latter two species are also acidophilic autotrophs, of morphology similar to *T. thiooxidans* [3].

A remarkable group of bacteria are the fruiting myxobacteria that have rod-shaped vegetative cells, flexible and weakly refractile, which multiply by binary transverse fission. Under appropriate conditions, the vegetative cells aggregate to form macroscopically visible fruiting bodies, often of considerable complexity, which bear resting structures. Myxobacteria are frequent and ubiquitous inhabitants of the soil, decaying wood and other plant materials, as well as in the dung of animals. Myxobacteria have been isolated from samples collected in the soil of different geographic regions: in tropical rain forests, in the arctic tundra, in steppes, deserts, in bays at sea level, as well as at high altitudes [4, 5].

All fruiting myxobacteria are strictly aerobic chemoheterotrophs. Some members of the genera *Archangium* and *Sorangium* are cellulose decomposers. However, most fruiting myxobacteria do not attack cellulose and do not grow on simple defined media. The simplest medium for *Myxococcus* strains consists of a mixture of amino acids. It has been observed that both growth and fructification of myxobacteria are markedly enhanced by the presence of other kinds of bacteria; many myxobacteria can kill and lyse microorganisms belonging to other groups (true bacteria, algae, yeasts and fungi). Many myxobacteria are thus predators killing their microbial prey by the secretion of antibiotics and subsequently digesting the host protein by means of extracellular hydrolases. The predacious character of the fruiting myxobacteria probably accounts for their abundant development on dung, which has a very high bacterial content [4].

Another peculiar group of bacteria are the cytophagas, discovered by Winogradsky in 1930. These bacteria can completely destroy the structure of the cellulose fibres. The cytophagas constitute a group of gliding unicellular rod-shaped bacteria, distinguishable from the fruiting myxobacteria by their inability to undergo aggregation and fructification. They are widely distributed in the soil, fresh water and the sea. The strictly aerobic cellulose-decomposing soil cytophagas are physiologically highly specialized: the only substrate they can use as a carbon and energy source is cellulose. Another peculiar feature is their failure to secrete an extracellular hydrolase for their initial attack on cellulose: the cells must be in direct contact with cellulose in order to decompose it. This behaviour suggests that the cellulase formed by the cytophagas is an exocellular enzyme, which is associated with the cell surface but cannot diffuse away from it, as does a truly extracellular hydrolytic enzyme. Some soil species can utilize chitin that is the principal polysaccharide constituent of the cell wall of many fungi and the cuticule of insects [4].

8.1.2 Actinomycetes

The actinomycetes constitute a group of bacteria that usually have a unicellular mycelium with long branching hyphae that may develop in the soil or on its surface. The aerial mycelium commonly breaks up into fragments that resemble bacteria. Some of the hyphae bear many asexual spores, called conidia.

The actinomycetes are widely distributed in nature; they are predominantly saprophytic but also include species forming parasitic or mutualistic associations with plants, animals and humans. They occur in soils, plant litter manure compost, biodeteriorated materials, fresh and salt water, and the live tissues of plants, animals and humans. The most widely distributed genera are coryneforms, *Mycobacterium, Nocardia, Rhodococcus* and *Streptomyces*, but other genera such as *Frankia* and *Thermoactinomyces* occupy important, clearly defined ecological niches. A detailed review of actinomycete ecology was published by Goodfellow and Williams [6], and a critical evaluation was presented by Williams et al. [7]. According to the latter, in the "age of biotechnology" developments in actinomycete ecology are therefore not solely a matter of academic interest.

Actinomycetes can at times be the dominant microflora in soils, manure heaps, and wherever plant residues are undergoing decomposition. Among the products of their activities are soil humus and humus-like materials.

Actinomycetes are mostly aerobic and grow best in neutral or alkaline soils most of them having a pH growth limit of near 5.0, which is somewhat higher than for most soil bacteria. They are able to grow abundantly on decaying vegetable matter which may become matter with their mycelia. A characteristic musty earthy odour is definite evidence for the presence of actinomycetes [2].

Both mesophilic and thermophilic actinomycetes are found in the soils, the latter growing best at about 50 to 65°C. Thermophilic actinomycetes are abundant in fermenting strawy manure heaps, moist hay and other vegetable materials. In the decomposition of such materials fast-growing bacteria and fungi are responsible for the initial stages of the degradation involving the readily available sugars and proteins. Then the actinomycetes utilize resistant materials. Actinomycetes play a very important role in humus formation, largely because of their ability to attack a variety of resistant substances such as cellulose, hemicellulose, keratin, chitin and oxalic acid. Little is known about their ability to decompose lignin. The various high-molecular weight plant substances are converted into humic acids under a wide variety of conditions. When many *Streptomyces* species undergo autolysis they form dark brown substances that have chemical and physical properties resembling humic acids [2].

The ability of actinomycetes to produce antibiotics was discovered in the "antibiotic era" during and after World War II and many antibiotics are now commercially produced by means of actinomycetes.

The actinomycetes of the genus *Rhodococcus* play an important role in nature. Rhodococci decompose compounds that are weakly assimilated by other microorganisms: hydrocarbons, xenobiotics, etc. Nesterenko and Kvasinkov [8] have established that rhodococci are widely distributed in Ukrainian soils, including oil-bearing soils.

8.1.3 Cyanobacteria

Cyanobacteria (formerly known as blue-green algae) are photoautotrophic microorganisms that are widely distributed in nature including the soils. They are widespread even in regions as dry as the Negev desert in Israel and as cold as deserts in Antarctica (particularly on the under surface of stones). This flora consists mainly of members of the genera *Schizothrix* and *Microcoleus* [1].

Cyanobacteria living in soils and most frequently isolated belong to the genera *Nostoc, Cylindrospermum* and *Anabaena.* Cyanobacteria are common constituents of neutral to alkaline soils and also of saline soils. Several cyanobacteria occurring in soils fix atmospheric nitrogen. Cyanobacteria living in symbiosis with fungi in the form of lichens are frequently found in desert soils of the southwestern USA. The alkalinity of these desert soils is doubtless a major factor in accounting for the observations. Furthermore, cyanobacteria have the ability to withstand both very wet and very dry conditions [2].

8.1.4 Fungi

The fungal population of soils constitutes a very heterogeneous group of organisms. The fungi known to occur in the soil cover the range from chytrids to agarics, from saprophytes to root parasites, and from parasites of amoebae to parasites of man [9].

In general, *Mucor, Penicillium, Trichoderma* and *Aspergillus* predominate in soil fungal flora. *Rhizopus, Zygorhynchus, Fusarium, Cephalosporium, Cladosporium*, and *Verticillium* occur commonly. All of these grow quickly and sporulate copiously and are therefore favoured when the dilution plate method is used. Direct examination of the soil shows that *Basidiomycetes* are numerous and that dark sterile hyphae (probably members of *Dematiaceae*) are common. The biomass of fungi in cultivated soils often exceeds that of any other group of organisms. Addition of organic matter to a soil stimulates the fungal flora [1].

All fungi are heterotrophs and are predominantly aerobic, and hence are usually found at or near the surface of any organic matter upon which they may be growing. In the soils they are limited largely to the plow layer, or A-horizon, but this is because an abundant supply of energy sources is available only in this upper region [2].

Many of the fungi attack cellulose and a few of them can decompose lignin which makes them competitors with bacteria and actinomycetes in this respect. Fungi have low nitrogen demands and obtain nitrogen either from the substances that they are decomposing or from inorganic nitrogen sources.

Many fungi are tolerant of unfavourable environmental factors. Although the majority of the fungal species are mesophilic, a few can tolerate temperatures in the thermophilic range. The most acid-resistant organisms to have been reported are two fungi described by Starkey and Waksman [10], *Acontium velatum* and a green organism belonging to the Dematiaceae, which were found growing at very acid pH values in 4% copper sulphate solution. Growth occurred well at pH 0.2 to 0.7 and slowly even at pH 0. The upper limit was not defined, as the two fungi quickly lowered the pH from 7 to 3, and then grew well. Although resistant to high Cu^{2+} concentrations, the fungi grew better in the absence of copper ions.

8.1.5 Algae

Algae are found in nearly all cultivated soils but they are found also in hot deserts as dry as the Negev desert (see also Section 8.1.3) and cold deserts of Antarctica. They are there represented by the coccoid *Chlorophyta*. The soil floras have been shown to be extensive and the algal biomass on surface soil must be considerable since it is frequently visible to the naked eye.

The soil algae include flagellate, coccoid, diatomaceous and filamentous species. *Chlorella* and the *Chlorococcum* of the *Chlorophyta*, together with certain diatoms, are frequently isolated from soil samples. *Chlamydomonas* and *Hormidium* are also widely distributed.

All algae are photoautotrophic organisms, although some species can live in the dark, utilizing carbohydrate substrates.

The main contribution of algae to soils and plant growth is in supplying a small amount of organic matter. This contribution is of minor importance in cultivated soils but it is likely to be of major importance in the initiation of colonization of soils that are devoid of organic matter. Usually, algae are present in such areas together with cyanobacteria that are able to fix nitrogen from the air [1, 2].

8.1.6 Protozoa

Protozoa are widely distributed in the soil. They generally occur in the water film surrounding soil particles. The rhizosphere of plants is also a favourable environment for protozoa because of the increased food supply in the form of bacteria, plant excretions and plant residues. Soil protozoa are usually smaller than fresh water forms. They exist both as motile and as encysted resting forms. Some are amoeboid, others are oval with cilia, and still others are small organisms that propel themselves by means of flagellae. Their food consists chiefly of bacteria but some species can also digest other organisms, including protozoa. Protozoa are aerobic organisms that require a moist soil for growth and thrive best in neutral soils well-supplied with various forms of organic matter. Available data resulting from extensive studies on soil protozoa led Allison to the conclusion that "protozoa are of minor importance in the large majority of soils. This applies to their contribution to organic matter breakdown and to the overall effects on crop production" (ref. [2], p. 59).

8.1.7 Interactions of soil microorganisms

A variety of interactions among members of soil populations have been recognized. Soil microorganisms may be involved in relationships such as symbiosis, competition, antibiosis, pathogenesis, or predation.

8.1.7.1 Interactions with plant roots

In the rhizosphere, the region of the soil under the influence of plant roots, many types of interactions occur. Because it is the region of the soil which provides the plant with its soluble nutrients, other soil organisms must affect the plant through this area. In the same area any effect of the root on other soil organisms must occur. This effect on the soil microflora is usually expressed as the R/S ratio, that is, the number of organisms in rhizosphere soil as compared with the number in the same soil beyond the influence of the root.

Bacterial response to the rhizosphere conditions is greater than that of other groups. Sometimes where a high bacterial response is recorded the R/S ratio for protozoa is also large. Fungal numbers estimated by the dilution plate count increase only slightly in the rhizosphere although more than do those of algae, which may be unchanged or even decreased [1].

Soil microorganisms can influence plant roots in a number of ways. One of them is the secretion of membrane-active antibiotics which stimulate further leakage of plant cell constituents into the soil. Microorganisms can also affect the availability of nutrients, compete with the plant for water and nutrients, etc.

Positive effects on the plant are produced by microorganisms that enter more intimate relationships with the plant roots. Such effects are known in the case of symbiotic nitrogen-fixing bacteria, actinomycetes and cyanobacteria as well as of symbiotic mycorrhizal fungi.

Bacteria of the genus *Rhizobium* occur in nodules on the roots of many legumes, but have also been found in one non-leguminous plant, *Trema aspera.*

Rhizobium occurs free-living, but cannot fix nitrogen when it is existing as a natural member of the soil population. The sequence of events in the infection of roots and formation of an active, nitrogen-fixing nodule reveals a complex series of interactions between symbiont and host.

Initially, free-living rhizobia aggregate around the root hairs, presumably in response to an unidentified attractant in root exudates. The host root then secretes extracellular polygalacturonase, which weakens the external plant cell wall adjacent to the bacteria, and it invaginates to form a structure called the infection thread. Bacteria become enclosed in the infection thread, which moves inward through the root cortex. At the same time, cortical cell division is stimulated to form the bulk of the eventual nodule tissue. The wall of the thread is cellulose, and entirely of host plant origin. The infection thread may branch and spread through the developing nodule tissue, the branches terminating in host cells which have previously become polyploid. The bacteria become deposited in the host cell where they become enclosed in vesicles of host membranes. They may undergo several divisions, but then swell to about 40 times the volume of the original bacterium to become "bacteroids", often with simple branches to give "Y" or "X" shapes. Finally, the host tissue synthesizes leghaemoglobin which colours the nodule pink. Only if this is formed can the nodules fix nitrogen [11]. The practical consequences of symbiotic nitrogen fixation are discussed in Section 8.1.9.2.

Mycorrhizae result from symbiotic colonization of fine roots by beneficial soil fungi. Only one species of fungus usually forms a mycorrhizal association with any particular root. The vast majority of economically important plants form mycorrhizae. On the basis of their morphology, these associations are divided into two major groups: ectomycorrhizae and endomycorrhizae. Endomycorrhizae are by far the most common, but ectomycorrhizae are formed on some important families of forest trees. Mycorrhizae of both groups are important contributors to the cycling of soil nutrients, particularly phosphorus. Plants grow poorly in areas without adequate mycorrhizal fungi. The growth of forest trees and certain agricultural plants can be stimulated by inoculating them with mycorrhizal fungi when such plants are growing on soils with low levels of mycorrhizal fungi and essential nutrients.

Ectomycorrhizae are formed by fungi belonging to higher *Basidiomycetes* (mushrooms and puffballs), *Ascomycetes* (cup fungi and truffles), and lower fungi of the family Endogonaceae. The host plants of these fungi are predominantly trees such as pine, hemlock, spruce, fir, oak, beech, willow and poplar.

Vesicular-arbuscular endomycorrhizal fungi occur on most food crops. This type of mycorrhizae are formed by certain fungal species of the family Endogonaceae. The vesicular-arbuscular endomycorrhizae significantly increase growth of plants on soils deficient in readily available phosphate; more information may be found elsewhere [12]. The significance of root microorganisms in the ecosystem has been reviewed by Newman [13].

8.1.7.2 Plant pathogens

The soil is a reservoir of plant pathogenic microorganisms, in particular root-infecting fungi. It has been observed that competition of plant pathogens with other soil organisms is of great importance. The causative agent of potato scab, *Streptomyces scabies*, can be suppressed by green manuring and it is thought that this is due to the antagonism of an increased population of free-living actinomycetes brought about by the green manuring [1].

Root pathogens occur also in non-crop vegetation. For example, *Phytophtora cinnamoni* which causes root rot of many woody species, is widespread in native forests in Australia and has caused the death of almost all the trees in some areas of forest. *P. cinnamoni* has killed many native chestnuts in the USA. *Poria weirii* causes widespread deaths among native conifers in the forests of western Washington and Oregon [13].

Agrobacterium tumefaciens is a peculiar soil bacterium that is pathogenic to plants and induces tumour growth on roots of infected plants. This bacterium, in addition to its chromosomal DNA, harbours a tumour-inducing plasmid (Ti plasmid). During the genetic transformation of plant cells by *A. tumefaciens*, a specific segment of DNA, the t-DNA, is recognized in and mobilized from the large Ti plasmid of the bacterium, transferred across the cell walls of the bacterium and plant cell, and integrated as an unaltered fragment into the plant nuclear genome. The t-DNA contains oncogenes, i.e., genes that control dedifferentiation and tumour growth [14, 15].

8.1.7.3 Antibiotics in soil

In laboratory experiments it is frequently found that antagonism is exhibited between microorganisms isolated from the soil. Further, the soil is the chief source of microorganisms producing antibiotics which are produced industrially. Nevertheless, a number of controversies on the production and function of antibiotics in natural environments may be found in the literature. Experiments and discussions have been focused on questions such as "Are antibiotics produced in nature?" and "Do antibiotics have a natural function?" or "Is one function that of inhibiting or killing competing organisms in nature?" [16].

Potentially, antibiotics should be produced in circumstances that permit growth of their producers. Such circumstances may be found in the soil, plants and plant materials (e.g., fruits), etc. Brian [17] advocated the competitive role of antibiotics against other species susceptible to their effects, and accumulated experimental data concerning the production of antibiotics and other secondary metabolites of microorganisms in natural environments.

A detailed review on the production and role of antibiotics in the soil was published by Gottlieb [18]. In spite of many examples of antibiotic production in soils, he was inclined to doubt whether antibiotics are "normally" produced and play a role in the ecology of soils in "normal" unaltered soil. He concluded with the view that the available data still do not allow us to accept the thesis that antibiotics are naturally produced in soil and function there in antagonistic capacities. Even if antibiotics were produced in normal soils some of them might not play an ecological role because of inactivating mechanisms in the soil such as biological degradation, adsorption on soil clays and reactions with the organic matter in the soil.

In contrast to these claims about what is "natural" and what is not, Demain [16], considered antibiotic production in unsterilized soils supplemented with natural plant material as "natural" situation. Similarly, the confirmed production of gliotoxin by *Trichoderma* on wheat straw in the soil, and in the soil immediately adjacent to the straw, should also be considered "natural", as well as patulin production in soils supplemented with alfalfa and clover or in contaminated apples and in fruit juices [19].

The production of antibiotics in natural conditions has been verified experimentally by many authors. Some examples are given in Table 8.3, reproduced from a book of the present author [20] in which a section is devoted to the "raison d'être" of antibiotic production in general and their ecological roles in particular. The production of antibiotics in nature thus seems to be well established.

Table 8.3. Production of antibiotics in nature [20]

Antibiotic	Producing organism	Conditions
Actinomycin	*Streptomyces antibioticus*	Unsterilized and unsupplemented soil
Alternaric acid	*Alternaria solani*	Inoculated unsterilized tomato fruits
Citreoviridin	*Penicillium citreo-viride*	Contaminated rice
Citrinin	*Penicillium citreo-viride*	Contaminated rice
Erythroskyrin	*Penicillium citreo-viride*	Contaminated rice
Frequentin	*Penicillium frequentans*	Inoculated, unsterilized, incubated in unsterilized soil
Gladiolic acid	*Penicillium gladioli*	Inoculated seeds
Gliotoxin	*Trichoderma* sp.	Inoculated into wheat straw and then incubated in soil; unautoclaved soil supplemented with clover
Heliomycin	*Streptomyces olivocinereus*	Unsterilized and unsupplemented soil
Patulin	*Penicillium expansum*	Inoculated or rotting apples
Patulin	*Byssochlamys* spp.	Fruits and fruit juices
Tenuazonic acid	*Alternaria* spp.	Infected cotton plants
Trichothecin	*Trichothecium roseum*	Unsterilized and unsupplemented soil; contaminated apples

The next two questions, of whether antibiotics have a natural function by inhibiting or by killing competing organisms in nature, may be considered simultaneously.

The actinomycetes producing ristomycin, rifamycin, lincomycin, tobramycin, rubomycin, carminomycin, olivomycin, bleomycin and actinomycin D were virtually insensitive to their own antibiotics at the concentrations close to those produced during the biosynthetic processes. At the same time other actinomycetous species close to the above organisms were suppressed to a significant extent by these antibiotics in the same concentrations. These findings were interpreted as indications that antibiotics may have a protective effect on the organisms producing them and play a significant role in the ecology of the actinomycetes [21].

In terms of possible allelochemical effects of fungal secondary metabolites, a hypothesis was presented by Martin [22]. It is known that many arthropods, especially insects and mites, have established close associations with fungi, and among such species the consumption of fungal mycellium (mycophagy) is common. According to the author, many of the secondary metabolites produced by such fungi are certainly potentially harmful to any insects which may consume them, and their presence clearly presents a challenge to the capacity of a consumer to detoxify them. For those insects which have mechanisms to counter the deleterious effects of such noxious secondary metabolites, and which are specialized fungus-feeders, the same substances may serve as attractants or as stimulants to feeding or oviposition.

Hence antibiotics and other secondary metabolites may be useful as factors participating in the manifold ecological relations by means of which the producer organisms are related to the other organisms of their biotope [23, 24].

8.1.7.4 Predacious soil microorganisms

In the soil habitat various forms of microbial predation are known. Protozoa prey on one another and also on bacteria, yeasts, algae, and some even on nematodes. The latter and other small animals also feed on bacteria.

Some myxobacteria kill eubacteria and other microorganisms with a secreted antibiotic, lyse the dead cells with an extracellular enzyme mixture and utilize the soluble products.

A number of fungi belonging to the *Hyphomycetes* and *Zygomycetes* trap soil nematodes, soil amoebae, and sometimes rotifers and subsequently invade and devour them. The members of the *Zoopagales* shed sticky conidia which adhere to the prey, usually an amoeba or other small soil animal, and put out germ tubes which penetrate into the body where a small thallus is formed. They are probably obligate predators [1].

More than 50 species of nematode-trapping fungi are known. Many are *Deuteromycetes* of the order *Moniliales.* The genera most commonly represented are *Arthrobotrys, Dactylaria, Dactylella,* and *Trichothecium.* They trap nematodes by either adhesion or occlusion. Some fungi capture nematodes through adhesion to virtually undifferentiated hyphae, but many fungi have, for this purpose, specialized networks of adhesive branches, stalked adhesive knobs or constricting rings. Adhesive networks are produced by hyphal branching. Certain species form one-celled sticky processes, and others produce spherical knobs on short stalks. Adhesive networks and knobs are coated with a mucilage and capture nematodes on contact by adhesion [25].

Some capture structures function mechanically. They are usually fashioned from three curved cells which join to form a closed ring at the end of a short stalk. A nematode that enters a non-constricting ring becomes firmly wedged and unable to escape. A number of species of nematode-trapping fungi produce constricting rings. When a nematode enters, the ring cells swell, obliterating the opening and constricting the nematode so that it cannot escape. Its surface is then penetrated and fungus hyphae ramify through the carcass and digest and absorb its content [25].

Initial attempts to exploit predaceous fungi for the biological control of a nematode-caused disease, root-knot of pineapple, were made just prior to World War II in Hawai. Perhaps, under certain conditions, the activities of nematode-trapping fungi can be directed against nematode parasites that are of economic significance.

8.1.8 Chemical transformations by soil microorganisms

"The biogeochemical cycles which operate on Earth are essential for the maintenance and continuation of life as we know it. Solar radiation provides the energy which is harnessed by photosynthesis. Relatively simple inorganic chemicals (supplied by soil minerals, natural waters and air) are utilized by autotrophs for their biochemical processes; these feed the heterotrophs. After death, the constituents of living organisms are mineralized again by microorganisms" [26].

The soil microorganisms, plant root system and soil fauna are responsible for chemical transformations in the soil which are important for its fertility and which ensure the removal of natural litter from the earth's surface. Some stages of the cycles of matter result in amelioration of the soil, whereas others decrease its fertility [1]. In the following sections, participation of soil microorganisms in the cycles of carbon, nitrogen, sulphur, phosphorus and other elements are discussed (see also Sections 2.1.2 and 4.2.9).

8.1.8.1 The carbon cycle

Organic residues added to the soil contain about 50% carbon which is eventually converted to carbon dioxide. Soil microorganisms are responsible for the evolution of about 95% of the gas which is then fixed mainly by green plants. A simplified representation of the carbon cycle is given in Fig. 4.8.

Plant and animal remains, representing the main types of carbon compounds added to the soil, contain the carbon included in high-molecular weight compounds. In plants the main types of these are cellulose, hemicellulose and lignin, followed by smaller quantities of fats, waxes and oils, proteins and nucleic acids. In invertebrates and fungi chitin occurs, whereas in bacteria it is peptidoglycan (murein).

Three general methods exist for the catabolism of organic compounds: aerobic respiration anaerobic respiration and fermentation.

On the surface of the soil, residues are attacked by bacteria, fungi and animals. In the soil the conditions for further decay are more favourable to microorganisms. The carbon in the residues is oxidized to carbon dioxide, incorporated in microbial cells and the reminder is incorporated into humus. Humus can be further decomposed by soil microflora.

In waterlogged anaerobic soils, organic matter can be converted (via organic acids, carbon dioxide and hydrogen) to methane by methanogenic bacteria. A methane oxidizing flora at the soil surface oxidizes most of the methane to carbon dioxide.

8.1.8.2 The nitrogen cycle

Almost all higher plants, animals and microorganisms depend on combined nitrogen for their nutrition. Combined nitrogen in the form of ammonia, nitrates, or organic compounds, is relatively scarce in the soil and water, and its concentration often becomes the limiting factor in the development of living organisms. Hence the nitrogen cycle is of paramount importance in the total turnover of this element in the biosphere [4].

The main features of the nitrogen cycle are illustrated schematically in Fig. 4.9. The nitrogen cycle is of huge importance for soil fertility.

Ammonification. Plants and algae assimilate nitrogen either as nitrate or ammonia. If nitrate is assimilated, it must be reduced in the cells to ammonia which is then used in the synthesis of nitrogenous organic compounds — amino acids, amino sugars, and purine and pyrimidine bases. These three types of compounds occur in organisms mainly in polymers. There is no significant excretion of reduced nitrogenous compounds by plants.

The organic nitrogenous compounds synthesized by autotrophic organisms serve as the nitrogen source for animals and humans. During their assimilation, complex nitrogenous compounds are hydrolysed, but the nitrogen remains largely in a reduced organic form. Animals excrete a significant quantity of nitrogenous compounds in their metabolism. The form in which nitrogen is excreted by various animals can be: ammonia (invertebrates), uric acid (reptiles and birds) or urea (mammals). In the soil the urea and uric acid are rapidly mineralized by special groups of microorganisms with the formation of ammonia and carbon dioxide.

Only part of the nitrogen stored inorganic compounds through plant growth is changed to ammonia by animals and the microbial ammonization of urea and uric acid. When an animal or a plant dies, its body constituents are attacked by microorganisms, and the nitrogenous compounds are decomposed with the liberation of ammonia. Part of it is assimilated by microorganisms themselves and converted again into cell constituents. These are ultimately converted to ammonia after the death of microorganisms. A wide variety of soil bacteria are capable of hydrolysing proteins. *Bacillus, Pseudomonas* and *Arthrobacter* species are of particular importance in the process. Aminopolysaccharides are broken down by a much restricted microflora, mostly by species of anaerobic *Clostridium.* Nucleic acids are broken down by fungi such as *Aspergillus* and *Penicillium*, and by bacteria such as *Clostridium, Bacillus* and *Achromobacter.* The main product of the breakdown of organic residues is ammonia.

Nitrification is the process of oxidation of ammonia to nitrite and nitrate by chemoautotrophs of the Gram-negative genera *Nitrosomonas* and *Nitrobacter* that employ nitrification as their sole source of energy. *Nitrosomonas* mediates oxidation of ammonia to nitrite according to the overall reaction:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

Nitrobacter converts nitrite to nitrate:

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

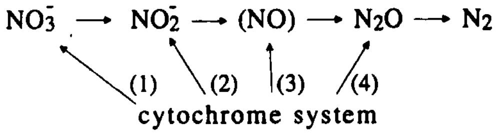
Nitrification takes place in most cultivated soils but in many forests, orchard, and grassland soils the nitrifying bacteria are inactive because of soil or climatic conditions. The plants in these situations must therefore assimilate ammonium nitrogen. Ammonium ions are chemically stable in acidic conditions and, as they may be bound to negatively charged clay particles, are not leached out of the soil. In contrast, nitrate and nitrite are easily leached out and nitrite is also converted in acidic soils to gaseous nitrogen and nitrous oxide thus causing a net loss of nitrogen. However, only a relative small portion of the ammonium ions bound to clay particles is exchangeable and available for assimilation. Above certain levels they may be toxic to plants and in very alkaline soils they may be volatilized [1].

Denitrification in the strict sense involves the dissimilatory reduction, by essentially aerobic bacteria, of nitrate or nitrite to the gaseous oxides (nitric oxide, NO, and nitrous oxide, N_2O), which may themselves be further reduced to nitrogen (N_2). Denitrification does not include assimilation of these ions by plants or microorganisms or loss by leaching. The products of denitrification are not assimilable by higher plants and most microorganisms, and thus this process is deleterious to soil fertility [1, 27].

The ionic nitrogen oxides as terminal electron acceptors in the absence of oxygen (anaerobic respiration) and the gaseous nitrogen species are major products of these reductive processes.

Interest in denitrification exists for several reasons. First, it is the major mechanism for the loss of fertilizer nitrogen, resulting in decreased efficiency of fertilizer use. Second, it is of great potential application in the removal of nitrogen from high-nitrogen waste materials such as animal residues. Third, denitrification contributes N_2O to the atmosphere, where it is involved in stratospheric reactions resulting in the depletion of ozone. And lastly, it is the mechanisms by which the global nitrogen cycle is balanced [27].

Biochemically, in denitrification electrons are transported via cytochromes to nitrogen oxide reductases. These reductases are indicated in the scheme below as follows: (1) nitrate reductase, (2) nitrite reductase, (3) nitric oxide reductase, and (4) nitrous oxide reductase.



A potential for denitrification exists in most habitats, but there is no information on which groups of organisms are responsible for the activities observed in particular systems. From their frequency of isolation, the *Pseudomonas* and *Alcalienes* groups are perhaps of greatest significance. Knowles [27] also described denitrifiers belonging to the genera *Achromobacter, Agrobacterium, Bacillus, Chromobacterium, Corynebacterium, Halobacterium, Hyphomicrobium, Moraxella (Kingella), Neisseria, Para-*

coccus (Micrococcus), Propionibacterium, Rhodopseudomonas, Thiobacillus, Vibrio and *Xanthomonas.*

Nitrogen fixation. Prokaryotic microorganisms capable of nitrogen fixation have representatives in many genera. Free-living nitrogen-fixing bacteria include members of *Klebsiella, Azotobacter, Clostridium, Rhodospirillum, Aspirillum*, and various cyanobacteria. Bacteria that fix nitrogen only when they are symbiotically associated with a plant include *Rhizobium* spp. (which nodulate legumes), certain actinomycetes (which nodulate *Comptonia, Alnus, Elaeagnus, Hippophae* and *Myrica*), and *Anabaena azollae* (which fixes nitrogen within the leaf pores of the water fern *Azolla*). No eukaryotic organisms have been shown to fix nitrogen [1, 28].

The assimilation of molecular nitrogen by nitrogen-fixing organisms is catalysed by the enzyme complex nitrogenase, which is made up of two soluble proteins called component I and component II. Component I is also known as MoFe protein or nitrogenase reductase. It has a molecular weight of 200,000 to 250,000 and contains 2 Mo atoms, 28 to 34 non-heme Fe atoms, and 26 to 28 acid-labile sulphides. Component II has a molecular weight of 55,000 to 65,000 and has four non-heme Fe atoms and four acid-labile sulphides [28]. In the process the nitrogen is reduced to ammonium ions. The process is accompanied by evolution of hydrogen. Between 12 and 36 ATP molecules are required for each N_2 molecule that is fixed.

Cyanobacteria known to fix nitrogen belong to more than 20 genera. The amount of nitrogen fixed by cyanobacteria range from a few kilograms per hectare per year in Temperate Zones to over 100 kg ha^{-1} yr^{-1} in some polar regions [29].

Free-living bacteria in Temperate Zones fix only 2 to 3 kg N ha^{-1} yr^{-1}. In the tropics, however, there is increasing evidence that nitrogen fixation by bacteria, particularly those growing in associative symbioses may be important. In Brazil, the nitrogen-fixing bacterium *Azotobacter paspali* lives in association with roots of the tropical forage plant *Paspalum notatum.* This association fixes 90 kg N ha^{-1} yr^{-1} [29].

The fixation of nitrogen by the symbionts legume — *Rhizobium* is of tremendous agricultural importance. Average amounts of nitrogen added to the soil by a leguminous crop are frequently between 120 and 600 kg N ha^{-1} yr^{-1} [1].

8.1.8.3 The sulphur cycle

Most soil sulphur is combined in organic compounds. Higher plants normally use sulphate ions although they can also assimilate sulphur-containing amino acids. Microorganisms can utilize most of the sulphur compounds and are important in the sulphur cycle (Fig. 4.10).

In aerobic conditions, soil microorganisms decompose organic sulphur-containing compounds to sulphate (mineralization) whereas in anaerobic conditions hydrogen sulphide is liberated (putrefaction).

Hydrogen sulphide is oxidized to sulphur by chemoautotrophic *Thiobacillus* and *Beggiatoa*. *Thiobacillus thiooxidans* oxidizes sulphur to sulphuric acid.

The organisms responsible for reducing sulphate in the soil are members of the genus *Desulfovibrio.*

8.1.8.4 Other transformations in soil

Phosphorus is necessary for all organisms as a constituent of nucleic acids, phospholipids and other organic phosphate compounds. Its frequent deficiency in soils must be supplemented with phosphate fertilizers. Phosphorus is liberated from organic matter during ammonification. Phosphate is also made available to plants as a result of the formation by microorganisms of organic acids which dissolve insoluble inorganic phosphate compounds in the soil.

Organisms require smaller amounts of other biogenic elements including trace elements such as iron, manganese, molybdenum, magnesium, zinc and copper. Little is known about the cycles of these elements in the soil.

Soil microorganisms may play a key role in modification of heavy metals added to the soil as a result of man's industrial and agricultural activity. For such modification to occur, soils must contain populations of microorganisms resistant to the toxic effects of a given metal and capable of altering the chemical form of the added metal. Drucker et al. [30] determined that the order of toxic effect (from the greatest to the least) was: Ag, Hg, Cr, Cd, Cu, Ni, Zn, Tl, Fe, Sn, W, Mo, Mn, As, Co, Sb, Pb.

The use of organic pesticides in agriculture is made with the tacit assumption of selective action, i.e. that the parasite is inhibited while the higher plant and non-parasitic microorganisms are unaffected. Most frequently, this is not the case. It has been shown that pesticides inhibit growth of soil cyanobacteria, bacteria and algae [31, 32]. Some organic fungicides have been shown to be mutagenic to bacteria. Although the introduction of systemic fungicides has resulted in better control of many plant diseases, their very effectiveness has at the same time posed new problems [32].

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8.2 Soil fauna

Soil fauna consists of a significant amount of animals of different size which are present in soil, some permanently, some temporarily. Some of them are of microscopic size, for example, protozoa which are discussed in detail within the framework of microorganisms. Microfauna covers also some metazoa, such as whirligig beetles or small worms. Macrofauna is represented by a rich groups of larger animals which are usually classified into arthropods and other animals. The greatest attention is focused on the components of fauna which occur in the arable land since they significantly influence its fertility and other properties. The main varieties are now discussed in turn.

Whirligig beetles (*Rotatoria*) — microscopically small worms present in high amounts particularly in soils with high reserves of organic matter. About 100 species of them have been described, but their importance in the soil is not well known. They require adequate soil moisture and move in a thin layer of water in soil pores, but some can live in a dry environment. Their food consists of soil humus, detritus, bacteria, algae, protozoa and small nematodes.

Nematoda are small worms with a prolonged body; they are present almost in all types of soils, sometimes in surprisingly high amounts. Under favourable conditions several millions of individuals can be present in the surface layer down to a depth of 5 cm on an area of 1 m^2, but sometimes only few thousands occur there. Depending on their method of nutrition they can be categorized into three groups:

- nematoda nourished by dead residues of plants and animals,
- nematoda eating bacteria, algae, protozoa or other nematoda,
- parasites living on the plant roots and sucking juice from them. In the case of over-reproduction they become very serious pests of plants.

Turbellaria are worms with a distinctly flat body which live on places with rich reserves of dead residues. Their size is from several mm to 3 cm, and they feed on microorganisms, nematoda and other small worms. Some of them are able to form cysts where they can survive both dry conditions and excessive moisture of soil.

Annelida are the most perfect worms with metameric segmentation. This is a very important group of soil animals; the most important are potworms and earthworms.

The potworms are small white worms which are not longer than 5 cm. They occur particularly in acid soils with a suitable content of organic matter. They require adequately wet, but also well aerated soils since they are demanding as regards oxygen. They like to move in existing cavities since their ability to burrow the soil is limited, and in this respect they are not so efficient as the earthworms. Their food consists of soil detritus, bacteria, fungi, algae, etc. They can be found in high amounts in manure and compost.

The earthworms have long been considered as the most important group of soil animals. They are concentrated particularly in the surface layers of soil, forming thus more than a half of the present biomass, but some species penetrate to a depth of several metres. Most species require a neutral reaction of soil whose acidity must not be below pH 4.5. They are rather sensitive to the environmental temperature, they die at –2°C. They flourish in wet soil, in dry weather they can move and burrow into it until the loss of moisture in their body does not exceed 18%, but they can survive even a loss of 70–75% of their normal body moisture. Because of remarkable sensitivity to moisture and temperature the earthworms are noted for their seasonal activity. Their influence on soil is mechanical (burrowing) and chemical (eating and excretion of non-digested organic residues). The paths and small channels are burrowed mostly in the upper layer of soil down to a depth of 60 to 120 cm, thus improving the physical properties of soil, they increase porosity, improve aeration and permeability of water. Hence, the total microclimate in the upper layer (the A horizon) is improved. The earthworms are very useful also because they enrich the soil with organic matter which they transport from the surface into the soil. Together with organic residues they also consume mineral substances which are transformed in their digestion tract, they are mixed there and enriched with calcium. The excreta are then solid, water-resistant structural aggregates consisting of inorganic and organic compounds of a humus nature, bound with calcium. The importance of the erathworms for soil fertilization was pointed out by Charles Darwin as early as 1881, and his assessment has proved to be surprisingly exact. The mass quantity passing through the digestion tract of the earthworms is undoubtedly important under suitable conditions. It can be expected that in the case of abundance of earthworms as much as 5–9 kg of dry soil matter per m^2 pass through their digestion tract per year. On an area of 1 ha they are able to transfer about 120 tons of soil per year excreting 15 to 20 tons of excreta [1–3]. As well as the transport of organic matter from the soil surface, earthworms bring a significant soil quantity from the bottom layers to the surface contributing thus to total mixing of soil.

Molluscs represent a very heterogeneous group of which the most numerous are snails and slugs. They are not typical soil organisms because they spend most of their life on the soil surface. They enter the soil only rarely, and even, then only the top layer. They eat organic residues of plants and animals, some predatory species also eat earthworms and other small animals. The fact that many of them eat various parts of vegetation from leaves up to reserve organs can be a problem because they cause serious damage to the crop. Their negative effects are not balanced by enrichment of soil with organic matter since as far as this is concerned they are much less efficient than the earthworms. They require moisture with a sufficient amount of calcium carbonate (in the case of snails) necessary for their shells.

Arthropoda include a great portion of the soil animals. The most important are mites, spring-tails, spiders and other groups of insects. They enrich the soil with organic matter to different degrees, and they help to humify it, contribute to mixing of soil and thus to the improvement of its physical and physico-chemical properties.

Acarina are wide-spread species including mites and ticks, they are present in all soils and in number they exceed all other groups of soil Arthropoda. However, their size is very small and their material and metabolic contribution to the transformations of organic matter in soil is not considered to be important. Some eat dead organic matter, others eggs of insect, filamentous fungi or other microorganisms, some are predaceous and eat other Arthropoda or worms. They speed up decomposition of organic matter also by distribution of bacteria and other microorganisms into different layers of soil and infect the bodies of newly dead plants and animals.

Spring-tails (Colembola) follow the Acarina in order of occurrence. The soil species are several mm long, and they occur under various soil conditions. They eat microorganisms, dead plants, residues and excreta of animals; some species are predators. The spring-tails are considered to be important co-producers of humus.

Chilopoda live in soil rich in plant residue, their main food consists of dead and living plants and fungi. Adult Chilopoda aerate soil by burrowing tunnels, young individuals can move only in the existing holes.

Diplopoda are related to Chilopoda, but they are mostly predaceous. They live both in forest and arable land, in moss and various hiding places. They hunt and eat the majority of small animals present in soil. Some burrow and loosen the soil, others use only existing tunnels and holes.

Coleoptera include a large group of insects living on the surface or inside the soil at different stages of their individual development. Some of them eat living and dead plants, microorganisms, decaying residues, etc., others are predaceous. Some are very serious pests for agricultural and forest growths, but many predaceous species are useful because they eat the pests.

Diptera occur in soil mostly at their larval stages, only rarely as an adult insect, which is usually without wings. Their larvae require quite a lot of moisture, some are able to burrow in the soil, but usually they use already existing tunnels and holes. They eat living and dead plants, residues of animals, excreta, fungi, etc. Some species are parasites on worms, molluscs or another insect. Their major effect on soil consists in speeding up degradation processes and the support of humus formation.

Isopoda are very sensitive to air currents, therefore their occurrence is limited to humid places such as wet leaves, irrigated gardens, greenhouses, etc. They eat decaying organic matter mostly of plant origin. They do not have any special effect on the soil properties.

Hymenoptera are represented particularly by various species of ants which often build complicated systems of corridors and cavities under the surface. They eat particularly dead and living insects, and help to mix upper and bottom soil layers.

Isoptera live mostly in tropical and subtropical regions, but they also occur in the mild zones. Like ants they often live in communities of many thousands, some species build high structures from material they bring from soil; other species live in the earth where they make complex tunnels and corridors. They eat particularly wood and other dead plants. Because of their remarkable voraciousness they speed up the decomposition of cellulose in the soil.

Vertebrata are represented by many species, of which the most important are moles, mice, fieldmice, susliks, hamsters, and rabbits. Their importance consists in loosening and transport of soil; the activity of some of them is exceptional. The most active ones are moles and small rodents, which — except for the favourable effects on soil — often represent a serious danger for crops. Some of them build nests under the ground in which they store remarkable quantities of plant material. Many vertebrata, including birds, snakes and lizards, eat other soil animals, thus indirectly influencing the soil conditions [1–5].

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9 Human exposure to toxic and hazardous substances in water, air and soil (Environmental biochemistry and toxicology)

9.1 Toxic substances

Toxic substances damage biological systems, disturbing the functioning of biochemical processes and resulting in detrimental, and even fatal effects. The study of toxic substances and their modes of action compose the science of toxicology. It is a branch of pharmacology, which investigates mutual relationships between chemical substances and biological objects. The mechanisms by which toxic substances affect biological systems and the overall results of these interactions are many and varied.

Toxicology is concerned with a complex study of the characteristics and effects of chemical substances and the application of knowledge obtained for the protection of man and of life in general. The considerable development of industry, especially the chemical industry and energy production, increases the risk of ecological catastrophes due to exhalates and accidental escapes of biologically highly efficient substances. Modern civilization, due to ill-considered use of the results of the scientific and technology development, gives rise to extreme increases of toxicological problems. The problems of industrial toxicology include those concerning not only man himself, but also water, air, soil and indeed the whole biosphere. Increased attention has been paid to the hygienic standardization of new chemical substances in the working environment, and the number of substances for which the maximum allowable concentrations have been established continues to increase. The research into chronic effects of low concentrations of chemical substances and of the mechanisms of the intoxication and biochemical reactions has been developed. Analytical methods for determining substances in the atmosphere and in biological material have been refined. It has been shown that together with the great development of industry and especially agrochemistry, the number of people threatened not only by traditional but also by new chemical substances is increasing.

In the fairly recent past, the study of the ***industrial toxicology*** included particularly changes due to the effects of substances known by their toxic effects in the classical sense. These were irritating vapours and gases, narcotics, substances damaging the liver, kidneys and blood, etc. The effects studied by industrial toxicology were fairly restricted as compared to a great variety of pharmacological effects. Current industrial toxicologists encounter ever more frequently phenomena at the boundary of normal and pathological conditions and at the boundary of physiological compensation reactions. In these cases, we do not speak about "poisoning", as such, preferring to use terms such as "increased exposure", "threatening by poisoning", etc.

Biological effects of a chemical substances are decisively affected by the following factors: physico-chemical characteristics, way of exposure, its frequency, duration, level and distribution in time, absorption, distribution in space and also in the organism, conversion and elimination, and possibly also ability of the organism to resist the damage. This ability depends on both hereditary and acquired characteristics of the organism.

Toxic substances cover a vast range of materials, including organic compounds, inorganic compounds, organometallic compounds, metals, trace elements in various forms, solvents, vapours, and compounds of plant or animal origin. By their very nature, pesticides constitute a large and important class of toxic substances.

The list of toxic substances is too long to be detailed. Particularly disturbing is the fact that in many cases it is not known whether a specific chemical compound belongs on this list. Thus, living things are being exposed to harmful chemicals that are not currently recognized as being toxic. On the other hand, important and useful chemicals are being regulated excessively because their harmlessness to humans has not been proven.

Toxic substances may be classified, according to their overall effects, as mutagens, carcinogens, or teratogens. They may also be classified chemically, using such categories as heavy metals, metal carbonyls and organochlorine compounds. Classification according to function, such as food additive, pesticide, or solvent, is also useful.

9.2 Routes of toxic substances through the body

The effects of toxic substances are acutely dependent upon the absorption, distribution and secretion of the toxicants [1]. Another important factor is the rate of metabolism, or biochemical transformation, of the toxic substances in the body.

The toxicity of a given substance depends on its physical and chemical characteristics, which determine the extent of its intake into the organism, its direct effects on the organism after resorption as well as secondary effects after its biotransformation, and lastly the excretion of the toxic substance or of its metabolites from the organism or, in contrast to this, its accumulation in body tissues. The toxicity may depend on the species of the organism, on the way of intake of the poisonous substance (exposure), and further it is dependent on the dose or possibly concentration and duration of the poisoning effect. In the toxic effects, there are also differences between individuals, particularly as regards sex and age, and in animals the effect also depends on the species and higher taxonomic groups. The effect of harmful and toxic substances which enter into the organism, is affected by several factors, the most important of them being the following:

(a) the substance itself, its structural and physico-chemical properties,

(b) the pattern of mutual interactions between the substance and organism,

(c) the organism exposed and its characteristics,

(d) variable subjective factors.

The influences of these factors on the toxic effect of the substance interfere with each other so that it is difficult to assess the separate contributions in the end result.

9.2.1 The absorption

By way of absorption, the substance enters the body and body liquids. Toxic substances are absorbed through the skin, lungs and gastrointestinal tract. The absorption depends on characteristics of the substance absorbed, on the means of its penetration into the organism, on the species of the organism and its characteristics, on the length of the gastrointestinal tract and rate of the digestion, on the substance concentration, on its dissociation at different pH values, and on the pH value of medium, etc. [2–4].

9.2.2 The distribution of substances in the organism

The distribution of the substance throughout the body starts after its entrance into the blood plasma. The distribution of each substance in the blood depends on its binding with blood proteins, blood cells and on the blood flow rate. It also depends on the penetration of substances through biological membranes. Substances penetrating rapidly through the membranes are distributed rapidly and in roughly equal concentrations in the whole organism.

Toxic substances are concentrated in special tissues. Certain substances achieve a maximal concentration at the site of their action (e.g. carbon monoxide exhibits a high affinity to haemoglobin); some other substances, on the other hand, are concentrated in certain organs where they are bound in different forms, thus forming a reservoir with a high content of the substance (*depot*). The site of their own toxic action may be, however, different from the accumulating organ.

Foreign substances entering into the organism are frequently bound to macromolecular substances by ionic bonds, hydrogen bonds or van der Waals forces. The amount of the substance bound is in equilibrium with the remaining free substance. Most foreign substances are bound to plasmatic proteins, e.g. to albumin, which represents a transport system (for calcium, copper, zinc, vitamin C, bilirubin, penicillin, streptomycin, tetracyclins, salicylates, barbiturates, sulphonamides, histamine). Among the various organs, particularly the liver and kidneys are able to bind foreign substances. Liver proteins firmly bind most carcinogens, azo dyes, and corticosteroids, whereas cadmium is bound, for example, to kidney proteins. The two organs also rapidly metabolize the substances absorbed [5, 6].

9.2.3 The excretion of toxic substances

The organism eliminates toxic substances or their metabolites through the kidneys, bile, lungs, saliva, stools and skin. The excretion by the kidneys is of the main importance. This mechanism is the same as that during the excretion of final products of primary and secondary metabolic pathways. Substances absorbed in the gastrointestinal tract are eliminated from the blood by the liver. These substances can be removed by the liver prior to reaching the circulation system. Substances which enter the body by inhalation are also eliminated from the lung (carbon monoxide, alcohol, volatile substances). The excretion system is not specialized and it operates on the basis of a simple diffusion [7–9].

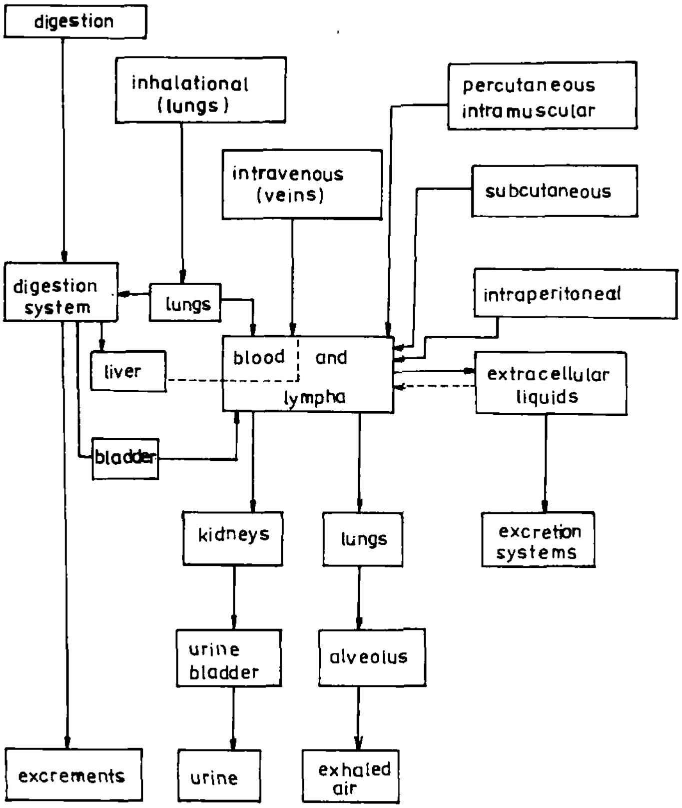

Fig. 9.1. Absorption, distribution and excretion paths of toxic substances

Absorption, distribution and excretion paths of toxic substances are shown in Fig. 9.1.

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9.3 Metabolism of toxic substances

Toxic substances entering the human organism undergo biological conversions catalysed by enzymes, are changed sponaneously under conditions present in the organism (pH, effects of the intestinal microflora, temperature), or react with certain compounds. Some substances are not converted in the organism and they are excreted in their original state. Toxic substances are more readily eliminated from the body if their water solubility is relatively high. Much of the body's metabolic action on these substances has the purpose of increasing the water solubility of lipophilic materials that would otherwise tend to accumulate in the body. The body uses mainly the following protective mechanisms for the removal of undesirable substances:

— it eliminates the substances in their unaltered forms by breathing and excretion,
— it modifies the substances to those more soluble in water and eliminates them through the kidneys,
— it modifies the substances, combines the metabolites obtained with primary metabolites with their further stepwise excretion,
— it makes the use of special protective mechanisms.

Harmful substances are metabolized most frequently in two-step reactions. In the first step, the substances are converted to more-water-soluble and thus also more reactive ones, which may be more easily excreted — *metabolic transformation*; in the second step, metabolites obtained in this way are bound to readily available primary metabolites in the body, which leads to a decrease of the toxicity. This process is called *conjugation*. In the course of the metabolic transformation of a substance, its biological characteristics are altered. In the case of a conversion of a toxic substance to a non-toxic or less toxic one, we speak of *detoxication* (e.g. CN^- to SCN^-); in the case of an increase of the toxicity we speak about an *intoxication* (e.g. the insecticide parathione is converted to highly toxically efficient paraoxone); the case of a change of a biologically inefficient substance to a biologically efficient one by action of enzymes is referred to the *activation* (this principle is used for administering certain pharmaceuticals in the form of "precursors of pharmaceuticals", which are changed in the organism to active substances, as for example proinsulin obtained from microorganisms, which is converted to active insulin in the organism).

Certain toxic substances are very similar to normal endogenous metabolites, so that the organism may incorporate them erroneously into its tissues. The process, where a biogenic substance is replaced by an abiogenic one (foreign to the organism) is named *lethal synthesis* (e.g. fluoroacetate can react with pyruvate instead of acetate, and fluorocitrate produced in this way blocks the enzyme aconitase in the Krebs cycle, thus causing a blockade of the energy production; ^{90}Sr can replace Ca in bones, which leads to permanent irradiation of the bone marrow with a disturbance of the haemopoiesis).

Most metabolic transformations of foreign substances in the body occur on the basis of catalysis by enzymes from the endoplasmatic reticulum, particularly liver cells, and only a small portion of these reactions occur in cells of the remaining tissues. Enzymes participating in the metabolic transformation of foreign substances are not commonly produced in the body and thus, the elimination and transformation of foreign substances, particularly those of a synthetic origin, is a slow process [1–4].

9.3.1 The mechanism of conversions affecting the fate of substances in the organism

The reactions converting foreign substances are as follows:
— oxidation (microsomal and non-microsomal),
— reduction,
— hydrolysis,
— conjugation.
Of these, oxidation and conjugation are the most frequently occurring reactions.

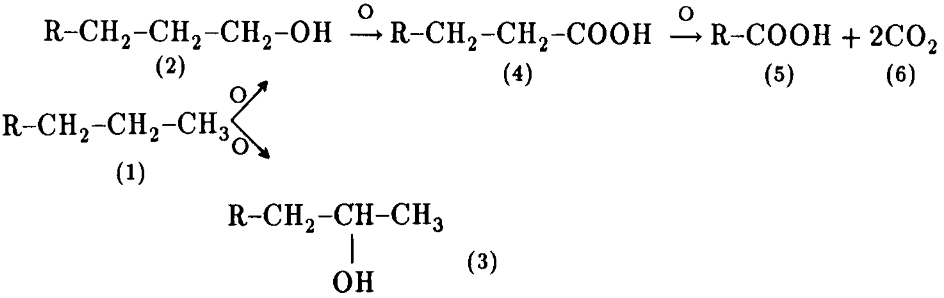
9.3.1.1 Oxidation

Oxidation is an extremely common reaction in all living systems. For the organism, it serves as a source of the energy necessary for synthetic processes and this type of reactions is simultaneously employed for removing toxic substances. According to the site of enzymes catalysing relevant reactions, we can consider two types of oxidation — *microsomal* and *non-microsomal*. The oxidation occurs particularly in liver cells and only a small proportion occurs in the skin or in other tissue.

Microsomal oxidation is catalysed by enzymes bound to microsomes of the endoplasmic reticulum. The enzymes may be located via fractionation of the liver cells. Enzymes catalysing this type of reactions are found in the microsomal fraction. The microsomal enzymes occupy an important position in an organism's biochemical system, since they catalyse not only the oxidation of fatty acids, the hydroxylation of steroids and the oxidation of terpenes and alkaloids, but also the oxidation of different pharmaceuticals, pesticides and carcinogenic polycyclic hydrocarbons. The ability of these chemical substances to intensify the synthesis of enzymes in liver microsomes is a general phenomenon which occurs in animals as well as in man [5].

For their activity, the enzymes of the microsomal fraction require the presence of $NaDPH_2$ (nicotine amide dinucleotide phosphate) and oxygen [6]. Microsomal oxidation includes the following processes:

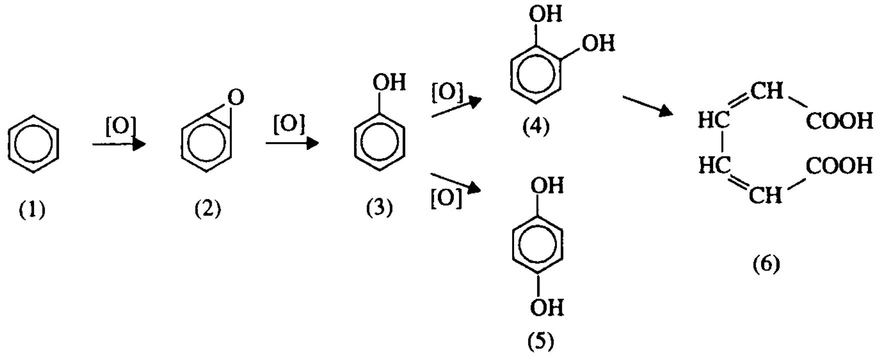
(a) *The oxidation of aliphatic and aromatic hydrocarbons.* By the oxidation of aliphatic and aromatic hydrocarbons (1), primary (2) and secondary alcohols (3), aldehydes, acids (4) or ketones are formed stepwise. A further oxidation of acids (4) results in splitting off two carbon atoms to yield a lower acid (5) and carbon dioxide (6)



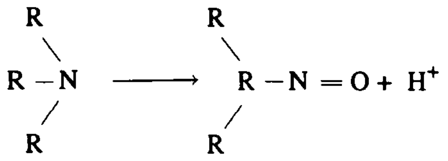
$$\underset{(2)}{R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH} \xrightarrow{O} \underset{(4)}{R\text{-}CH_2\text{-}CH_2\text{-}COOH} \xrightarrow{O} \underset{(5)}{R\text{-}COOH} + \underset{(6)}{2CO_2}$$

$$\underset{(1)}{R\text{-}CH_2\text{-}CH_2\text{-}CH_3} \xrightarrow{O} \underset{(3)}{R\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_3}$$

Aromatic substances are oxidized to hydroxyderivatives and dihydroxyderivatives. Benzene (1) is converted through an instable epoxidic form (2) to phenol (3) which is further oxidized to form pyrocatechol (4) or hydroquinone (5). The muconic acid (6) is the terminal oxidation degree, being formed by opening the benzene ring. In this way, not only monocyclic but also polycyclic hydrocarbons are oxidized, such as quinoline, indol and coumarins. Some substances are even oxidized to water and carbon dioxide

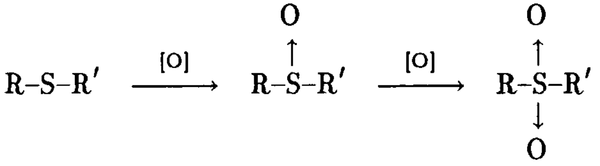


(b) *Oxidation of nitrogen and sulphur.* Nitrogen of primary, secondary and tertiary aliphatic as well aromatic amines yields *N*-oxides after oxidation



$$\underset{R}{\overset{R}{R-N}} \longrightarrow \underset{R}{\overset{R}{R-N}}=O + H^+$$

The oxidation of sulphur in aliphatic and aromatic sulphides (1) results in corresponding sulphoxides (2) and sulphones (3)



$$R\text{-}S\text{-}R' \xrightarrow{[O]} R\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}R' \xrightarrow{[O]} R\text{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{-}R'$$

(1) (2) (3)

(c) *The dealkylation* of *O*-, *S*-, *N*-. This reaction occurs during the metabolic transformation in the body for the separation of the *O*-, *S*-, *N*-alkyl group, forming corresponding phenols, thiols or amines and simultaneously aldehyde or possibly acetyl.

The non-microsomal oxidation is catalysed by enzymes that are free in the cellular plasma or by relatively non-specific enzymes present in the mitochondrial fraction of the homogenized tissue of liver cells. Two of these enzymes which are particularly important are *monoaminooxidase*, catalysing the metabolism of primary amines and controlling the level of biogenic amines, and *diaminooxidase*, catalysing selectively the oxidation of one out of two amino groups of diamines. Aliphatic alcohols are oxidized by the *alcohol dehydrogenase* to aldehydes. This reaction is reversible and the same enzyme participates in the reduction of aldehydes and ketones to alcohols [7].

$$CH_3\text{-}CH_2\text{-}OH + NAD \underset{\text{dehydrogenase}}{\overset{\text{alcohol}}{\rightleftarrows}} CH_3CHO + NADH_2$$

9.3.1.2 Hydrolysis

Hydrolysis occurs during the metabolism of esters and amides. The reactions are catalysed by *esterases* and *amidases* occurring in the liver and in the blood plasma. These enzymes split esters to acids and alcohol, and amides to the corresponding acids and ammonia [8]

$$\text{R–COOR}' + H_2O \xrightarrow{\text{esterase}} \text{R–COOH} + \text{R}'\text{–OH}$$

$$\text{R–CONH}_2 + H_2O \xrightarrow{\text{amidase}} \text{R–COOH} + NH_3$$

9.3.1.3 Reduction

Reduction occurs less frequently in the organism than oxidation. Aromatic nitroderivatives (1) are reduced through hydroxylamine (2) to amines (3) by action of *nitroreductases* occurring in the microsomal and soluble fraction of the liver cells

$$\underset{(1)}{\text{Ar–NO}_2} \rightarrow \underset{(2)}{\text{Ar–NH–OH}} \rightarrow \underset{(3)}{\text{Ar–NH}_2}$$

Alcohols can also be reduced, disulphides are reduced to mercaptans, hydroxamic acids to amides, sulphones to sulphoxides, and chloral to trichloroethanol [9].

9.3.1.4 Conjugation

Conjugation is a reaction leading most frequently to the detoxication of foreign substances. As a result of evolutionary history, this type of the detoxication is most fully developed in higher organisms. The conjugated components are bound to coenzymes in the organism and from them they are tranferred enzymatically to foreign substances.

It is a matter of general knowledge that metabolic transformations exhibit no phylogenic dependence, however, certain reactions are typical for certain species. The conjugation reactions exhibit an obvious phylogenic dependence, which can also be observed in particular development stages of man.

A typical reaction for the metabolism of foreign substances in the body is their binding to readily available endogenous substrates — acids. In this reaction, foreign substances are bound, with the help of original or transformed functional groups, to acids (acetic, glucuronic, sulphuric, amino acids). Molecules are thus formed, which are more polar, less soluble in fats and more easily excreted from the body than the original substances.

The reaction with *glucuronic acid* is the most common type of conjugation reaction. The products formed are called *glucuronides.* Depending on the type of the substance reacting with glucuronic acid, we can consider several types of glucuronides. In the case of the formation of glucuronides from primary, secondary and tertiary alcohols and phenols, i.e. substances having hydroxyl groups, *ether-type glucuronides* are formed. In the conjugation of substances having a carboxylic group with glucuronic acid, *ester-type glucuronides* are obtained. The esteric bond serves for binding carboxylic groups on aromatic rings, whereas on the aliphatic chain this bond occurs only exceptionally. Further types of glucuronides which may be formed are as follows: *aminoesters* (from aromatic amines), *N-glucuronides* (from substances with sulphonamide groups), *S-glucuronides* (from thiophene, 2-mercaptobenzothiazole).

The formation of glucuronides is one of the most important microsomal conjugations, occurring particularly in the liver and, to a lesser extent, in the kidneys, gastrointestinal tract and skin. Glucuronides are not excreted directly from the organism, since most animal tissues contain the *enzyme β-glucuronidase*, hydrolysing conjugates with the simultaneous formation of *aglycone* and *glucuronic acid.* It is possible that the enzyme facilitates the release of carcinogens bound in conjugates (polycyclic hydrocarbons), which can partially explain the development of cancer in intestines.

In contrast to these conjugation reactions, the formation of *sulphate esters* is probably an extramicrosomal process, catalysed by relevant enzymes in the presence of the coenzyme 3-phosphoadenosine-5-phosphosulphate. In this case, *sulphuric acid* is conjugated with primary aliphatic alcohols to produce *alkyl sulphates*, which are normal components of urine.

A further type of conjugation reactions concerns the reactions serving to remove aromatic amines and sulphonamides as well as aromatic amino acids bound to *acetic acids.* The products obtained are named *acetyl derivatives* and they are catalysed by *acetyl transferases.* The process is referred to as *acetylation* and the amino group of a given chemical substance always reacts with acetic acid.

The conjugation of foreign substances having carboxylic groups with *amino acids* occurs very frequently. This type of reaction is considered as *peptidic conjugation* and in this process, aromatic carboxylic acid always reacts via its carboxylic group with the amino acid, with the participation of *acetyl coenzyme A* and *ATP.* Besides the carboxylic group bound directly to an aromatic ring (benzene, naphthalene, thiophene, furane or pyrimidine), carboxyl separated from the aromatic ring by the group $-CH_2-$ or $-CH=CH-$ can also take part in the reaction. The bond formed during this reaction is considered as the *peptidic bond -CO-NH-* and it serves as a basis for the formation of proteins by connecting amino acids into long peptidic chains.

A variety of detoxication systems and reactions are invariably used in the removal of toxic substances from the organism [10].

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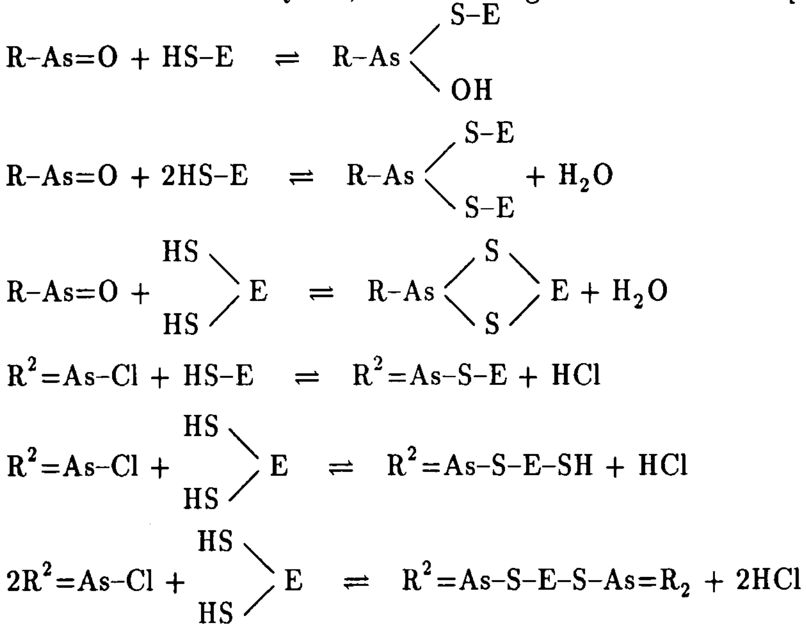
9.4 Disturbance of enzyme action

The disturbance of the activity of enzymes — biocatalysts, which affect the course of metabolic processes in all living cells — can lead to serious or even fatal consequences for the organisms involved.

The catalytic effects of enzymes (which are in general characterized as globular proteins) are due to their characteristic three-dimensional orientation of chemical groups at sites named active centres, which serve for binding, activating and converting a certain substrate. In many enzymes, the active centre is, however, insufficient for the specific binding of the substrate and thus, a coenzyme has to participate in the process (organic molecules of non-protein character) or possibly some inorganic cation or anion serving as an activator.

The activity of enzymes can be either reduced or even completely stopped by the action of inhibitors, also referred to as enzymatic poisons. These are substances, which can be bound to active centres of enzymes, thus preventing any catalytic activity. They can also be bound at a distance from the active centres, and then the enzymes are inactivated indirectly due to changes induced in their tertiary structure; they can also react with a given important component of coenzymes, with activators or directly with the substrate, thus hindering the enzymatic conversion of the substrate. In the case where the inhibitor can be removed, with recovery of the enzyme activity, we refer to reversible inhibition. Irreversible inhibition can also occur and in this case the enzyme activity cannot be recovered by any intervention.

Important functional groups, which are frequently present in active centres of enzymes are $-SH$ and $-SCH_3$ groups of amino acids cysteine and methionine. Of the various components which can react with these groups, we can mention compounds of arsenic or heavy metal ions (Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, etc.). Below, we present reactions, which may occur between different arsenicals and enzymes, thus resulting in their inhibition [1]:



$$(1)\quad \mathrm{R{-}As{=}O} + \mathrm{HS{-}E} \rightleftharpoons \mathrm{R{-}As}\begin{array}{l}\diagup\,\mathrm{S{-}E}\\ \diagdown\,\mathrm{OH}\end{array}$$

$$(2)\quad \mathrm{R{-}As{=}O} + 2\mathrm{HS{-}E} \rightleftharpoons \mathrm{R{-}As}\begin{array}{l}\diagup\,\mathrm{S{-}E}\\ \diagdown\,\mathrm{S{-}E}\end{array} + \mathrm{H_2O}$$

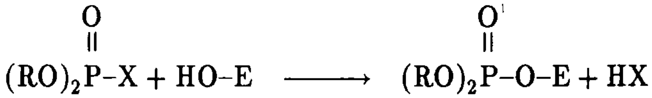
$$(3)\quad \mathrm{R{-}As{=}O} + \begin{array}{r}\mathrm{HS}\diagdown\\ \mathrm{HS}\diagup\end{array}\mathrm{E} \rightleftharpoons \mathrm{R{-}As}\begin{array}{c}\diagup\,\mathrm{S}\,\diagdown\\ \diagdown\,\mathrm{S}\,\diagup\end{array}\mathrm{E} + \mathrm{H_2O}$$

$$(4)\quad \mathrm{R^2{=}As{-}Cl} + \mathrm{HS{-}E} \rightleftharpoons \mathrm{R^2{=}As{-}S{-}E} + \mathrm{HCl}$$

$$(5)\quad \mathrm{R^2{=}As{-}Cl} + \begin{array}{r}\mathrm{HS}\diagdown\\ \mathrm{HS}\diagup\end{array}\mathrm{E} \rightleftharpoons \mathrm{R^2{=}As{-}S{-}E{-}SH} + \mathrm{HCl}$$

$$(6)\quad 2\mathrm{R^2{=}As{-}Cl} + \begin{array}{r}\mathrm{HS}\diagdown\\ \mathrm{HS}\diagup\end{array}\mathrm{E} \rightleftharpoons \mathrm{R^2{=}As{-}S{-}E{-}S{-}As{=}R_2} + 2\mathrm{HCl}$$

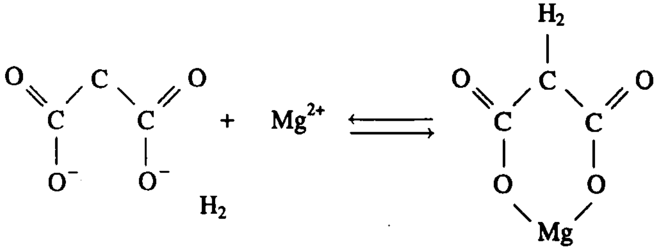
A further functional group which can have a basic role in the enzyme active centre is the OH group. A well known example of enzyme inhibition by binding the inhibitor with the OH group is the irreversible inhibition of acetylcholine esterase (enzyme splitting acetylcholine) by organophosphate esters based on the phosphorylation of the esteric site, i.e. the serine hydroxyl group. The reaction corresponds to the acetylation of the site in the normal process for the enzymatic hydrolysis of the true substrate acetylcholine [2]:



$$(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{–}X + HO\text{–}E \longrightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{–}O\text{–}E + HX$$

However, in sharp contrast to the acetylated acetylcholine esterase, which is unstable and hydrolysed very rapidly (the half-life is about 0.1 ms), the phosphorylated enzyme is much more stable by a factor of at least 10^7.

Many enzymes are dependent on dissociable metal ions for their activity, and the operation of most of the important metabolic systems thus requires the presence of these cofactors. For example, the list of enzymes requiring Mg^{2+} is a long one and includes the oxidases and decarboxylases for the keto acids, most of the enzymes involved in phosphate metabolism, some dehydrogenases, some peptidases, phosphoglucomutase and enolase. These enzymes may be inhibited with inhibitors forming stable complexes with Mg^{2+} ions. For example, malonate and other dicarboxylic compounds are able to chelate effectively with Mg^{2+} and other metal ions, and their inhibition may result from the reduction of metal ion concentration in the medium or the removal of the metal ions from the enzyme [3]:



Enzymes having metals as their components can also be inhibited by a substitution of one of these metal ions by another ion with the same charge and a similar size. For example, the toxic effect of cadmium is due to a substitution for zinc, which is a common component in metalloenzymes. The Zn^{2+} and Cd^{2+} ions are chemically similar, however, the cadmium-containing enzyme does not function properly. The Cd^{2+} ions can result, for instance, in the inhibition of amylase, adenosine triphosphatase, alcohol dehydrogenase, glutamic-oxalacetic transaminase, carbonic anhydrase and peptidase activity in carboxypeptidase [4].

Particular groups of chemically similar inhibitors can inhibit the enzymes via several mechanisms. For example, quinones (some of them are used as fungicides — chloranil, dichlon) can inhibit enzymes by the following mechanisms: (1) oxidation of enzyme groups, (2) reaction with enzyme -SH groups, (3) complexing with metal ions, (4) reaction with substrates or cofactors, (5) production of hydrogen peroxide (the oxidation of hydroquinones by O_2 often forms H_2O_2, which could be the inhibitory agent), (6) non-specific binding through the aromatic rings (more important for the polycyclic quinones), (7) competition with quinonoid or polyphenolic substrates [1].

These examples are presented only to emphasize the wide range of possibilities of inhibition of enzymes by toxic substances.

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9.5 Damage to the genetic material — DNA

Toxic substances damaging nucleic acids exert an even more serious impact on the offspring of organisms involved than enzymatic poisons.

Deoxyribonucleic acid (DNA), and in the case of a virus ribonucleic acid (RNA), represent the genetic material comprising the complete information necessary for the existence and reproduction of living matter. DNA, which is the most important component of chromosomes present in nuclei of cells, is a critical target site for many toxic substances with a biogenetic action and it can also be damaged by action of certain physical agents (different types of radiation).

We will discuss in more detail the toxic effects of substances with a biogenetic action, which form the carcinogens, mutagens and teratogens; some of these substances fall simultaneously into two or even into all the three of the groups. All such substances alter the genetic code of cells, causing mutations. Carcinogens can induce changes in any type of cell and the effect is manifested mainly on the organism involved with limited transfer to the offspring. Mutagens affect germ cells and the effect is manifested in further generations (mutants). Teratogens attack somatic cells of the embryo in the organogenesis period [1].

For a better understanding of the detrimental effects of the above-mentioned substances, we will first characterize deoxyribonucleic acid itself. The DNA molecule is formed by two polynucleotide chains, which are coiled in an antiparallel arrangement to form a double helix (Fig. 9.2). Each monomer of the chain of DNA, the nucleotide, consists of a purine or pyrimidine base (adenine, guanine, cytosine or thymine), deoxyribose and moiety of phosphoric acid, forming the phosphodiesteric bond with the neighbouring monomer (Fig. 9.3). Two polynucleotide chains are mutually connected via hydrogen bonds between purine and pyrimidine bases, their pairing being governed by their spatial structure and from this standpoint, only pairing of adenine with thymine (A–T) and guanine with cytosine (G–C) is possible. The order of these paired bases and thus also of paired nucleotides in the DNA molecule provides the genetic information [2].

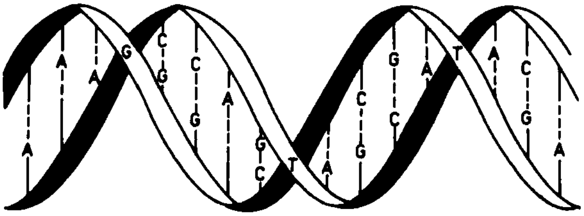

Fig. 9.2. Schematic diagram of a DNA double helix with complementary bases connected via hydrogen bonds. A — adenine, T — thymine, G — guanine, C — cytosine

Mutations caused by substances with biogenetic effects may be divided into gene (point) mutations characterized by small changes of DNA (only one pair or at most several nucleotides are hit) and chromosomal mutations, visible under a conventional microscope (e.g. chromosome breaks, deletions, translocations, etc.). Depending on the mechanism of the effects of genotoxic substances, the mutation can result from (1) the substitution of analogues of bases, (2) the chemical conversion of DNA and of its nucleotides, (3) binding of chemical substances to DNA and (4) DNA depolymerization [3].

An example of mutation caused by the substitution of analogues of bases is the substitution of thymine by 5-bromouracil, which is one of the well-known substances leading to point mutations by altering the nucleotide. 5-Bromouracil, in its common keto configuration is paired with adenine. 5-Bromouracil paired in this way may be converted by a tautomeric transition to a rarely occurring enol configuration and in a further replication cycle (where the genetic information is doubled during the cell division), it may

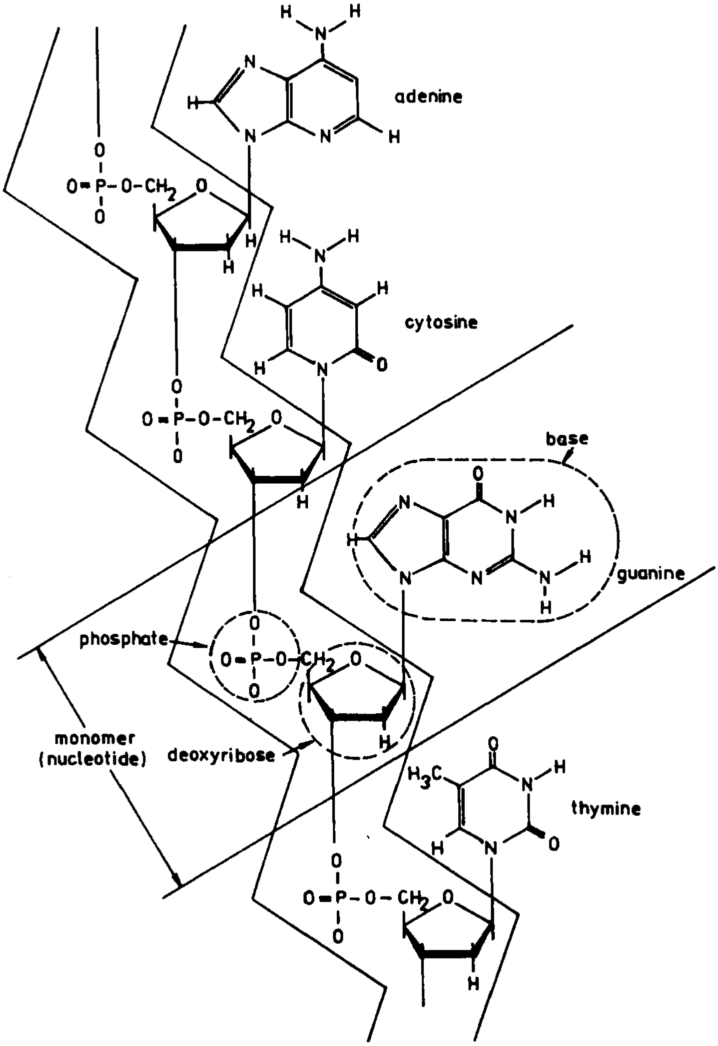

Fig. 9.3. A part of one polynucleotide helix from the DNA molecule. The monomer indicated consists of the purine base guainine, deoxyribose and a moiety of phosphoric acid forming a phosphodiesteric bond with the neighbouring monomer

be paired with guanine (Fig. 9.4) which is then paired with cytosine in a subsequent replication. Thus, the original pair A–T is replaced during three replication cycles by the pair G–C, which represents a modification of the genetic information. It should be noted that the organisms containing 5-bromouracil-substituted DNA are much more sensitive to chemical and physical damage than organisms containing normal DNA.

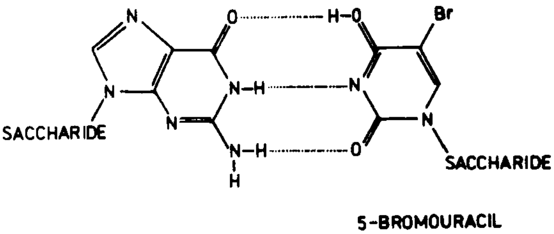

Fig. 9.4. Pairing of the enol form of 5-bromouracil with guanine

Point mutations can also be caused by alkylation substances, which induce chemical conversions of original nucleotides. DNA bases are the critical target site again, since their original pairing may be disturbed by their alkylation. For example, alkylated guanine is paired with thymine instead of cytosine, which results in a change of the genetic information in further replication cycles. Bis(2-chloroethyl)sulphide, diethyl sulphate, diazomethane, ethylmethane sulphonate and ethyleneimines, are examples of known alkylation agents [3].

On the basis of binding a chemical substances to DNA it is possible to explain the carcinogenic effect of benzo[*a*]pyrene, which, after its metabolic activation to diolepoxide, is bound by a covalent bond to a free primary guanine amino group (see p. 143). To a lesser extent, it can also react with a ketone-group oxygen or with a particular nitrogen atom in the guanine heterocyclic ring. It was shown that this interaction changes the configuration of the DNA molecule in the vicinity of the target guanine, so that it is "locally denatured" at these sites and it loses its double helix character. The whole cell is transformed to a neoplastic cell as a result of these changes at a molecular level [4].

Some substances induce a depurinization and depyrimidinization of DNA chains, thus making the DNA deoxyribosephosphate skeleton labile with a subsequent depolymerization of the molecule. The partial DNA depolymerization can also result from an inhibition of the repair of single-chain breaks in DNA, which results in chromosomal breaks. This mechanism of the action is assumed to be the case with caffeine, whose mutagenic effect was observed in mammal cells [3].

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9.6 The ecotoxicology of water pollutants

9.6.1 Heavy metals

Heavy metals are among the most toxic contaminants of natural waters. This toxicity is very serious mainly with respect to their long time of residence in the solution, since in surface waters, there are no suitable conditions for their conversion to insoluble substances. The danger of the contamination of surface waters with toxic metals is increased when wastewaters contain complexing substances, which bind metals strongly, so that they cannot be removed during the wastewater treatment. Metals bound in complex substances are less toxic as compared to their effects in the form of free ions, however, by the action of changes of medium and biological processes the complexes are decomposed and the toxic properties of the metals may then be fully manifested. The effect of heavy metal ions is moderated only by their adsorption on sedimenting substances and by their great dilution [1].

Heavy metals in waters inhibit the growth of organisms and the activity of enzymes, which is manifested by detrimental effects on self-cleaning processes in flows and reservoirs and on aerobic as well as anaerobic biological processes in wastewater treatment plants. The measure of the toxic effects of heavy metals on aquatic microorganisms can be followed, for example, on the basis of their effects on the biochemical oxygen demand values (BOD). From the study of the effects of certain heavy metals on the BOD_5 value, at concentrations of the metal of 10 mg l^{-1}, it was possible to list the metallic cations in the following order of decreasing toxicity: $Hg^{2+} > Ag^{+} > Cu^{2+} > Cd^{2+} > Pb^{2+} > Mo^{6+} > Fe^{2+} > V^{5+} > Ba^{2+}$. Hg^{2+} decreased the original value $BOD_5 = 120.8$ mg l^{-1} to 0.0 mg l^{-1} and Ba^{2+} only to 93.7 mg l^{-1} [2].

The effect of heavy metals can also be well observed on fish. Salts of lead, zinc, copper, mercury, silver, nickel and cadmium disturb the mucous membrane on the gills, thus involving the breathing process. The fish involved start to move the gills rapidly, and after that the motion becomes irregular, the rate gradually decreases and the fish die [3]. Toxic metals and their compounds can induce disturbances of the gastrointestinal tract, central nervous system, haemopoietic system, etc., the toxicity of the heavy metals depending on many factors such as the species, age and sex of the organism exposed, temperature, pH and water composition, valency of the element, chemical form, presence of other metals and compounds (synergistic and antagonistic effects).

Heavy metal ions are concentrated in nutritional chains with a possibility of a fatal involvement only of a higher member of the chain by the accumulation of the toxic metal in organisms, such as occurs even in man (the diseases itai-itai, minamata).

Below, we consider the more important heavy metals, whose presence in water results in an increased danger for living organisms, including man.

9.6.1.1 Lead

Lead is a dangerous water contaminant. In the marine environment it is present in higher concentrations in coastal waters as compared to deep waters. Most lead is accumulated in sediments and a portion of this element is removed from water by organisms, with accumulation in their bodies. Concentrations of 20 $\mu g\ kg^{-1}$ were determined in marine fish, but even as high a concentration as 1 $mg\ kg^{-1}$ was also observed (depending on the fish species, localities, etc.) [4]. The lead content in fresh-water fish is in general higher by several orders of magnitude than that in marine fish; concentrations of 0.2 to 2.5 $mg\ kg^{-1}$ have been determined [5].

The values of toxicity threshold for lead in the form of lead acetate were established for the bacterium *Pseudomonas putida* as 1.8 $mg\ l^{-1}$ Pb, for green algae *Scendesmus quadricauda* 3.7 $mg\ l^{-1}$ and for the protozoan *Entosiphon sulcatum* 0.02 $mg\ l^{-1}$ [6]. The chronic lead toxicity values for fish generally range from 5.6 $\mu g\ l^{-1}$ for rainbow trout (*Salmo gairdneri*) to 92 $\mu g\ l^{-1}$ for bluegill sunfish (*Lepomis macrochirus*). It has been observed that rainbow trout exposed to 13 $\mu g\ l^{-1}$ Pb for at least one week had significant increases in red blood cells (RBC), decreases in RBC volume and RBC iron content, and decreases in RBC δ-aminolevulinic acid dehydratase activity. Decreased haemoglobin content and inhibition of glutamic-oxalacetic transaminase (GOT) activity in brook trout (*Salvelinus fontinalis*) have been reported after 56-day exposure to 58 $\mu g\ l^{-1}$ Pb. The ninety-six-hour LC_{50} value for rainbow trout was 1.170 $\mu g\ l^{-1}$ Pb (hardness = 28 $mg\ l^{-1}$ as $CaCO_3$) and for bluegill sunfish 23.8 $\mu g\ l^{-1}$ Pb (hardness = 20 $mg\ l^{-1}$) [7].

Man can also be threatened by lead-contaminated water, seafoods or fresh-water fish. After absorption in the organism, lead is transported by the blood to the soft tissues, the highest concentrations being found in the liver and kidneys. Some, however, is transported to other organs such as the brain, lung, spleen and heart. Deposition of lead takes place in bone (where more than 90 per cent of the total body lead is found) as relatively insoluble lead phosphates. During the alteration of the acid-base metabolism of the body, lead may be mobilized from the bone and pass into soft tissues. Thus, tissue exposure to lead may be twofold; firstly in the acute phase of lead absorption, and secondly after mobilization from the bone [8].

Biochemical effects of lead result in changes of the activity of enzymes, where lead may be bound to both functional and structural proteins or it can displace essential metals from biological molecules and destroy the structural function relationships of nucleic acids. The poisoning with lead can involve the haemopoietic system, central nervous system (encephalopathy), kidneys, gastrointestinal tract, cardiovascular system, etc.

According to the WHO, the maximum permissible lead concentration in drinking water is 0.1 mg l^{-1} [9].

9.6.1.2 Mercury

The occurrence of a number of mass poisonings with alkyl mercurials (Minamata and Niigata in Japan, Iraq, Pakistan, Guatemala) has led to increased attention to the study of the contamination of the environment with mercury and of its conversion in, and toxic effects on living organisms. The hydrosphere is polluted with mercury by fallout and washing out from the atmosphere, by industrial releases in wastewaters, by rinsing pesticides containing mercury used in the agriculture as well as by dissolving mercury-bearing minerals. After snow or rain precipitations as much as 80% of mercury is removed from the atmosphere [4].

The formation of alkylmercurials from elementary mercury and from its inorganic substances in waters of oceans and lakes is the basic element in the whole chain of mercury conversion in the nature. In the upper sedimentation layers of the sea or lake bottom, methylation of elementary mercury or of mercuric ions occurs with the formation of methyl mercury. The methyl mercury is retained by small aquatic organisms which either serve as feed for fish or die, and during their decomposition dimethyl mercury vapours are released into the atmosphere. In the atmosphere, in acid medium (acid rain) dimethyl mercury can be demethylated to form methyl mercury, which can re-enter the nutritional chain in water.

The alkylmercurials are accumulated in the fish meat. Mercury exhibits one of the highest accumulation coefficients and in the meat of fish specimens living in waters polluted with mercury the concentrations of methyl mercury may even exceed 10 mg kg^{-1}. In Minamata and Niigata the contaminated fish contained methyl mercury in concentrations of 1 to

20 mg kg^{-1} and people eating predominantly fish meat reached a daily intake as high as 5 mg of methyl mercury [10].

A very sensitive indicator of the presence of mercury in water is the rainbow trout (*Salmo gairdneri*) which was observed to take up mercury strongly at a mercuric chloride concentration of 0.2 $\mu g\ l^{-1}$ (hardness = 112.4 mg l^{-1}). The lowest chronic toxicity value reported was 0.5 $\mu g\ l^{-1}$ methyl mercury for brook trout (*Salvelinus fontinalis*). The bioconcentration of mercury in brook trout has been shown to occur at water concentrations down to 0.03 $\mu g\ l^{-1}$ and the ninety-six-hour LC_{50} value for brook trout was 65 $\mu g\ l^{-1}$ methyl mercuric chloride [7]. The values of toxicity thresholds for mercury in the form of mercuric chloride were established for the bacterium *Pseudomonas putida* (10 $\mu g\ l^{-1}$ Hg), for green algae *Scendesmus quadricauda* (70 $\mu g\ l^{-1}$) and for the protozoan *Entosiphon sulcatum* (18 $\mu g\ l^{-1}$) [6].

Methyl mercury, which caused the above-mentioned mass poisoning events, is one of the most toxic forms of mercury. After its peroral administration almost 100% is absorbed in the gastrointestinal tract. In the blood, more than 90% of methyl mercury is bound to erythrocytes. The distribution of methyl mercury from the blood into particular organs is slow. It has a remarkable affinity for the brain tissue, the concentration of methyl mercury in the brain being higher by a factor of 3 to 6 than that in the blood, depending on the dose administered. Methyl mercury is eliminated from the organism mainly in faeces (more than 90%) and urine. In man, receiving a non-toxic dose of methyl mercury, the biological half-life is about 70 days.

Chronic intoxications can be considered in the case of a daily intake of about 1 mg of methyl mercury for one year. In the case of the poisoning in Minamata and Niigata in Japan, where the daily intake was as high as 5 mg, acute manifestations occurred in one or two months. During the Minamata outbreak, nerves and muscles were damaged, the field of view was narrowed, and disturbances of hearing occurred, etc. Pathological examinations suggest a damage of the brain cortex with a degeneration of neurons.

Biochemical effects of mercury and its compounds are mainly due to the reactions of Hg^{2+} ions with SH-groups of biomolecules with a subsequent change of the permeability of cell membranes and damage of intracellular enzymes [10].

The maximum permissible mercury concentration in drinking water, according to WHO, is 0.001 mg l^{-1} [9].

9.6.1.3 Arsenic

Arsenic is present essentially in all ground- and sea waters in low concentrations, however, regions with higher arsenic concentrations in waters are also known. A region of thermal springs, Vaiotapo in New Zealand, is known from the literature, where an endemic poisoning due to the milk from cows drinking water from these springs was described. In Taiwan, in regions where the inhabitants used drinking water from artesian wells with high arsenic content, nearly 20% of 37,000 villagers showed evidence of arsenic poisoning. The ground- as well as surface waters are, however, more frequently polluted with arsenic in the vicinity of mines, dumps, metallurgical works, etc. Thus, for example, at Reichenstein in Silesia, where the groundwater was polluted during mining ores of non-ferrous metals, the so-called "Reichenstein disease" (ulcers in the mouth, digestive complaints, neuritis and skin changes are the common symptoms) occurred. In sea water, higher arsenic concentrations were observed in the vicinity of outlets of canalization systems from industrial areas [10, 11].

Arsenic shows a remarkable tendency to become accumulated in aquatic organisms. For example crustaceans caught along the southeast coast of the USA contained 42 $\mu g\ g^{-1}$ of arsenic and in the liver of the perch caught in continental waters of the USA more than 40 $\mu g\ g^{-1}$ were found [10]. In spite of the accumulation ability, arsenic is not frequently dangerous to the nutritional chains, since in muscle tissues of organisms it is bound to organic substances, which are characterized by a low toxicity. The organic-bound arsenic, for example in crab meat eaten by the man is excreted in unaltered form. Harmful effects of arsenic on fish are manifested at concentrations in water of 1 to 4 $mg\ l^{-1}$ [9].

Elementary arsenic is not toxic. Its inorganic compounds, arsenic trioxide, arsenites and arsenates are, however, strongly toxic [7]. For mammals as well as for aquatic organisms, As(III) compounds are more toxic than As(V) compounds. Inorganic compounds of arsenic are absorbed in the gastrointestinal tract and in breathing organs and to a lesser extent, they are absorbed through the skin. They are then distributed by the blood into the whole organism. The pattern of distribution in the organism depends on the form of arsenic ingested. Arsenites in human body have a particular affinity for the hair, nails and skin. Arsenic has been found to enter the hair roots within 30 minutes of ingestion [11]. From the human body, inorganic arsenic is excreted mainly in the urine, with a biological half-life of about 10 hours. The major portion is, however, excreted after a biotransformation in the form of mono- and dimethylarsenic acids, with a half-life of about 30 hours [10].

Biochemical effects of arsenic are caused by blocking the SH-groups of proteins, which is most serious in enzymes containing sulphur (mainly hydrolases) and also by a chemical similarity between arsenic and phosphorus. Arsenic disturbs the metabolism of glycides and lipids, with considerable damage to the oxidative phosphorylation, etc.

Acute poisoning by arsenic compounds can occur with a gastrointestinal syndrome or, in the case of enormous doses, with a paralytic syndrome and strong cephalalgia, rapid unconsciousness and interruption of the blood circulation and breathing. During chronic poisoning, particularly changes on the skin and mucous membranes, neurological changes (polyneuritis and paralysis) and haematological changes (anaemia) were described. Inorganic arsenic compounds are also characterized by carcinogenic effects with a demonstrated occurrence of skin and lung cancer in man [10].

The maximum permissible arsenic concentration in drinking water, according to WHO, is 0.05 mg l^{-1} [9].

9.6.1.4 Copper

Copper is an essential trace element which participates in many oxidation-reduction enzyme systems, however, its presence in water exerts toxic effects on aquatic organisms already at very low concentrations. Copper avoidance concentrations for salmonids range from 0.1 to 70 μg l^{-1}. Reduced critical swimming speeds in rainbow trout (*Salmo gairdneri*) were found at 10 μg l^{-1} Cu depending on hardness, pH, and time of exposure. Coho salmon (*Oncorhynchus kisutch*) had temporary increases in cortisol levels after a 2-hour exposure to 15 μg l^{-1} Cu. Concentrations of 38 to 39 and 67 to 69 μg l^{-1} Cu caused significant increases in red blood cell count, haemoglobin, haematocrit, plasma glutamic oxalacetic transaminase (GOT), and total protein in brook trout (*Salvelinus fontinalis*) after 6 and 21 days of exposure, respectively. The ninety-six-hour LC_{50} value for rainbow trout was 17 μg l^{-1} Cu (hardness = 24 mg l^{-1}), for northern squawfish (*Ptychocheilus oregonensis*) it was 18 μg l^{-1} Cu (hardness = 20–30 mg l^{-1}) and for coho salmon it was 19 μg l^{-1} Cu (hardness = 24 mg l^{-1}). The value of the toxicity threshold for the bacterium *Pseudomonas putida* was established as 0.03 mg l^{-1} Cu, that for green algae *Scendesmus quadricauda* 1.1 mg l^{-1} Cu and for the protozoan *Entosiphon sulcatum*, 0.11 mg l^{-1} Cu. A concentration of 22 μg l^{-1} Cu (hardness = 45.3 mg l^{-1}) caused reproductive impairment in *Daphnia magna* after a 3-week exposure [7, 6].

Toxic effects of copper in man are manifested only at higher concentrations. Copper is only moderately absorbed and its major portion is excreted with faeces and partially with the urine. An amount of 1 g of copper sulphate induces vomiting in adults. At a concentration in the blood of 8 mg l^{-1}, icterus and renal damage were observed, whereas at a concentration of 3 mg l^{-1}, only gastrointestinal problems were encountered. In children exposed to copper in foodstuffs and drinking water with high copper contents, diarrhoea occurred with a considerable decrease of body weight, and liver tests also demonstrated pathological changes. The normal healthy condition was rapidly recovered after the exposure had ended [10].

Water with a higher content of copper is characterized by a "bitter", "metallic" taste. According to WHO, the highest permissible copper concentration in drinking water is 0.05 mg l^{-1} [9].

9.6.1.5 Cadmium

Cadmium is a very dangerous water pollutant with a high toxicity for aquatic organisms as well as for man. During a tragic accident in Japan, where water and rice fields were polluted with cadmium in the vicinity of a very large metallurgical complex, the dangerous disease itai-itai occurred, characterized by long-term effects and by many fatal cases.

The values of toxicity thresholds for cadmium in the form of cadmium nitrate were established for the bacterium *Pseudomonas putida* (80 μg l^{-1}), for green algae *Scendesmus qudricauda* (31 μg l^{-1}) and for protozoan *Entosiphon sulcatum* (11 μg l^{-1}) [6]. Chronic toxicity values for the cladoceran *Daphnia magna* ranged between 0.15 and 0.44 μg l^{-1} and for the brook trout (*Salvelinus fontinalis*) between 1.7 and 9.2 μg l^{-1}, depending on the water hardness. In the minnow (*Phoxinus phoxinus*) vertebral fractures were noted at 7.5 μg l^{-1} Cd. In the flounder (*Pleuronectes flesus*) a concentration of 100 μg l^{-1} Cd caused changes of blood plasma electrolyte (potassium, calcium and magnesium) concentrations. The ninety-six-hour LC_{50} value for rainbow trout (*Salmo gairdneri*) was 1.0 μg l^{-1} (hardness = 24 mg l^{-1}) and for coho salmon (*Oncorhynchus kisutch*) 1.8 μg l^{-1} (hardness = 23 mg l^{-1}) [7].

Cadmium is accumulated extraordinarily strongly in the human body. In newborn infants, the total cadmium amount is usually approximately 1 μg and by the 50th year of life the total amounts may be as high as 20 to 30 mg. In man, the value of the cadmium biological half-life ranges between 10 and 30 years. The kidneys, liver, lung and testes are the critical organs for cadmium, and in the case of long-term exposures a major portion of this element is accumulated in the kidneys [5, 10].

A cadmium concentration in drinking water of about 15 mg l^{-1} induces vomiting. A daily cadmium intake exceeding 1 mg results in acute poisoning with the following main symptoms: nausea, vomitus, diarrhoea, spasma of the gastrointestinal tract, cephalalgia and intense salivation. Shock from loss of liquids, acute failure of the kidneys, heart and lung and eventually death result from very high exposures. In the case of the disease itai-itai (translated as "ouch-ouch") the daily cadmium intake in the population involved was about 600 μg and the disease was fatal in nearly one half of the cases. Calcium losses, demineralization and osteomalacia occurred, which led to painful fractures, destruction of vertebrae and reduction of the skeleton size [9, 10].

The toxic effects of cadmiun are further manifested by a negative action on the metabolism of iron, copper and zinc which results in a deficiency of these metals with relevant disturbances. Cadmium also exerts teratogenic, mutagenic and carcinogenic effects [10].

According to WHO, the maximum permissible cadmium concentration in drinking water is 0.01 mg l^{-1} [9].

9.6.2 Carbon disulphide and hydrogen sulphide

Natural waters may be contaminated with carbon disulphide and hydrogen sulphide from wastewaters from the chemical industry and more frequently by hydrogen sulphide formed during the anaerobic decomposition of organic matter.

Among the aquatic organisms, fish are most sensitive to the presence of carbon disulphide and hydrogen sulphide. Carbon disulphide is less toxic and according to a certain data in the literature it was not harmful for certain fish species even at concentrations of 100 mg l^{-1}, whereas some other species died even after a one-hour exposure at this concentration. In other experiments with fish species *Alburnus alburnus* and *Alburmoides bipunctatus*, the fish died at a carbon disulphide concentration of 30 mg l^{-1} in several hours. For the species *Gambusia affinis* the lethal concentration at pH 7.4 to 8.0 was shown to be 0.162 mg l^{-1} during a 24-hour exposure, and even lower in the case of longer exposures.

More data are available about hydrogen sulphide toxicity. According to a majority of authors, hydrogen sulphide was not harmful in concentrations of 1 to 2 mg l^{-1}, however, fish species having higher requirements for water purity (such as trout) only tolerated concentrations of 0.3 to 0.5 mg l^{-1}.

In experiments with the fish species *Alburnus alburnus* and *Alburmoides bipunctatus*, the fish individuals died after only 20, 15 and 3 min at concentrations of 3, 5 and 10 mg l^{-1}, respectively [12, 13].

During the investigation of effects of carbon disulphide on green organisms, considerable changes after a 24-hour action on water rich in green organisms were obtained, in comparison with a control, only at a concentration of 100 mg l^{-1}. Hydrogen sulphide was harmful to the green organisms at a concentration exceeding 10 mg l^{-1}.

Bacteria were most resistant to the effects of carbon disulphide and hydrogen sulphide. In the case of carbon disulphide, the metabolism of bacteria remained unaffected even at a concentration of 2000 mg l^{-1}. In the case of hydrogen sulphide, at a concentration of 2300 mg l^{-1}, the multiplication of bacteria was normal, however, the rate of growth was inhibited in comparison with a control [13].

The presence of carbon disulphide and hydrogen sulphide is of course readily detected by their unpleasant smell at concentrations which are well below toxic concentrations. Water containing carbon disulphide as well as hydrogen sulphide irritates the skin, and both compounds may be absorbed through the skin [14].

9.6.3 Nitrates and nitrites

Excess amounts of nitrates in surface waters disturb natural equilibria and when present in drinking water, they are also hazardous to human health. In the presence of phosphates, nitrates cause eutrophization: overpopulation of aquatic vegetation, which reduces the oxygen content in water during its decomposition, and later leads to the production of ammonia, thus threatening the life of aquatic organisms.

In a non-reducing medium and at low concentrations, nitrates are not dangerous to the adult, healthy man and thus, primary toxicity is not generally a problem. This is connected with their rapid elimination by the kidneys. In the case of higher amounts of nitrates ingested, secondary toxicity may be manifested, which results from their reduction to nitrites. The nitrate ion NO_3^-, which is extraordinarily stable and which is only a very weak oxidizing agent in solutions, may be converted to the nitrite ion NO_2^- by certain bacteria of the mouth microflora, which contain the enzyme nitrate reductase. Of the total amount of nitrates ingested, approximately 80% is excreted by the kidneys, the remaining portion is mostly converted to ammonia compounds in the intestine and a small fraction is transported through the salivary glands into the mouth cavity. It was demonstrated that the amount of nitrates ingested is proportional to their concentration in the saliva, which also results in a proportionality of the amount of nitrites formed.

The toxic effect of nitrites in the human organism after their absorption through the intestinal wall into the blood is particularly due to the possibility of inducing methaemoglobinaemia. In this, nitrites react with haemoglobin by oxidizing the haemoglobin Fe^{2+} ion to the Fe^{3+} ion, thus converting the red haemoglobin to dark brown methaemoglobin:

$$\begin{aligned} HNO_2 &\rightarrow OH^- + NO^+ \\ Fe^{2+} + NO^+ &\rightarrow Fe^{3+} + NO \end{aligned}$$

In contrast to haemoglobin, methaemoglobin is unable to transfer oxygen. The extent of the effect depends on the methaemoglobin concentration in the blood and it is manifested by the grey-blue to blue-violet colour of mucous membranes and skin of marginal parts of the body (mainly of the lips), by an increased pulse frequency, difficult breathing and diarrhoea. In adults, methaemoglobinaemia can be induced by about 0.5 g KNO_2 and a dose of 4 g KNO_2 can be lethal. The disease is very serious in very young suckling children, whose blood contains haemoglobin F (foetal haemoglobin) instead of haemoglobin A. Haemoglobin F is much more liable to oxidation than haemoglobin A, and, in addition to this in the erythrocytes of suckling children, the enzymatic system, which could convert the methaemoglobin formed back to haemoglobin, is still insufficiently developed.

Numerous cases of poisoning with nitrites from drinking water (mainly from individual sources) are recorded in the literature, many of them with fatal consequences. A content of nitrites above 30 mg l^{-1} is considered as suspect and 40 mg l^{-1} results in methaemoglobinaemia in suckling children.

Nitrates and nitrites can give rise to other effects. They are, for example, able to decompose carotene. Nitrates affect the activity of the thyroid gland, which plays an important role in the conversion of carotene to vitamin A. The interactions of nitrites with amines are, however, much more dangerous, since they result in the production of *N*-nitroso compounds. Many of these compounds damage the liver and exhibit teratogenic and carcinogenic effects [5, 15].

9.6.4 Cyanides

Cyanides are among the most toxic substances of wastewaters and they can be leached out into natural waters. They can occur either as simple cyanides (NaCN, HCN), or as complex cyanides of various metals. Simple, water-soluble cyanides readily release hydrogen cyanide even in a neutral medium. HCN is a very weak and water-soluble acid. Hydrogen cyanide acts very rapidly as a poison and it exerts lethal effects even in very low amounts. The toxicity of complex cyanides is much lower than that of simple cyanides, on account of the stability of the complexes.

Cyanides exert very different effects on different organisms, higher organisms being much more sensitive to their toxic effect than lower organisms. For example, bacteria are able to resist, without losing their biological activity, cyanide concentrations which are already lethal for Protozoa. Bacteria serve as food for Protozoa and thus, the Protozoa decay with an overpopulation of bacteria. The effect on fishes is usually considered when establishing the maximal allowable cyanide concentration in surface waters. The toxicity of cyanide compounds for fishes is set out in Table 9.1 [1].

Table 9.1. Toxicity of cyanide compounds for fishes [1]

Compound	Concentration CN^- ($mg\ l^{-1}$)	Fish species	Effect
NaCN	2.0	White fish	Death in 17 min
	1.0	Trout, minnow	100% mortality in 20 min
	0.8	Minnow (10–16 cm), carp (30–40 cm)	100% mortality in 24 h
	0.3–0.7	Minnow (10–16 cm), carp (30–40 cm)	25% mortality in 24 h
	0.3	Minnow (10–16 cm), carp (30–40 cm)	No effect
	0.05	Trout	100% mortality in 24 h
	0.02	Trout	No effect
KCN	0.14	Trout	Mortality
$K_3[Fe(CN)_6]$	17	Minnow	No effect for 24 h
$K_4[Fe(CN)_6]$	17	Minnow	No effect for 70 days

The effect of the CN^- anion is based on blocking the tissue respiration or, more precisely, by blocking the cytochrome. After ingestion, it is rapidly absorbed by the stomach mucous membrane, however, it can also be absorbed by intact skin. It is metabolized mainly to SCN^-. The course of the acute poisoning depends on the amount of the substance ingested. In man, small doses result in cephalalgias, nausea, dizziness, accelerated breathing and unconsciousness. The breathing in irregualr and the patient dies in spasms by the asphyxia. Doses of 0.2 to 0.3 g KCN or 0.05 to 0.06 g HCN are lethal to man [14].

9.6.5 pH

In recent years, as a result of acid rain and snowfall, the pH of water has decreased in many natural waters, a phenomenon which is mostly discussed in relation to harmful effects on fish. Anions of most acids exert a low toxicity, so that the toxicity of acids is essentially given by the pH value. If the pH of water drops below 5, the biological equilibrium is disturbed, the self-purification capacity of the river or lake is reduced, the fish feeding base is diminished and a toxic effect of H^+ ions on the fish occurs. The allowable pH range, which is not threatening to fish and other aquatic organisms, is 5.5 to 9.0. In mountain waters and clean brooks (in trout waters), the organisms can more readily resist a decrease of pH below 5.5 than an increase above 9. Fishes from intermediate zones are able to tolerate even a pH increase above 9 and a short-term increase above 10. The pH increase resulting from assimilation is not as harmful for the fish as that resulting from pollution by wastewaters, for which it is also necessary to take into account the detrimental effects of their components [1].

In the toxic effect of acid waters on fish the gills are the primary target of elevated hydrogen ion activity. On the basis of observations on salmonid fishes seven major effects of pH upon the gills (ranked in approximate order of their occurrence with declining pH) were identified: inhibition of Na^+ and Cl^- uptake mechanisms, increased ion permeability and diffusional ion efflux, increased hydrogen ion permeation of the gills, enhanced mucus production and release, mucus coagulation and precipitation, inhibition of gas transfer across the gills, and damage to and separation of gill epithelial layers [16].

The fish sensitivity to the decrease of water pH differs, however, within the salmonids. The most sensitive to acid stress are the brown trout (*Salmo trutta*) and rainbow trout (*Salmo gairdneri*), whereas the brook trout (*Salvelinus fontinalis*), is generally regarded as the least sensitive. Even greater acid tolerances are seen among such teleosts as the white sucker (*Catostomus commersoni*), the perch (*Perca* sp.), the roach (*Rutilus rutilus*), and the characinid fish of the Amazon Basin. All of these species, as a rule, can survive at pH levels to most salmonids [16].

9.6.6 Radioactive substances

Most aquatic organisms are able to accumulate radioactive substances to a considerable extent. The plankton has a concentration of radioactive substances higher by a factor of 2 to 10^4 as compared to the concentration in the water, for fish this factor is about 500 to 800. The accumulation of radioactive substances in aquatic organisms also represents a danger for man. For example, in the isles of the Pacific Ocean about 2/3 of ^{90}Sr enter the human organism from fish [17].

^{90}Sr is an example of those radionuclides that are in soluble form and are chemically analogous to essential nutrient elements, and therefore follow ecological pathways in a fashion similar to their nutrient analogues. ^{90}Sr, ^{140}Ba, ^{226}Ra and ^{45}Ca will behave like calcium; ^{137}Cs, ^{86}Rb and ^{40}K will generally follow the movement of potassium; ^{131}I will resemble the movement of non-radioactive iodine, etc.

The danger from radioactive substances is mainly due to the detrimental effects of the emitted ionizing radiation; however, there are also toxic effects at the level of biochemical reactions. The most important effects of radioactive radiation from accumulated radionuclides are manifested at a much later date in the form of genetic consequences. There are also local effects, since the radionuclides are frequently accumulated in a certain critical organ (^{90}Sr in bones, ^{137}Cs in muscles, etc.). Thus, the local radiation dose can exceed by a factor as high as 50 the mean whole-body dose. In many cases, tumour growth may be induced.

In the case of internal contamination of organisms, long-term irradiation is typical, which depends on the activity of the radionuclides incorporated. The activity of radionuclides gradually decreases due to radioactive decay and to the excretion of a portion of the amount accumulated. Thus, when evaluating the danger to the organism from a given radionuclide, it is necessary to consider its physical as well as its biological half-life [18].

The physical half-life T_{ph} is the time necessary for the decay of one half of the inital number of radioactive atoms.

The biological half-life T_{b} is the time in which one half of the administered amount of the radionuclide is excreted.

The actual decrease of the radionuclide amount in the organism is, however, expressed by the effective half-life, T_{ef}, i.e. the time necessary for reducing the activity of the radionuclide in the organism to one half of the initial amount. It holds that:

$$\frac{1}{T_{\text{ef}}} = \frac{1}{T_{\text{ph}}} + \frac{1}{T_{\text{b}}}$$

Table 9.2. The categorization of radionuclides according to their relative radiotoxicity [19]

Radiotoxicity group	Radionuclides
A Very highly toxic	^{90}Sr+^{90}Y, ^{210}Pb+^{210}Bi, ^{210}Po, ^{211}At, ^{226}Ra+ daughters, ^{228}Ra, ^{227}Ac, transuranium elements
B Very toxic	^{45}Ca, ^{59}Fe,^{89}Sr, ^{91}Y, ^{107}Ru+^{106}Rh, ^{110m}Ag, ^{126}I, ^{129}I, ^{131}I, ^{134}Cs, ^{140}Ba+^{140}La, ^{144}Ce+^{144}Pr, ^{151}Sm, ^{152}Eu, ^{154}Eu, ^{170}Tu, ^{207}Bi, ^{223}Ra, ^{228}Ac, ^{227}Th, ^{228}Th, ^{230}Th, ^{232}Th, ^{234}Th, ^{230}Pa, ^{231}Pa, ^{230}U to ^{238}U
C Intermediate toxicity	^{14}C, ^{16}N, ^{22}Na, ^{24}Na, ^{31}Si, ^{32}P, ^{35}S, ^{36}Cl, ^{42}K, ^{47}Ca, ^{46}Sc, ^{47}Sc, ^{48}Sc, ^{48}V, ^{52}Mn, ^{64}Mn, ^{56}Mn, ^{55}Fe, ^{58}Co, ^{60}Co, ^{59}Ni, ^{63}Ni, ^{65}Ni, ^{64}Cu, ^{65}Zn, ^{69m}Zn, ^{72}Ga, ^{73}As, ^{74}As, ^{76}As, ^{77}As, ^{75}Se, ^{82}Br, ^{87}Kr, ^{88}Kr, ^{86}Rb,^{88}Rb, ^{85}Sr, ^{89}Sr, ^{91}Sr, ^{92}Sr, ^{91}Y, ^{92}Y, ^{93}Y, ^{93}Zr+^{93}Nb, ^{95}Zr+^{95}Nb, ^{99}Mo, ^{96}Tc, ^{97m}Tc, ^{97}Tc, ^{99}Tc, ^{103}Ru, ^{105}Ru, ^{105}RH, ^{103}Pd+^{103}Rh, ^{109}Pd, ^{105}Ag, ^{111}Ag, ^{109}Cd+^{109}Ag, ^{115}Cd, ^{115m}Cd, ^{114m}In, ^{113}Sn, ^{122}Sb, ^{124}Sb, ^{125}Sb, ^{125m}Te, ^{127m}Te, ^{129}Te, ^{132}Te, ^{133}I, ^{134}I, ^{135}I, ^{135}Cs, ^{136}Cs, ^{137}Cs+^{137}Ba, ^{131}Ba, ^{141}Ce, ^{143}Ce, ^{142}Pr, ^{143}Pr, ^{146}Nd, ^{149}Nd, ^{147}Pm, ^{153}Sm, ^{152m}Eu, ^{155}Eu, ^{153}Gd, ^{159}Gd, ^{160}Tb, ^{166}Dy, ^{166}Ho, ^{169}Er, ^{171}Er, ^{171}Tu, ^{175}Yb, ^{177}Lu, ^{181}Hf, ^{182}Ta, ^{181}W, ^{185}W, ^{187}W, ^{183}Re, ^{186}Re, ^{188}Re, ^{191}Os, ^{190}Ir, ^{192}Ir, ^{194}Ir, ^{191}Pt, ^{193}Pt, ^{197}Pt, ^{196}Au, ^{198}Au, ^{199}Au, ^{197m}Hg, ^{197}Hg, ^{203}Hg, ^{200}Te, ^{202}Te, ^{204}Te, ^{203}Pb, ^{212}Pb, ^{206}Bi, ^{231}Th, ^{233}Pa, ^{240}U
D Moderate toxicity	^{3}H, ^{7}Be, ^{13}N, ^{17}N, ^{18}F, ^{38}Ca, ^{37}Ar, ^{41}Ar, ^{51}Cr, ^{58m}Co, ^{69}Zn, ^{71}Ge, ^{77}Kr, ^{85}Kr, ^{85m}Kr, ^{87}Rb, ^{85m}Sr, ^{91m}Y, ^{97}Nb, ^{96m}Tc, ^{97}Ru, ^{103m}Rh, ^{113m}In, ^{115m}In, ^{115}In, ^{129}Sb, ^{133}Te, ^{131m}Xe, ^{133}Xe, ^{135}Xe, ^{131}Cs, ^{134m}Cs, ^{139}Ba, ^{141}La, ^{142}La, ^{145}Ce, ^{145}Pr, ^{146}Pr, ^{144}Nd, ^{147}Sm, ^{165}Dy, ^{187}Re, ^{193m}Pt, ^{201}Tl, natural U and Th

Besides the physical and biological half-lives of particular radionuclides, their radiotoxicity further depends on the type and energy of the radiation emitted and on the metabolism of the given element. Those radionuclides are particularly dangerous, which are characterized by a long half-life, high ionization ability of radiation, selective accumulation in a certain type of the organism and a long residence time in the organism. From this standpoint, it is possible to categorize radionuclides into four groups according to their relative radiotoxicity (Table 9.2) [19].

We now discuss those radiotoxic elements which present particular hazards in hydrochemistry and water technology.

Strontium has several radioactive nuclides, formed during nuclear reactions, ^{90}Sr being the most dangerous one. ^{90}Sr is characterized by all the features connected with harmful effects on living organism. It is produced with a high yield during the fission reaction, it has a long half-life (T = 28 years) and a good solubility of most compounds in water. It is present everywhere on the earth's surface and it occurs in food chains. Its metabolism is similar to that of calcium and thus, it is deposited particularly in the bones and its beta-radiation damages the bone marrow, and hence also haemopoiesis [14]. The effective half-life of ^{90}Sr related to the whole organism is 5700 days [20]. The maximum permissible concentration for ^{90}Sr in water is 0.37 Bq ml^{-1}for its soluble form and for insoluble forms, 37 Bq ml^{-1} [21].

^{90}Sr itself is a fairly soft beta-emitter ($E_{\max\beta}$ = 0.6 MeV). However, its daughter ^{90}Y, which has a half-life of 64 hours emits very hard beta-rays with $E_{\max\beta}$ = 2.26 MeV. ^{90}Y has a rather short half-life, but its radiation is dangerous, since this radionuclide is produced continuously from ^{90}Sr accumulated in the skeleton, emitting radiation with a high ionization density [17].

In the case of uranium and its compounds, the chemical toxicity also needs to be considered. The distribution in the organism and the metabolism of uranium compounds are considerably affected by its valency. Uranyl ions $(UO_2)^{2+}$ are particularly toxic, forming complexes with a number of biochemically important substances. On the basis of the formation of uranyl complexes with phosphates it is possible to explain the disturbing effects in the metabolism of glycides. U^{6+} is deposited particularly in the kidneys and bones, U^{4+} mainly in the liver. Acute poisoning with uranium compounds is manifested primarily by damage to the kidney, chronic poisoning by damaging the haemopoiesis [14]. The effective half-life for ^{232}U, ^{233}U, ^{234}U, ^{235}U, ^{236}U and ^{238}U related to the whole organism is reported to be 100 days [20]. The maximum permissible concentration for natural uranium in water is 18.5 Bq ml^{-1} for both soluble and insoluble forms [21].

Radium also has a similar metabolism to calcium and as much as 99% of radium administered is deposited in the skeleton. It is dangerous particularly due to its radioactivity, the biochemical effects being of a smaller importance. Among the various isotopes, ^{226} Ra with a half-life of 1620 years is the most important one; it emits alpha particles. After ^{226}Ra incorporation, the early changes are negligible, included those of the blood count. Later changes are localized in bones. These involve a destruction of the bones, frequently complicated by infections and tumours in the bone or in its close vicinity. Osteosarcomas and carcinomas are produced [17]. The effective half-life of ^{226}Ra related to the bone is 16,000 days [20]. The maximum permissible concentration for ^{226}Ra in water is 14.8×10^{-3} Bq ml^{-1} for its soluble form and 33.3 Bq ml^{-1} for its insoluble form [21].

Plutonium is dangerous mainly on account of its radioactivity, in the case of an internal contamination. ^{239}Pu has a very long half-life (2.44×10^4 years), and it emits alpha-particles (E_α = 5.15 MeV (72%), 5.13 MeV (17%), 5.10 MeV (11%)) with a soft gamma-ray component [22]. It is deposited particularly in the bones and it is excreted with the urine. It damages the liver, haemopoiesis and it also frequently induces osteosarcomas [14]. The ^{239}Pu effective half-life, related to the bones is 72,000 days [20]. The maximum permissible concentration for ^{239}Pu in water is 3.7 Bq ml^{-1} for the soluble form and 29.6 Bq ml^{-1} for its insoluble form [21].

9.6.7 Phenol and related compounds

Phenol and its compounds are characterized by a highly toxic effect on aquatic organisms, the fish being most sensitive of these. Before the manifestation of their toxicity, however, the smell and taste of the fish is affected. For example *o*-chlorophenol caused an unpleasant fish smell already at a concentration of 0.015 mg l^{-1} and according to further data from the literature the fish gained this smell after 1.4 days at a concentration of 0.1 mg l^{-1}, after two days at a concentration of 0.01 mg l^{-1}, after 5 days at a concentration of 0.001 mg l^{-1} and after 11 days at a concentration of 0.0001 mg l^{-1}. The threshold phenol concentration affecting the hygienic regime of water flows was found to be 0.3 mg l^{-1}, however, according to the organoleptic parameter, for cresols the threshold concentration was found to be 0.0002 to 0.001 mg l^{-1}, and for the above-mentioned chlorophenols 0.0004 mg l^{-1} is recommended as the highest permissible concentration. The toxicity of phenol and certain phenol compounds for aquatic organisms is summarized in Table 9.3 [23].

On account of the high toxicity and considerable stability of phenols, these compounds lead to important problems in wastewater treatment. The biological treatment of water flows was inhibited by phenol at a concentration of 75 mg l^{-1}; hydroquinone at a concentration of 15 mg l^{-1} inhibited the biochemical treatment of wastewaters and the threshold concentration of the effect of 2,4-dinitrophenol on the biological treatment was found to be 20 mg l^{-1}; *m*-aminophenol at a concentration of 1 mg l^{-1} inhibited the BOD (biochemical oxygen demand) and nitrification of wastewaters.

Table 9.3. The toxicity of phenol and certain phenol compounds for aquatic organisms [23]

Compound	Concentration ($mg\ l^{-1}$)	Object studied	Effect
Phenol	0.01	Carp	Distrophic changes of the myocardium, kidney and liver
	0.2	Fish	Toxic
	0.5–1.0	Trout	Death
	1.0–5.0	Tench	Death
	5.0	Trout	Death after 10 h
	5.0–10.0	Daphnia	Death
	25.0	Crustaceans, genus *Gammarus*	Death
	40.0	Algae *Scendesmus*	Toxic
o-Cresol	2.3	Embryos of salmonid fish	Death after 24 h
	10.0	Perch	Toxic at 15°C
	17.0	Perch	Death after 10 min at 18°C
m-Cresol	6.5	Embryos of salmonid fish	Death after 24 h
p-Cresol	4.0	Embryos of salmonid fish	Death after 24 h
2,5-Xylenol	2.0	Perch	Toxic
	20.0	Minnow	Death after 5 to 7 min
	<100.0	*Escherichia coli*	Death
2,4-Dinitrophenol	0.5–1.0	Minnow	Death in distilled water after 6 h
	35–38	Minnow	Death in water with high contents of Ca + Mg after 6 h
Hydroquinone (1,4-benzenediol)	0.2	Carp, perch	Toxic
	0.5	Daphnia	Death
	4.0	Algae *Scendesmus*	Toxic
α-Naphthol	0.3	Plankton	Toxic
β-Naphthol	0.2	Fish	Toxic

Phenol and its compounds are characterized by mutagenic (e.g. phenol, *m*-aminophenol, hydroquinone) as well as teratogenic (dinitrophenol) effects. They irritate the skin and mucous membrane (cresols, hydroquinone) and they penetrate easily into the organism. Their effect is manifested by acute as well as chronic poisoning of the central nervous system with a simultaneous involvement of the liver and kidneys [23, 24].

The man, however, is only very slightly threatened by phenols occurring in water, since their above-mentioned organoleptic characteristics reveal their presence already in negligible concentrations, which are not toxic for the man.

9.6.8 Pesticides

The hydrosphere is one of the main regions for the accumulation and transport of pesticides. Pesticides are toxic not only for the target organisms, they affect all living organisms, fish and other aquatic organisms being very sensitive to them. The damage to the water economy are on the one hand direct, i.e. fish mortality and, on the other hand, indirect — destruction of lower aquatic organisms, which leads to a reduction or to a complete destruction of the fish feeding base. Either instantaneous or long-term pesticide effects need to be considered. For example, the fishes affected by certain insecticides applied against mosquito larvae may die immediately, or in the case of a lower dosage they can suffer from serious physiological disturbances. The accumulation of pesticides in organisms is dangerous, and is characteristic particularly for chlorinated organic compounds accumulating in the fat. During starvation or during diseases, these pesticides (particularly DDT) may be released into the blood and the amounts released can exceed the lethal dose.

The concentration of pesticides in nutritional chains is more dangerous, where the victim of poisoning need not come into direct contact with pesticides. This occurred, for example, in Clear Lake in California, where a population of divers was nearly completely destroyed due to the application of DDD against mosquito larvae. The preparation was applied into water of the lake, with a surface of 18,600 ha, in 1949, 1954 and 1957 to a total amount of 54,800 kg. Several months after the second application, ever more frequent death of the birds was observed, and they stopped coming back to the lake in the winter period. Analyses of the fat of dead divers demonstrated an unusually high content of DDD, 1600 mg kg^{-1}. In a more profound study it was shown that DDD is accumulated in the following order in increasing amounts: plankton < small fish < large fish < divers. The mean concentration of this substance in the plankton was 5.3 mg kg^{-1}; in muscles of small plankton-eating or plant-eating fish 5 to 8 mg kg^{-1}, and in fish predators 1 to 196 mg kg^{-1}. In older fish individuals the amounts of DDD accumulated were higher by a factor of 2 to 5 as compared to young fish. The DDD content in the fish fat was much higher than that in the

Table 9.4. 48-hour TL_m ($\mu g\ l^{-1}$) values of pesticides from static bioassay for various types of fresh-water organisms [27]

Pesticide	Stream invertebrate^a		Cladocerans^b		Fish^c		Gammar lacustris^d TL_m
	Species	TL_m	Species	TL	Species	TL_m	
Chlorinated hydrocarbons							
Aldrin*	*Pteronarcys californica*	100	*Daphnia pulex*	28	Rainbow trout	3	12,000
Heptachlor*	*Peteronareella badia*	4	*D. pulex*	42	Rainbow trout	9	100
Endrin*	*P. californica*	0.8	*D. pulex*	20	Bluegill	0.2	4.7
Benzene hexachloride (lindane)	*P. californica*	8	*D. pulex*	460	Rainbow trout	18	88
DDT*	*P. californica*	19	*D. pulex*	0.36	Bass	2.1	2.1
DDD (TDE)*	*P. californica*	1,100	*D. pulex*	3.2	Rainbow trout	9	1.8
Chlordane*	*P. californica*	55	*Simocephalus serrulatus*	20	Rainbow trout	10	80
Organophosphates							
Dichlorvos* (DDVP)	*P. californica*	10	*D. pulex*	0.07	Bluegill	700	1
Disulfoton (di-syston)	*P. californica*	18			Bluegill	40	70
Malathion*	*P. badia*	6	*D. pulex*	1.8	Brook trout	19.5	1.8
Parathion*	*P. californica*	11	*D. pulex*	0.4	Bluegill	47	6
Diazinon*	*P. californica*	60	*D. pulex*	0.9	Bluegill	30	500
Trichlorfon* (dipterex)	*P. badia*	22	*D. magna*	8.1	Rainbow trout	160	60
TEPP*					Fathead	390	52

Carbamates							
Carbaryl (sevin)	*P. californica*	1.3	*D. pulex*	6.4	Brown trout	1,500	22
Zectran	*P. californica*	16	*D. pulex*	10	Rainbow trout	8,000	76
Triazines							
Ametryne					Rainbow trout	3,400	
Atrazine			*D. magna*	3,600	Rainbow trout	12,600	
Simazine	*P.californica*	50,000			Rainbow trout	5,000	21,000
Organic acids							
Dalapon	*P. californica* Very low toxicity		*D. magma*	6,000			Very low toxicity
Dicamba					Non-toxic		5,800
Endothal, copper					Rainbow trout	290	
2,4-D, BEE	*P. californica*	1,800			Bluegill	2,100	760
Miscellaneous							
Diuron	*P. californica*	2,800	*D. pulex*	1,400	Rainbow trout	4,300	380
Rotenone	*P. californica*	900	*D. pulex*	10	Bluegill	22	350
Sodium arsenite	*P. californica* Very low toxicity		*S. serrulatus*	1,400	Rainbow trout	36,500	
Dinitrocresol	*P. californica*	560			Rainbow trout	210	

• Becomes bound to soil when used according to directions, but highly toxic (reflected in numbers) when added directly to water.

[a] — Stonefly bioassay was done at Denver, Colorado, and at Salt Lake City, Utah. Denver tests were in soft water (35 mg l^{-1} TDS), non-aerated, 60 F. Salt Lake City tests were in hard water (150 mg l^{-1} TDS), aerated, 48–50 F. Response was death.

[b] — *Daphnia pulex* and *Simocephalus serrulatus* bioassay was done at Denver, Colorado, in soft water (35 mg l^{-1} TDS), non-aerated, 60 F. *Daphnia magna* bioassay was done at Pennsylvania State University in hard water (146 mg l^{-1} TDS), non-aerated, 68 F. Response was immobilization.

[c] — Fish bioassay was done at Denver, Colorado, and at Rome, N. Y. Denver tests were with 2-inch fish in soft water (35 mg l^{-1} TDS), non-aerated; trout at 55 F; other species at 65 F. Rome tests were with 2–2.5-inch fish in soft water (6 mg l^{-1} TA: pH 5.85–6.4), 60 F. Response was death.

[d] — Gammarus bioassay was done at Denver, Colorado, in soft water (35 mg l^{-1} TDS), non-aerated, 60 F. Response was death.

muscle tissue. No obvious damage to the fish was observed, but the divers were shown to be a species very sensitive to the toxic effect of DDD [25].

The high sensitivity of fish to the presence of toxic substances in water is due particularly to their way of their breathing, when large amounts of water pass through the gills and thus, the possibility of the toxic effects of pesticides and of the accumulation of lipophilic chlorinated organic compounds in the fish body are increased. Molluscs take up their nutrients by continuous filtration of water, which also results in their high sensitivity even to low concentrations of chlorinated organic substances or similar foreign lipophilic substances present in water [26]. Different fish species react in different ways to a given pesticide. Salmonidae are very sensitive and Caprinidae are much more resistant. This also means an increased danger of the intoxication following the application of pesticides in the vicinity of trout waters.

Many factors affect the toxic effects and processes of the detoxication of pesticides in water. Pesticides well soluble in water, such as those from the group of organic compounds of phosphorus, urea derivatives, triazines, carbamates and phenoxyacetic compounds, readily participate in chemical and biological processes with their rather rapid decomposition. Sparingly soluble pesticides (particularly chlorinated organic compounds) are mostly characterized by their long biological half-life and they participate mainly in sorption and sedimentation processes. Very fine particles of water-insoluble pesticides are adsorbed in suspensions as well as in the zooplankton and phytoplankton. Their persistence and accumulation in nutritional chains increases the danger of toxic effects [25].

Water temperature is a very important factor affecting the toxicity of pesticides. In general, the poisoning of the fish with pesticides increases with increasing temperature. Water pH, affecting particularly the hydrolysis of pesticides and water hardness is also an important factor. Pesticides that are water-soluble and dissociated react with calcium, magnesium and with the other metals present in natural waters. These reactions can result in their detoxication and removal from water by their sedimentation. Toxicological investigations suggest that in waters with high calcium and magnesium contents the toxic levels of pesticides are usually higher than those in soft waters. The toxicity and detoxication of pesticides in water is further affected by the content of dissolved oxygen, solar radiation, content of organic compounds and ammonia, etc.

The extent of the threat to aquatic organisms by particular groups of pesticides categorized according to chemical composition is shown in Table 9.4 [27]. From the table it is obvious that chlorinated hydrocarbons and organophosphates are the most dangerous pesticides, and they also represent a considerable hazard to man.

9.6.8.1 Chlorinated hydrocarbons

Chlorinated hydrocarbons represent a wide group of substances, characterized in general by their long persistence (see Table 9.5) and high accumulation in organisms, which greatly increases their relative toxicity in addition to their direct acute effect. For example, the danger of endrin, DDT and DDD for aquatic organisms is shown not only by their TL_m values (see Table 9.4), but also the fact that these pesticides are not decomposed in waters for 8 weeks. During the process of water self-cleaning, the chlorinated hydrocarbons accumulate at the bottom of reservoirs and they are also bound in the plankton, entering into nutritional chains in this way. Their concentration in the nutritional chains represents an extensive danger for living organisms, as shown in the example of the mortality of birds

Table 9.5. General levels of persistence of commonly used pesticides [28]

Pesticide	Persistence in	
	water	fish
Chlorinated hydrocarbons		
Methoxychlor	Yes	ca 1 week
Heptachlor	Yes	ca 1 month
Dieldrin	Yes	ca 1 month
Toxaphene	Yes	> 6 months
DDD	Yes	> 6 months
DDT	Yes	> 5 months
Organophosphates		
Malathion	Variable	< 1 day
Parathion	No	< 1 week
Dursban	Yes	< 1 week
Guthion	No	< 1 week
Diazinon	No	< 1 week
Miscellaneous		
2,4-D	No	< 1 week
Dichlobenil	No	< 2 weeks
Diquat	No	< 3 weeks
Endothal salt	No	< 3 weeks
Simazine	Yes	< 3 weeks
Sodium arsenite	Yes	> 16 weeks

on Clear Lake. The bioaccumulation of chlorinated hydrocarbons can also be observed in man, the greatest contribution coming from their occurrence in drinking water or from eating polluted fish. The form of chlorinated hydrocarbons is also an important factor for their intake level. For example, when DDT is dissolved in plant or animal fat, its intake is increased by a factor of 1.5 to 10 [25].

The accumulation of chlorinated hydrocarbons in organisms depends on the dose, type of organism and its detoxication capacity, age, sex, way of penetration into the organism, interactions with the other substances, etc. A greater accumulation of pesticides occurs when administering smaller doses over short-time intervals as compared to one total dose.

In the initial period after the penetration into the organism, pesticides are distributed by the blood circulation so that their concentration in particular tissues depends on the level of the blood supply. For example, in the liver or in the brain, their concentration is higher than that in the fat tissue. The final distribution of chlorinated hydrocarbons is, however, governed by their solubility in fats which is much higher than that in water, so that concentrations in the lipid tissue may be higher by a factor of 100 to 300 as compared to those in the blood.

A portion of pesticides administered is accumulated in an unaltered form, and a further fraction may undergo different biotransformations. For example, DDT can be partially metabolized to DDA, DDD or DDE depending on the organism. HCH is accumulated in the form of alpha, beta, gamma and delta isomers. The accumulation of compounds in the organism is also altered on changing their chemical structure.

The most common chlorinated hydrocarbons used as insecticides may be listed in order of their decreasing rate of accumulation as follows: heptachloroepoxide > dieldrin > endrin > DDT > lindane [25].

The mechanism of the effect of DDT and similar substances on living organisms is explained on the basis of their disturbance of the K^+, Na^+ and Mg^{2+} transport through the membrane of neurons, which probably also disturbs the transfer of nervous impulses. This results in a negative effect on the function of the nervous system, including the brain. DDT also negatively affects the metabolism of Ca^{2+} and estrogenic hormones, the effect being manifested in disturbances of reproduction, a decrease in fertility and the survival of the offspring. There is probably a similar disturbing effect on the energy metabolism of the cell [29]. DDT and other chlorinated hydrocarbons (HCH, chlordan, dieldrin, kamfechlor) induce important changes in the liver of animals, which lead to a formation of tumours in certain species [25].

9.6.8.2 Organophosphates

Organic compounds of phosphorus, together with the chlorinated hydrocarbons, are among the most frequently used insecticides. Their insecticidal characteristics were discovered in the course of World War II during the study of new military poisonous substances. Many of them are thus also strongly toxic for man as well as for other mammals. For example, one of the first produced organophosphate insecticides, tetraethyldiphosphate (TEPP) is the most toxic substance ever used in agriculture (1 g of TEPP can cause the death of 16 people) [26].

Organophosphates have different toxicities for different aquatic organisms (see Table 9.4), their toxicity being lower for fish than for lower aquatic organisms. Thus, in the contamination of water with organophosphates, the fish may be threatened secondarily, i.e. by a reduction or destruction of nutrition.

One advantage of organophosphate insecticides lies in their fairly rapid biological and chemical degradation in plants and animals to non-toxic substances. They are also not accumulated in nutritional chains. The persistence of chlorinated hydrocarbons, organophosphates and of the other commonly used pesticides in water and fish is presented in Table 9.5 [28].

The insecticide effect and toxicity of organophosphate pesticides is generally accepted as being due to the phosphorylation of acetylcholine esterase, which results in blocking of this enzyme splitting acetylcholine, which is of a vital importance, being the substance which transfers nervous impulses by a chemical mechanism. Esters of organic substances of phosphorus bind acetylcholine esterase immediately, whereas thiophosphates can bind it only after metabolic conversions, changing the bond P=S to P=O. The conversion of parathione to paraoxone is as an example of this activation. Organophosphates also inhibit choline esterase, aliesterases and so-called "serine proteinases", which results in an induction of many physiological effects. From the clinical standpoint, these effects may be classed in general into the muscarine effect (increased secretion of glands, reduced heart activity, involvement of unstriped muscles), nicotine effect (muscule effects — spasms of striated muscles, gradual decreases of the heart activity and paralysis) and central nervous effect (various disturbances of the CNS, spasms or even coma) [5, 24, 25].

9.6.9 Carcinogenic substances

The hydrosphere is becoming ever more polluted with substances which are considered to be carcinogenic, i.e. able to induce tumour growth in animal organisms, accompanied by all the various malignant manifestations. Different carcinogenic substances threaten different degrees of danger. According to Shabad [30] and Litvinov [31] they may be categorized into the following four groups:

Group I includes the strongest (so-called obligate) carcinogens, which are invariably capable of inducing cancer disease in man, their carcinogenic action having been repeatedly demonstrated in experiments on animals (e.g. β-naphthylamine, benzo[*a*]pyrene).

Group II contains the strong carcinogens — substances inducing tumours in a fairly short time in most laboratory animals, the carcinogenic effect on the man being probable (e.g. aminoazo compounds, nitrosoamines).

Group III includes moderate carcinogens. These are many substances inducing tumours in a smaller fraction of experimental animals (up to 20%) and during their long-term action, i.e. in the second half of the life of these animals. Their carcinogenic effects on the man are still a matter of debate.

Group IV includes weak carcinogens, which have induced tumours in certain laboratory animals, however, in general the experiments with these substances have so far yielded controversial results.

On the basis of preliminary analysis of data extracted from the literature it was found that doses of carcinogenic substances inducing malignant growth vary over a millionfold range. The range of the potency of carcinogens in animals is shown in Fig. 9.5 [32]. The doses reported are effective in 50% of animals during their lifetime.

It needs to be emphasized that only the carcinogenic action of pure substances has been considered. Living organisms, however, come into contact with mixtures of substances, where the carcinogenicity of one substance may be affected by the other compounds and also by physical factors (such as ultraviolet radiation).

We now consider the most important carcinogens dangerous to animals and man. The strongest carcinogens occurring in nature include the aflatoxins, which are easily formed in different food products — metabolic products of Algae *Aspergillus flavus* and *Aspergillus parasiticus*. The hepatocarcinogenic effect of their most important representative, aflatoxin B_1, was first discovered in 1960 on trout caught in California [33]. The carcinogenic effects of certain aflatoxins on rainbow trout (*Salmo gairdneri*),

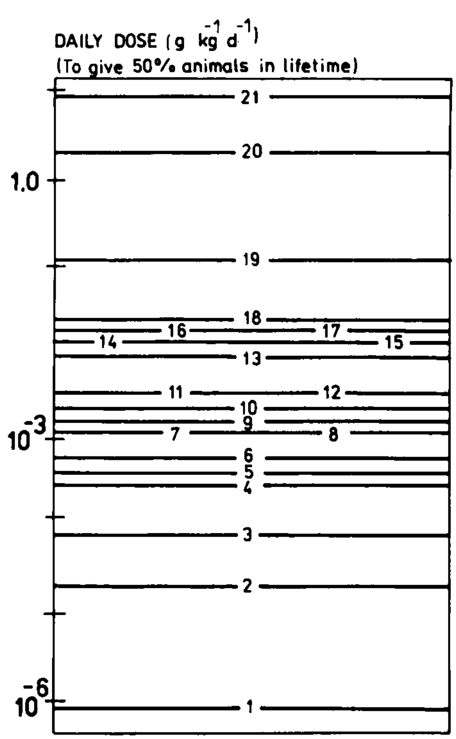

Fig. 9.5. Range of the potency of carcinogens in animals [32]. 1 — aflatoxin B_1, 2 — sterigmatocystine, 3 — 3-methylcholanthrene, 4 — dimethylnitrosoamine, 5 — propyleneimine, 6 — dibromochloropropane, 7 — nitrosopyrrolidine, 8 — 2-acetylaminofluorene, 9 — propane sultone, 10 — tris (2,3-dibromopropyl)phosphate, 11 — dibenzo-[*a*,*h*]anthracene, 12 — benzidine, 13 — urethane, 14 — 4,4′-methylenebis(2-chloroaniline), 15 — carbon tetrachloride, 16 — β-naphthylamine, 17 — safrole, 18 — methyl methanesulphonate, 19 — metronidazole, 20 — trichloroethylene, 21 — saccharin

which became the most extensively used aquatic species for toxicological (carcinogenic) research, are summarized in Table 9.6.

The effect of aflatoxins, which belong to the most important toxins of all, is particularly hepatotoxic under acute as well as chronic conditions. During experiments on animals it was found that in the course of the chronic action of aflatoxins, heavy damage to the liver occurs with a final occurrence of hepatomas and adenocarcinomas, partially with metastases in the lung and kidneys. In numerous studies, the carcinogenic effect of aflatoxins was demonstrated on the basis of a direct interaction with nucleic acids. The knowledge gained by the study of effects of aflatoxins on human embryonic lung and liver tissues indicate that the pathogenic effects of aflatoxins should also be considered in man. This is also suggested by epidemiological studies in certain areas of Africa, indicating a strikingly frequent occurrence

Table 9.6. Carcinogenic effect of certain aflatoxins on rainbow trout (*Salmo gairdneri*) [34]

Carcinogen	Route of exposure	Dose	Time	12-month incidence of hepatocellular carcinoma	%
Aflatoxin B_1	Dietary	6 ppb/in diet	12 mo	102/148	70
	Embryo (21 d)	0.5 ppm/in water	60 min	79/120	66
Aflatoxicol	Dietary	29 ppb/in diet	12 mo	46/57	81
	Embryo (14 d)	0.5 ppm/in water	60 min	58/100	58
Aflatoxin G_1	Dietary	20 ppb/in diet	16 mo	7/40[a]	17
	Embryo (21 d)	5.0 ppm/in water	60 min	7/30[a]	23
Aflatoxin M_1	Dietary	4 ppb	12 mo	6/46	13
Aflatoxin Q_1	Dietary	100 ppb	12 mo	12/113	11

[a] 15 months

of primary cancer of the liver at localities where increased humidity and temperature present natural conditions favouring the growth of moulds on foodstuffs [24].

N-nitrosoamines are an important group of carcinogenic substances which are extensively distributed in aqueous systems. Their occurrence is also supported by the possibility of their production from precursors present in waters (e.g. through reactions of nitrites with secondary amines present in the phytoplankton or with certain pesticides). The persistence and stability of *N*-nitrosoamines in waters facilitates their entrance into the life cycle. Out of about 300 *N*-nitroso compounds tested, carcinogenicity to animals was found in 87% [35]. The carcinogenic effects of certain *N*-nitrosoamines on rainbow trout are shown in Table 9.7 [34]. From the results it can be seen that the *N*-nitroso compounds tested in the rainbow trout most frequently induced hepatocellular carcinoma.

N-nitrosoamines are considered as important factors in the pathogenesis of human tumours of the gastrointestinal and breathing tract. In experiments on animals it was found that effects of repeated lower doses is more dangerous then that of higher single doses. The mechanism of the primary carcinogenic effect of *N*-nitroso compounds at a molecular level is based on the alkylation of nucleic acids, particularly at the *N*-7 site of guanine [15, 24].

Polycyclic aromatic hydrocarbons are a large group of carcinogens, which enter the hydrosphere in the case of an escape of petroleum products. In general, since these substances can hardly be decomposed biologically, they are accumulated in aquatic organisms, and through the nutritional chain they are thus potentially hazardous to the man. In oysters collected

Table 9.7. Carcinogenic effects of certain *N*-nitrosamines on rainbow trout (*Salmo gairdneri*) [34]

Carcinogen	Route of exposure	Dose	Time	Tumor type* and 12-month incidence		%
Dimethylnitrosoamine	Dietary	800ppm/in diet	12 mo	HC	44/60	73
	Embryo (21d)	2000ppm/in water	24 h	HC	57/59	97
Diethylnitrosoamine	Dietary	1100ppm/in diet	12 mo	HC	44/80	55
	Embryo (21d)	2700pp/in water	24 h	HC	68/79	86
2,6-Dimethylnitrosomorpholine	Dietary	1556ppm/in diet	18 mo	HC[a]	77/113	68
	Dietary	1556ppm/in diet	18 mo	GPA	53/113	47
	Dietary	1556ppm/in diet	18 mo	SPA	4/113	4
	Embryo (21d)	3900ppm/in water	24 h	HC	23/59	39
Nitrosomorpholine	Embryo (21d)	3100ppm/in water	24 h	HC	9/61	15
Nitrosopyrolidine	Embryo (21d)	2700ppm/in water	24 h	HC	1/58	2
N-Methyl-N'-nitro-*N*-nitrosoguanidine	Dietary	500ppm/in diet	18 mo	GPA[a]	110/110	100
	Embryo (21 d)	100ppm/in water	60 min	HC	51/60	85
	Embryo (21d)	100ppm/in water	60 min	NB	5/60	8
	Embryo (19d)	10ppm/in water	24 h	GPA[b]	5/25	20
	Embryo (19d)	10ppm/in water	24 h	SPA[b]	2/25	8
	Fry (swim up)	50ppm/in water	30 min	HC	15/24	63
	Fry (swim up)	50ppm/in water	30 min	NB	9/24	38
	Fry (swim up)	50ppm/in water	30 min	GPA	15/24	63
	Fry (swim up)	50ppm/in water	30 min	SPA	11/24	46

*HC — hepatocellular carcinoma, GPA — gastric papillary adenoma, SPA — swimbladder papillary adenoma, NB — nephroblastoma.

[a] 18 months.

[b] 24 months.

in polluted zones, the level of aromatic hydrocarbons was approximately 1 mg kg^{-1}. Further reports present data showing that the amount of benzopyrene type polycyclic hydrocarbons is 9 μg per 100 g of dry matter of bivalves, and in zones with high degrees of pollution as much as 100 μg per 100 g. Among the petroleum hydrocarbons, the highest accumulation in sea organisms was found for mono-, di- and trimethylnaphthene and also for benzopyrenes [33].

Polycyclic aromatic hydrocarbons act as procarcinogens, which can induce, after their metabolic activation, malignant tumours (see the case of the metabolic activation of benzo[*a*]pyrene on p. 143). It is important to note that these compounds have different effects on fish, rodents and man. Thus, some polycyclic aromatic hydrocarbons, which are considered as the strongest carcinogens with respect to their effect on man and mammals, exert either low or zero carcinogenic activity in the case of fishes as main aquatic organisms. For example, 7,12-dimethylbenz[*a*]anthracene and 3-methylcholanthrene were both non-carcinogenic to guppies [36]; benzo[*a*]pyrene, which was administered in diet (1000 ppm) for 18 months to rainbow trout, induced hepatocellular carcinoma in only 22 individuals out of 111 animals [34].

Polychlorinated biphenyls (PCBs) are also pollutants commonly found in aquatic species today, exerting a carcinogenic activity. The PCBs were shown to cause neoplastic changes in the livers of rats and mice as well as adenocarcinoma of glandular stomach in rats. When fed to rainbow trout at 100 ppm for 1 year, PCBs cause no primary effect, however they have been shown to modify the carcinogenic responsiveness of this aquatic species. In the rainbow trout, the PCBs enhance the hepatocarcinogenicity of diethylnitrosamine, yet they inhibit the incidence of liver tumours resulting from aflatoxin B_1 [37].

A further large group of substances, exerting weak carcinogenic effects, which are, however, widely distributed in the hydrosphere, are pesticides. The danger of pesticides for living organism is considerably potentiated by their bioaccumulation.

Certain heavy metals exert carcinogenic effects on animals as well as on man. An endemic occurrence of skin cancer was recorded in Argentina in the Córdoba Province, in connection with a contamination of the groundwater by arsenic from waste rocks after mining silver [10]. In Taiwan it was found that the rate of the occurrence of skin cancer increased depending on the arsenic content in wells. Some authors ascribe a considerable importance to the carcinogenic effect of cadmium, supported by experiments on laboratory animals as well as by studies of persons exposed to cadmium. Nickel and chromium also yielded positive results in experiments on animals; particularly certain chromium substances (chromous acid, chromates) seem to be carcinogenic and they also form ulcers on the skin of sea fish caught in areas polluted with industrial wastes [33].

9.6.10 Tensides

A large fraction of tensides, which are ever more used, eventually enters wastewaters. The content of tensides in municipal wastewaters is between 10 and 20 mg per litre, which has a negative effect on the biological purification of these waters. The low biological degradability of many synthetic tensides increases the probability of their escape into natural waters. On the recipient level the tensides form foam, preventing the contact of water with air. The amount of oxygen dissolved in water decreases, which results in the destruction of aquatic organisms as well as in a deterioration of the self-cleaning capacity of water flows. During the contamination of flows by synthetic detergents, a considerable amount of phosphates also enters the water (phosphates being an important active admixture in detergents), which causes water eutrophization.

Tensides exert toxic effects on aquatic microorganisms, animals as well as plants. Alkylbenzenesulphonate in a concentration of 3 mg l^{-1} was found to suppress the growth of the phytoplankton. Bacteria-degrading polysaccharides were sensitive to concentrations of tensides exceeding 3 mg l^{-1} and those degrading proteins to tensides at concentrations exceeding 7 mg l^{-1}. A similar sensitivity was observed for aquatic Algae, unicellular species being mostly more sensitive than multicellular ones [38].

In the case of animals, for example the *Daphnia magna* died at a concentration of tensides of 5 mg l^{-1} in 10 to 100 hours, whereas the worms *Tubificidae* species and *Chironomus* resisted concentrations up to 10 mg l^{-1} without serious consequences. For fish, concentrations of 4 to 6 mg l^{-1} of alkylbenzenesulphonate, 10 to 12 mg l^{-1} of tetrapropylenebenzenesulphonate and 1 to 3 mg l^{-1} of tensides with C_{12} to C_{14} + ethyleneoxide units was critical [38].

As regards plants, for example the *Batrachium aquatile* was unable to grow in the presence of 1 mg l^{-1} of detergents in water and for *Potamogeton* the concentration of 2.5 mg l^{-1} was critical [3].

In the toxic action of tensides, besides the toxicity which follows from the chemical structure of tensides, its physico-chemical effect is important, since it leads to the hydration and swelling of cells. The cell swelling is increased on decreasing the water surface tension (with increasing concentration of tensides), and thus, metabolic processes in cells are suppressed. With a long-term burden or excess swelling the cells are destroyed. Bacteria, moulds and yeast cells, which have firm cellular walls are more sensitive to tenside effects than, for example, protozoa, which have elastic cell walls, which allow limited changes of the cell shape [38].

A case of ducks living on waters containing detergents was also described. Their feathers were moistened, since detergents suppressed the ability of glands to produce fats which provide the impregnation of the feathers. Thus, some of the ducks were drowned [3].

An important factor in the contamination of waters with tensides for living organisms as well as for man is the ability of these substances to increase the solubility of other, sparingly soluble toxic organic substances.

9.6.11 Petroleum substances

Petroleum and its products exert negative effects on living organisms via physical, chemical, or combined interactions. In the physical action, the hydrophobic character of petroleum substances is of importance. The surfaces of bodies of lower organisms are protected from the aquatic medium by a membrane, which is also hydrophobic. These membranes consist of lipoids, which very easily retain hydrophobic substances. As a result of this petroleum substances can penetrate into bodies of organisms, preventing oxygen uptake and forming mucous layers (in fish, for example, on the gills), which leads to the death of the organisms. The formation of an oil film on the water surface restricts the oxygen transfer from the air, which reduces the re-areation and the oxygen content in water, thus threatening the life of aquatic organisms and deteriorating the self-cleaning capacity of the flow. The oil film also destroys aquatic insects searching for food on the water surface, as well as aquatic birds. The deposit of petroleum substances cannot be removed from the feathers of birds; the feathers thus lose (due to altered surface tension) their thermal and insulating characteristics. Thus, the birds die quickly from pneumonia or due to the disturbed thermoregulation, since they are no longer insulated from the aquatic medium by the air layer between the feathers. An additional effect is that of poisoning by petroleum substances which enter the gastrointestinal tract [3, 39].

The chemical action of petroleum products on organisms depends on their chemical composition, which is in turn dependent on the type of petroleum, on the method of its treatment, on the distillation fraction and also on any additives. Petroleum itself contains about 100 different chemical compounds. They are characterized by different solubilities — benzene derivatives are water-soluble up to a concentration of approximately 100 mg l^{-1}, naphthalenes up to about 30 mg l^{-1} and hydrocarbons with a higher formula mass are water-insoluble. The solubility increases the hazardous character of toxic substances. In general, petroleum products are only slowly degraded biologically and it is highly probable that the most toxic substances are decomposed most slowly and the products of their degradation can be even more harmful than the initial substances [4].

In many cases simultaneous physical and chemical interactions of petroleum components with living organisms are manifested, so that we can consider a physico-chemical action.

Harmful effects of petroleum result mainly from the content of fractions of aromatic hydrocarbons with low boiling points, which are toxic for nearly all organisms. Aliphatic hydrocarbons are assumed to exert no toxic effects on microorganisms. Different toxicities of petroleum components for particular organisms may cause changes in the relative representation of organisms living in natural waters in the case of the pollution with petroleum. In experiments, where petroleum from Libya and mixture of African and Asian petroleum were added to different types of sweet waters, a rapid change to the α-mesosaprobic type was observed in both cases. Due to the action of the petroleum toxic effects, the number of species of aquatic organisms decreased [40]. The toxic concentrations of petroleum and certain of its fractions for the daphnia, worms and fish are given in Table 9.8 [39].

Table 9.8. Toxic concentrations of the petroleum and certain petroleum fractions for daphnia, worms and fish [39]

Substance	LC_{50} (mg l^{-1})		Organism
	in 24 h	in 48 h	
Petroleum	12.1	5.0	Daphnia
	124.5	92.5	Fish
	768.0	519.0	Worms
Gas oil	5.3	0.4	Daphnia
	131.8	78.8	Fish
	380.2	237.4	Worms
Kerosene	7.9	2.8	Daphnia
	22.4	12.0	Fish
	138.0	42.2	Worms
Petrol	0.09	—	Daphnia
	2.5	—	Fish
	25.0	—	Worms

Petroleum which penetrates into natural waters undergoes various changes. About 40% of petroleum is sedimented, 40% resides in water in the form of an emulsion and 20% forms a surface film. The processes of the self-cleaning of water flows containing petroleum are very slow and the bacterial oxidation of petroleum products at the bottom is slower by a factor of about 10 as compared to this process on the surface. The conversions of petroleum components in water is greatly affected by temperature. At lower temperatures petroleum shows increased stability. For example, non-refined petroleum was toxic in experimental flows at low temperatures for 2 months. After 2 to 7 days the amount of emulsified petroleum products in water was decreased by 40 and 15% at temperatures of 20 and 5°C, respectively [23].

Petroleum components inhibit the process of the biochemical cleaning of wastewaters in activation reservoirs at 50 mg l^{-1} and thus, specific procedures are usually employed for the treatment of waters containing petroleum.

Toxic effects of petroleum components on living organisms were observed on birds and fish. The individuals followed exhibited excess excitation and sensitivity, with loss of equilibrium, difficulty in moving and breathing, and subsequent death. Dissection of these birds demonstrated extensive changes in internal organs: hyperaemia of the liver, enlarged adrenal glands, impermeable mucous membranes, and destroyed intestinal flora [3].

On the surface of the human body, petroleum components exert irritating, and in the course of a long contact, pathogenic effects. They remove fat substances from the skin, thus reducing its protective ability; they can result in a strong irritation and formation of a rash. In the case of a several-year occupational exposure, eczemas and carcinomas may develop. The carcinogenic action comes particularly from aromates with higher boiling points (polycyclic substances with 4 to 6 benzene rings). Even higher carcinogenic efficiency is characteristic of components of the tar fraction. During the inhalation of petroleum hydrocarbons, particularly a narcotic effect is manifested, which is frequently accompanied by spasms. In the case of chronic action of aromate vapours, haemopoiesis may be damaged [39, 40].

Direct danger to man through the ingestion of petroleum substances occurring in water is negligible, since they affect the sensory characteristics of water even in negligible concentrations, so that they cannot be involuntarily ingested; the threshold concentration of the taste of petroleum components in water is 0.1 mg l^{-1}, that of petrol smell is as low as 0.05 μg l^{-1} [23].

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9.7 The ecotoxicology of air pollutants

The majority of toxic substances in the air are present in the gaseous state, a smaller portion being in the form of aerosols and dust. The substances from the air enter the organism via the respiratory tract (*inhalation*). In contrast to toxic substances occurring in water, pollutants in the atmosphere exert continuous and long-term effects. They represent a health hazard and catastrophic events can sometimes occur. They affect the cardiovascular and respiratory systems (Table 9.9). They also exert negative effects on the nervous system, increasing its instability.

Harmful effects of pollutants may very frequently be *synergistic*. In the atmosphere, interactions between the pollutants present occur, forming new compounds which exert qualitatively as well as quantitatively different harmful effects as compared to the inital compounds. Many pollutants are carcinogenic, potentiate carcinogenic processes or contribute to the induction of genetic disturbances.

A considerable amount of data is now available about contributions to the occurrence of diseases in city populations. The diseases which belong to this category are as follows: (1) acute non-specific upper respiratory disease, (2) chronic bronchitis, (3) chronic obstructive ventilatory disease, (4) pulmonary emphysema, (5) bronchial asthma, and (6) lung cancer [1]. The development of these diseases is slow, with a permanent deterioration of the health condition of the persons involved. This slowly developing effect, which frequently results in diseases that are often untreatable, can be considered as chronic.

Table 9.9. Toxic effects of substances occurring in the atmosphere

Pollutant	Source of pollution	Effect
CO	Forest fires, decomposition of organic matter, combustion of solid fuels, exhaust gases	Involvement of the blood circulation, haemoglobin, deterioration of heart diseases and diseases of the respiratory system, cephalalgias, increased fatigue
SO_x	Combustion of sulphur in coal, petroleum and oils, treatment of sulphur ores	Irritation of eyes and lung, deterioration of diseases of the respiratory system, increased mortality from other diseases
NO_x	High-temperature decomposition of N-substances in fuels of motor vehicles and in the coal, decomposition of organic substances	Irritation of the lung, deterioration of diseases of the heart and respiratory system, cyanosis, inhibition of plant growth, participation in carcinogenesis
Hydrocarbons	Imperfect combustion of fuels, industrial solvents, petroleum exploitation	Damage to the respiratory system, carcinogenesis, damage to haemoglobin, blood cells, CNS
Photochemical oxidants	Effects of solar radiation on hydrocarbons and NO_x	Deterioration of heart diseases, diseases of the respiratory tract, irritation of the eyes, of the repiratory system, increased fatigue
Asbestos	Mining and treatment of asbestos	Damage to the respiratory system, deterioration of diseases of the heart and of the respiratory system, fibrosis and lung cancer
Dust, soot, oils	Forest fires, combustion of coal, transportation, building industry	Deterioration of diseases of the heart and respiratory system, irritation of mucous membranes, induction of cancer
Metals and their compounds	Mining and treatment of ores and metal compounds, exhaust gases	Diseases of the respiratory system, nervous system, induction of tumour diseases, teratogenic effect
H_2S	Petroleum refinement, chemical industry, microbial processes, agriculture	Irritation of the eyes and respiratory system, physic disturbances, damage to the lung
NH_3, H_2SO_4, HNO_3	Chemical industry, fertilizers, agriculture	Damage to mucous membranes, deteriorated breathing and diseases of the respiratory system, irritation of the lung, eyes and skin
HF	Production of aluminium and fertilizers, chemical industry	Inflammations of the skin, eyes and mucous membranes, loss of calcium
Pesticides	Production and distribution in the industry, agriculture	Induction of cancer diseases, damage to reproduction processes, genetic defects
Radioactive substances	Natural sources, mining of radioactive ores, fission processes, nuclear experiments	Induction of tumours and genetic defects, depression of the organism resistance, damage to the eyes and skin

9.7.1 Reducing pollutants

Sulphur compounds and smoke are reducing pollutants, which may give rise to serious situations under certain meteorological conditions. This has initiated many experimental toxicological studies dealing with the effect of different components of this complex on animals and man. It has also prompted many epidemiological surveys concerning the effect of commonly occurring levels of these pollutants in the environment on populations. The results from these two research fields are summarized in two reports issued by the institution National Air Pollution Central Administration (at the present time supervised by the Environmental Protection Agency): Air Quality Criteria for Sulphur Oxides (USDHEW, 1969b) [3] and Air Quality Criteria for Particulate Matter (USDHEW, 1969a) [2].

9.7.1.1 Sulphur dioxide

Sulphur dioxide is the main harmful substance emitted by industry, as regards its amounts in the atmosphere. The amount of sulphur emitted into the atmosphere, mainly as sulphur dioxide, is even greater than that utilized in the conversion to sulphuric acid or other sulphur compounds. This results particularly from high contents of sulphur in the coal and petroleum burned and from an insufficient retention of sulphur dioxide from combustion products. Sulphur dioxide affects plants as well as animals. It is of primary importance in industrial toxicology from the local, regional and also global standpoints.

Sulphur dioxide exerts an acute effect on plants, which is manifested by a distinctly delimited damage to parts of leaves, which become white or brown, and a chronic effect, which leads to a reduction in photosynthesis. There are large differences in the sensitivity of different species. For example, cotton plants and spinach are very sensitive to sulphur dioxide, cereals, fruit and evergreen trees show a middle sensitivity, and potatoes and maize are fairly resistant.

Irritation effects are characteristic in animals and man. On account of its high solubility in water, these effects are manifested particularly by irritation of the upper respiratory pathways.

For an understanding of the complex biological effect of sulphur dioxide, it is necessary to consider its mechanism from a number of different standpoints. The atmospheric chemical reactions of sulphur dioxide remain subject to some confusion. Many factors, including temperature, humidity, light intensity, atmospheric transport, and surface characteristics of particulate matter, may influence these reactions. Therefore, the study of these reactions under simulated atmospheric conditions is quite difficult. Like many other gaseous pollutants, sulphur dioxide undergoes chemical reactions resulting in the formation of particulate matter, which then settles or is scavenged from the atmosphere by rainfall or other processes. It is well known that high levels of air pollution are commonly accompanied by a marked increase in aerosol particles and a consequent reduction in visibility. Reaction products of sulphur dioxide are thought to be responsible for some aerosol formation. Whatever the processes involved, much of the sulphur dioxide in the atmosphere is ultimately oxidized to sulphuric acid and sulphates, particularly ammonium sulphate and ammonium hydrogen sulphate.

Some of the possible ways in which sulphur dioxide may react in the atmosphere are as follows: (1) photochemical reactions, (2) photochemical and chemical reactions in the presence of nitrogen oxides and/or hydrocarbons, particularly alkenes (olefins), (3) chemical processes in water droplets, particularly those containing metal salts and ammonia, and (4) reactions on solid particles in the atmosphere. Bearing in mind that the atmosphere is a highly dynamic system with great variations in temperature, composition, humidity, and intensity of sunlight it is understandable that different processes may predominate under various atmospheric conditions.

Photochemical reactions are probably involved in some of the processes resulting in the *atmospheric oxidation of* SO_2. Light with wavelengths above 218.0 nm is not sufficiently energetic to bring about the photodissociation of SO_2:

$$SO_2 + h\nu \rightarrow SO + O \tag{1}$$

The lower atmosphere receives only light at wavelengths exceeding 290 nm. In the region of 300–400 nm, solar radiation is absorbed to produce excited electron states in SO_2. A weak absorption band with a maximum around 384 nm is thought to produce an excited triplet state,

$$SO_2 + h\nu \rightarrow {}^3SO_2 \tag{2}$$

and a stronger absorption band with a maximum around 294 nm produces an excited singlet state (Eq. 3).

$$SO_2 + h\nu \rightarrow {}^1SO_2 \tag{3}$$

In darkness and at SO_2 concentration of only a few parts per million in pure air, the oxidation of SO_2 to SO_3 and subsequent formation of H_2SO_4 is too slow to measure. However, in sunlight at SO_2 concentrations of 5–30 ppm and a relative humidity of 32–91%, the overal reaction

$$SO_2 + 1/2O_2 + H_2O \rightarrow H_2SO_4 \qquad (4)$$

occurs to an extent of about 0.1% (of SO_2) per hour. Possibly the photochemical excitation of SO_2 (Eqs. 2 and/or 3) is involved in the overall reaction. Several possible reaction paths have been postulated for the overall reaction, but the identities of the intermediate products remain very much in doubt. It is obvious that the oxidation of SO_2 at the parts-per-milion level in an otherwise unpolluted atmosphere is a slow process. In general, other pollutant species must be involved in the process in an atmosphere undergoing SO_2 pollution.

The presence of hydrocarbons and nitrogen oxides greatly increases the oxidation rate of atmospheric SO_2. *Hydrocarbons, nitrogen oxides*, and *ultraviolet light* are the factors necessary for the formation of *photochemical smog*. This disagreeable condition is characterized by high levels of various oxidizing species (*photochemical oxidants*) capable of oxidizing SO_2.

In relatively dry atmosphere, it is probable that sulphur dioxide is oxidized by *reactions occurring inside water aerosol droplets*, frequently with H_2O_2 as the oxidizing agent. This oxidation process is much faster *in the presence of ammonia*, which reacts with sulphur dioxide to produce bisulphite ion and sulphite ion in solution:

$$NH_3 + SO_2 + H_2O \rightarrow NH_4^+ + HSO_3^- \qquad (5)$$

$$NH_3 + HSO_3^- \rightarrow NH_4^+ + SO_3^{2-} \qquad (6)$$

Laboratory studies have shown that ions of iron(II), iron(III), nickel(II), copper(II), and especially manganese(II) catalyse the oxidation of sulphur dioxide to sulphate in water droplets.

The importance of aqueous-phase oxidation of sulphur dioxide in the atmosphere has been emphasized by a detailed study of the available data for SO_2 oxidation. It was concluded that only about 20% of the SO_2 oxidized in the atmosphere is oxidized by homogeneous gas-phase reaction and the remaining 80% is oxidized in the liquid phase. The same study concluded that about half of the SO_2 in the atmosphere is removed by oxidation to sulphate or sulphuric acid and the other half is removed by dry and wet deposition of SO_2 on land, vegetation, and water.

Heterogeneous reactions on *solid particles* may also play a role in the removal of sulphur dioxide from the atmosphere. In atmospheric photochemical reactions, such particles may function as *nucleation centres.* Thus, they act as catalysts and grow in size by accumulating reaction products. The final result would be the production of an aerosol with a composition unlike that of the original particle. Little research has been done on the role that solid particles play in the oxidation of sulphur dioxide under conditions like those found in the atmosphere. Soot particles, which consist of elemental carbon contaminated with polycyclic aromatic hydrocarbons produced in the incomplete combustion of carbonacetous fuels, have been shown to catalyse the oxidation of sulphur dioxide to sulphates.

Oxides of metals such as aluminium, calcium, chromium, iron, lead, or vanadium may also serve as catalysts for the heterogeneous oxidation of sulphur dioxide. These oxides may also adsorb sulphur dioxide [4].

The effect of SO_2 on mortality and lung pathology was experimentally studied particularly on mice, guinea pigs and insects. The concentration ranges used in these experiments were 10 to 1000 ppm. In mice, 45-day action of sulphur dioxide at a concentration of 25 ppm induced no mortality of experimental animals. At concentrations of 130 ppm, 50% of guinea pigs died after 154 hours. The mice were more resistant as compared to guinea pigs and for their 50% mortality an 847-hour exposure to a concentration of 150 ppm was necessary. These species-related sensitivity differences varied at concentrations of about 1000 ppm, where the 50% mortality in mice was observed after 4 hours, and in guinea pigs after 20 hours. Concentrations below 33 ppm showed no negative effects on the health condition of the experimental animals. In contrast to this, high concentrations induced coughing, moderate dyspnoea, rhinitis, lacrimation and adjunctivitis. Pathological changes were characterized by negligible to small pulmonary oedemas, lung haemorrhages and light to moderate visceral congestion.

The observed lung pathology was dependent on the length of the exposure. Under normal conditions, pulmonary oedemas and areas of consolidation occurred after the action of sulphur dioxide. In guinea pigs two mechanisms were observed which could possibly lead to the mortality of the experimental animals. In the case of rapidly dying animals, there were histopathological changes in the form of the occlusion of the bronchioles and venous congestion with little or no fluid in the alveoli. The animals surviving for two to four hours had fluid in the alveoli, distended bronchioles, and a partial desquamation of the mucosal membranes.

During a chronic exposure of rats to high concentrations of sulphur dioxide, the hypertrophy of goblet cells and mucous glands was observed, similar to chronic bronchitis [5]. In the course of the chronic exposure (5 hours daily, 5 days in the week for three months at a concentration of 300 to 400 ppm) an increased number of mucus-secreting cells occurred in the main bronchi, where these cells also occur under normal conditions and in peripheral airways, where they are otherwise absent. It is of interest that these changes can be induced by the irritation itself without effects of the infection. In this case, the infection is not the essential factor for the excess formation of mucus secreting cells, characteristic for chronic bronchitis. After terminating the exposure, the excess of these cells persists for at least three months.

On the basis of the sulphur dioxide solubility in water it is assumed that this gas will pass fairly rapidly through the upper respiratory ways. Experiments of this type were also performed on larger animals (dogs and rabbits) as well as on man [6]. The use of $^{35}SO_2$ made it possible to trace the sulphur dioxide absorption in doses of 0.05 to 700 ppm. It was found that at concentrations of 20 ppm, 90 to 98% of sulphur dioxide did not penetrate through the upper respiratory ways of rabbits. These results were in agreement with those in dogs and man. At concentrations below 1 ppm, only 2 to 10% of sulphur dioxide did not penetrate beyond the trachea. The results of experiments with $^{35}SO_2$ demonstrated that the sulphur dioxide inhaled is transported very rapidly into the whole body [7]. The sulphur dioxide inhaled is removed only slowly through the respiratory tract. The radioactivity in the respiratory tract can be detected at most for one week after the exposure. A portion of ^{35}S is incorporated into proteins [8].

The basic physiological response of the organism to sulphur dioxide inhalation is a mild degree of bronchial constriction, which is reflected in a measurable increase of the flow resistance. This type of the reaction was demonstrated on guinea pigs, dogs and cats [9].

The most sensitive criterion of the response to the exposure to sulphur dioxide is the degree of flow resistance, which is directly related to the sulphur dioxide concentration. The decrease of the resistance degree is accompanied by reduction in the compliance of the lung. Simultaneously, on increasing the degree of resistance and compliance of the lung, a statistically significant decrease in breathing frequency occurs at concentrations of about 25 ppm. An increase in tidal volume occurs, which is, however, insufficient to compensate for the reduced breathing frequency.

Toxic effects of sulphur dioxide on man. Opinions concerning chronic effects of sulphur dioxide on man are not uniform. According to certain data, chronic bronchitis with a subsequent lung emphysema and myocardial dilatation [9] are the most serious consequence of long-term and repeated irritation. According to this concept, after the absorption of sulphur dioxide a metabolic acidosis occurs with a reduction in the alkali reserve, with compensating excretion of ammonia in the urine and alkalies in the saliva, affecting the metabolism of proteins and glycides and with an insufficiency of B and C vitamins. It also probably adversely affects blood formation as it can lead to methaemoglobin formation [10, 11]. It can react with nucleic acids [12]. Its detrimental effect on the teeth is obvious, and is similar to that of sulphuric acid.

The effect of sulphur dioxide on the skin is irritation, and it is increased by sweating. It is possibly also absorbed through the skin. Its effect is only rarely considered in connection with allergic skin diseases and with asthma [13].

Sulphur dioxide can be detected with a high sensitivity more by the taste than by the smell — from a concentration of about 1 ppm. A concentration of 2 to 5 ppm can be observed quite distinctly, and it exerts irritating effects particularly on persons who are not adapted to it, since those coming regularly into contact with sulphur dioxide have a reduced sensitivity of the smell and taste sensors. A habituation was also observed in animals. A concentration of about 10 ppm irritates immediately and distinctly, that of about 20 ppm irritates eyes strongly, inducing coughing in persons who are not used to sulphur dioxide. Such individuals cannot withstand a concentration of 50 ppm. Exposures to about 30 ppm with temporary peaks of 100 ppm, repeated during a two-year occupational exposure resulted in increased occurrence of the inflammation of the nasopharynx, changes of the smell and taste, and fatigue [11]. After a long-term exposure to concentrations of 25 ppm, no health problems were observed according to certain authors, however, according to other authors, work at concentrations of 10 to 20 ppm leads to heavy damage to the respiratory tract after several years [9]. Several years occupational exposure to concentrations of 30 to 100 ppm of sulphur dioxide is considered as threatening to health. A concentration of 500 ppm is considered as dangerous after just a short exposure. A concentration of 1000 ppm irritates the moist skin within a few minutes [11].

9.7.2 Photochemical pollutants

The main photochemical pollutants are *ozone*, *nitrogen oxides*, *aldehydes*, *carbon monoxide*, *peroxyacetyl nitrates* and *hydrocarbons*. They are of interest from the standpoint of their participation in chemical reactions, which result in *photochemical smog* production.

9.7.2.1 Ozone

Ozone is an irritating agent for the respiratory system, and it can even cause a fatal pulmonary oedema from inhalation in sufficient concentrations. For this reason, it may be considered as strong irritating agent for the lungs. For different species of animals, the LC_{50} for a three-hour exposure period varies from 51.7 ppm for guinea pigs to 21.0 ppm for mice. Lower concentrations induce different pathological lung conditions. In mice exposed to 3.2 ppm of ozone for 4 hours, general lung oedema occurs and at 1 ppm it is possible to observe hyperaemia and excess leucocytes in lung capillaries [14]. In rats exposed to 2 ppm of ozone for 3 hours, a decrease of the water content in the lung was observed with a decrease of the respiratory air volume and of the oxygen intake.

In an environment with higher ozone concentrations, changes of the breathing pattern occur, shallow, rapid breathing being the most characteristic symptom. In rabbits exposed to 15 ppm of ozone for 30 min the oxygen intake was reduced. The volume of the respired air as well as the oxygen intake remained below the values before the exposure, for a further two days [14].

The effect of a two-hour exposure to ozone on the breathing of guinea pigs was followed in concentrations of 0.34 to 1.35 ppm [15]. The first detectable effects were an increased breathing frequency and decreased volume of the respired air. These changes were observed at all the ozone concentrations. Higher concentrations resulted in more intense changes and the reaction occurred sooner. The breathing frequency and the respired air volume recovered to normal values after terminating the exposure. Ozone concentrations of 0.34 or 0.68 ppm showed no effect on the degree of resistance. At higher concentrations the degree of resistance was increased and the values before the exposure were recovered in 90 min.

Reactions of ozone with proteins can be observed in vitro as well as in vivo [14, 16]. The primary reaction of ozone with egg albumin is similar to its denaturation. Changes of the UV-light absorption, particularly in the tyrosine spectrum, and a reduced solubility occur. These structural changes are sufficient to induce the production of antibodies when the ozonized proteins are injected into rabbits. The exposure of rabbits to an environment containing 10 ppm ozone for one hour weekly for six weeks induced the formation of antibodies in the blood serum in detectable amounts. These antibodies reacted very strongly with ozone-treated egg albumin and weakly with thermally denaturated egg albumin. They did not react with native egg albumin.

In lung cells of rats exposed for 45 min to an ozone concentration of 9 ppm changes in DNA and RNA were observed [17]. After one-hour exposure, the amount of the lung RNA increased rapidly and between the second and sixth hour of the exposure it was negligibly reduced below normal values with a rapid development of oedema and acute inflammatory reactions. The amount of DNA remains unaltered up to one hour of exposure, after that it increases, reaching a maximal value at the fourth hour of the exposure. The normal RNA value is recovered six hours later. Similar changes in the DNA and RNA amounts can also be observed in the liver.

Ozone exerts a toxic action by forming free radicals. The formation of these radicals can be accomplished by a reaction of ozone with SH-groups [18] or by a reaction of ozone with unsaturated fatty acids. It is assumed that ozone can cause a lipidic peroxidation under in vitro as well as in vivo conditions [19].

Following repeated exposures of animals to low ozone levels for a time longer than one year, chronic damage to the lung occurs. Daily exposures neigligibly above 1 ppm for one year induce emphysematous and fibrotic changes in the rodent lung. In the lung of rabbits exposed only one hour weekly to tolerable ozone doses, there was increasing damage to the alveolar walls, leading to emphysema, which was observed as an ultimate damage in other species of animals exposed to higher concentrations.

After one-year exposure to low ozone doses, excess ageing of rabbits was observed. Ozone can affect the ageing process due to the dependence of this process on irreversible cross-linking of macromolecules. Lipoperoxidation can also play a role in this process.

In sensitive strains of mice, ozone can increase the formation of lung tumours [20].

On exposing animals to ozone prior to immunological tests with aerosols containing an infectious agent, it is possible to increase the infection occurrence as compared to controls [21]. It is assumed that in this case, protective mechanisms are inhibited, such as the mucociliary streaming or phagocytosis.

Toxic effects of ozone on man. Ozone belongs to the class of substances which are strongly toxic to man. It exerts irritating effects on respiratory organs and on the central nervous system.

Laboratory tests demonstrated detectable effects of ozone already at exposures of 0.3 to 0.8 ppm [22, 23]. In an atmosphere with a concentration of 1 ppm, coughing and fatigue occurs after 1 hour, at concentrations of 1 to 10 ppm cephalalgia and unconsciousness; and death occurs, at concentrations exceeding 1000 ppm, in several minutes. The manifestations occurring just after the exposure may vary. After a latency period lung oedema can occur and after exposures to lower concentrations pneumonia may be observed.

The characteristic smell of ozone can be detected from concentrations of about 0.015 ppm. In low concentrations it is pleasant, higher concentrations are unpleasantly irritating. The irritation of eyes occurs after three hours at concentrations of 0.2 ppm; that of the skin occurs in 1 min at a concentration of 100 ppm [24].

A physical burden during the exposure increases remarkably the sensitivity to ozone. Considerable tolerance may be developed. Nitrogen oxides do not affect the ozone toxicity.

Daily, but short-term exposure to ozone, at concentrations exceeding 5 ppm which may be the case during electric welding, can lead to serious damage to the lung. The action of ozone, due to the structure of its free radical, is similar to that of ionizing radiation (radiomimetic effect) and thus serious damage to health is a strong possibility. Ozone seems to be one of the most hazardous substances of photochemical smog, which is produced by action of atmospheric oxygen and solar radiation on an atmosphere polluted with hydrocarbons and nitrogen oxide [25].

9.7.2.2 Nitrogen dioxide

Nitrogen dioxide also belongs to the group of agents irritating the respiratory tract. Due to its low solubility in water it is only slightly absorbed in the upper airways and thus, the lungs are only very slightly protected. The damage after the exposure can occur even in peripheral parts of the lung. After exposure to high concentrations of nitrogen dioxide death occurs as a result of lung oedema. During an initial exposure to low nitrogen dioxide concentrations a certain tolerance to higher concentrations can be developed, which could be otherwise fatal due to lung oedema. The tolerance developed in this case is referred to as the cross tolerance between nitrogen dioxide, ozone and the remaining agents inducing the oedemas. Low concentrations of nitrogen dioxide damage the lungs after a longer time of the exposure.

Short-term exposures of rats to a concentration of 0.5 ppm of nitrogen dioxide for 4 hours or to 1 ppm for one hour were sufficient to induce reversible histological changes in the lung [26]. In the lung of rats killed immediately after the exposure, there was a disorientation and tearing of mast cells and loss of cytoplasmic granules. The changes were observed particularly in the pleura, bronchi and in surrounding tissues, the greatest damage being observed in the mediastinum. These changes were reversible and they disappeared in animals as soon as 24 hours after the exposure. The release of the granular material and lung mast cells is explained as a result of an acute inflammatory reaction.

During the exposure of rabbits for 4 hours daily for six days to 0.25 ppm of nitrogen dioxide, structural changes in the lung collagen were observed, via electron microscopy [27]. These changes were observable even 7 days after terminating the exposure, which indicates slow recovery.

An emphysema-like damage to the lung occurs after chronic exposures to nitrogen dioxide.

Rats exposed to an atmosphere containing 0.8 or 2 ppm of nitrogen oxide exhibited only moderately accelerated breathing without obvious problems. Their lung was rather coarse and it was different from the lung of controls only by a negligible inflation. They were able to contact in spite of the fact that in the lung from rats exposed to 2 ppm, there was a certain amount of residual air, so that their weight was increased by about 20% as compared to controls. The lung of rats exposed to 2 ppm showed histological changes in the bronchiolar epithelium. The cells were wider and more uniform in comparison with controls with either reduced numbers or a lack of cilia. In the group of animals exposed to 0.8 ppm, there were similar cellular changes. A 16-week exposure to 4 ppm did not greatly change the lung volume. The terminal bronchiolar epithelium was high and hypertrophic. After exposures to 10–25 ppm of nitrogen dioxide the lung remained large, filled with air and heavy; however, neither lung oedema nor increase of the blood volume were detected. The animals died due to respiratory failure. The development of emphysema-like lungs was accompanied by the enlargement of the thoracic cage, with dorsal kyphosis.

Emphysema-like lesions were also observed in the lungs of beagle dogs exposed to 25 ppm of nitrogen dioxide for six months [28].

During acute as well as chronic exposures to higher concentrations of nitrogen dioxide, biochemical changes were observed in addition to the histological damage. The exposure to 1 ppm of nitrogen dioxide for 1 hour induced changes in the production of collagen and elastin in the rabbit lung [31].

Nitrogen dioxide, similarly to ozone, can induce lipidic peroxidation, which can be demonstrated after a 4-hour exposure to 1 ppm in rat lung lipidic extracts [32]. The maximal peroxidation was observed 24 hours after the exposure and it persisted for at least a further 24 hours. The peroxidation was increased on exposing the animals to nitrogen dioxide six times daily. This supports the presence of a cumulative action. The increased peroxidation in surface and tissue lipids was also observed in rats which received a diet poor in vitamin E.

In different species of experimental animals (mice, hamsters, rabbits, squirrel monkeys) it was shown that short as well as long exposures to nitrogen dioxide were able to increase the tendency to the infection of the respiratory tract by bacteria (bacterial pneumonia) or by the influenza virus [33, 34].

Changes in the lung function occur after the exposure of animals or man to nitrogen oxide. In general, the changes are similar to those occurring after the exposure to ozone. The breathing frequency is increased with a simultaneous decrease of compliance of the lung, which are the main changes in the mechanical behaviour of the lung. The degree of the lung resistance is only slightly altered.

During long-term exposures, chronic increases of the breathing frequency and decreases of the lung appliance were observed.

Toxic effects of nitrogen dioxide on man. Irritation is the main effect of nitrogen dioxide on man [35, 36]. Its smell can be recognized already at concentrations of 5 ppm, at concentrations of 10 to 20 ppm it exerts a weakly irritating effect after some time, at 60 ppm an immediate, irritating effect occurs, and exposure to concentrations of 100 to 150 ppm for 30 to 60 min is possible, but is dangerous to human life. A concentration of 300 ppm induces immediately strong coughing and it is very dangerous even in the case of a short exposure [11]. The upper safe limits are considered to be: 60-minute exposure at 10 ppm, 30-minute exposure at 20 ppm, 15-minute exposure at 25 ppm and only 5-minute exposure at 35 ppm [29].

A latency period is typical for poisoning with nitrogen dioxide or with nitrous gases (a mixture of higher nitrogen oxides, particularly nitrogen oxide and nitrogen dioxide where the latter is predominant at normal temperatures). Immediately after the exposure, weaker or stronger manifestations of the irritation, mainly coughing, occur. These manifestations need not necessarily occur after the inhalation. The patient involved feels alright in this case, and the clinical manifestation of the poisoning may occur only after 5 to 72 hours [30]. The latency period can also be shorter. After a long exposure, serious manifestations may occur immediately. The breathing problems can be preceded by a decrease in the blood pressure and an increase of the blood density.

The following types may be considered in the case of acute poisoning:

(1) irritation type — this is the most common and it is accompanied by lung oedema or pneumonia;

(2) reversible type — this is characterized by breathing problems, cyanosis, vomiting, dizziness, and drowsiness leading to unconsciousness. Methaemoglobin can be detected in the blood. Lung oedema and pneumonia occur in the case of the reversible type;

(3) the shock type is manifested in an exposure to high concentrations — shock occurs with rapid interruption of breathing, spasms and death;

(4) the combined type is a combination of the above-mentioned types.

In the case of repeated long-term exposures, nitrogen dioxide induces conjunctivitis, inflammations of the nasopharynx and bronchitis. It also damages the teeth. Its effects on the health are similar to those of the remaining irritating substances. Increases of the erythrocyte count, and decreases of the resistance against infections are sometimes reported after its action. A carcinogenic effect also cannot be precluded.

9.7.2.3 Aldehydes

Besides the various other substances with toxic effects, polluted air may also contain aldehydes, which are formed as reaction products of hydrocarbon photooxidation. The reactions of aldehydes are not very rapid, so that they are accumulated in concentrations of about 0.2 ppm in the photochemical smog. Formaldehyde and acrolein are the most important compounds in this group. Their irritating nature obviously contributes to the increase of the smog smell and to its irritating effects on the eyes. According to estimates, formaldehyde represents a fraction of 50% out of all the aldehydes in the polluted air. Acrolein is more irritating than formaldehyde and forms about 5% of the aldehydes.

9.7.2.3.1 Formaldehyde

Formaldehyde is an irritating substance, which irritates mucous membranes of the nose, upper airways and eyes due to its high solubility. Concentrations of 0.5 to 1 ppm can be detected on the basis of its smell, levels of 2 to 3 ppm exert a moderate irritation, and most people do not withstand concentrations of 4 to 5 ppm [37].

The effects of low formaldehyde concentrations on breathing was followed on guinea pigs [38]. The animals exposed to 0.3 ppm for 1 hour to higher formaldehyde concentrations showed an increased pulmonary flow resistance accompanied by a moderate decrease of the lung compliance.

The breathing frequency and volume per minute were decreased, however, the changes of those factors were not statistically significant up to concentrations exceeding 10 ppm. The general manifestations of the damage to the respiratory system with fomaldehyde are rather similar to those caused by sulphur dioxide, being dissimilar to the damage resulting from the action of ozone and nitrogen oxides. Concentrations of 0.05 ppm induced no changes in the breathing system. Below a concentration of 50 ppm the changes were reversible and recovery was achieved one hour after the exposure.

9.7.2.3.2 Acrolein

Acrolein ($CH_2=CH-CHO$) is a more irritating aldehyde than formaldehyde on account of its unsaturated nature. It irritates eyes and mucous membranes of the respiratory tract already at concentrations below 1 ppm.

The acrolein effect on the breathing system was also followed in guinea pigs [39]. It was found that during an exposure to 0.6 ppm and above, the degree of the pulmonary flow resistance and the respired air volume are increased, with decreasing breathing frequency. The acrolein effects were reversible.

The inhalation of acrolein also affected certain enzymes of the rat liver [40]. After a 40-hour continuous exposure to a low acrolein concentration (2.1 ppm), an increased activity of the alkaline phosphatase was observed. The exposure to 4 ppm for 4, 8 and 20 hours resulted in increased values of the alkaline phosphates of the liver as compared to controls — 135, 222 and 253%, respectively. The activity of the liver alkaline phosphatases and tyrosine-ketoglutanate transaminases were increased in rats 5 to 10 hours after an injection or inhalation of acrolein. The results of research indicate the irritating effect of acrolein in stimulating the pituitary–adrenal system, which induces a hypersecretion of glucocorticoids conditioning the induction or stimulation of the synthesis of larger amounts of protein enzymes of the liver.

9.7.2.4 Carbon monoxide

Mankind encountered the effects of *carbon monoxide* as far back as prehistoric times. It is the most common poison with a suffocation action. It is second to carbon dioxide with respect to the amounts of industrial emissions. Carbon monoxide toxicity is due to its affinity to haemoglobin. This affinity is higher by a factor of 200 than that of oxygen. Haemoglobin in combination with carbon monoxide forms *carboxyhaemoglobin* (COHb) and thus, it can completely reduce the total content of oxygen transported by the circulating blood.

The bond of haemoglobin to carbon monoxide is stronger than the bond to oxygen. There are two mechanisms of the asphyxiant action in poisoning with carbon monoxide, as follows: a decrease of the amount of haemoglobin which is able to transport oxygen and a reduction of the ability of haemoglobin to release oxygen to make it available to tissues.

Besides this main effect, which leads to suffocation, carbon monoxide also exerts other effects. They are, however, of a lower importance in a comparison with the effect on haemoglobin. It is possible to consider effects on myoglobin and on the other tetrapyrol substances. Many enzymes containing trace elements modify their activity by the action of carbon monoxide [41]. An increase of the activity of aspartate-aminotransferase and of the lactate concentration can be used for the indication of acute poisoning [42].

The effect on the nervous system is given not only by the asphyxiant action. Even at a concentration of COHb in the blood below 5%, changes in the higher activity of the nervous system were observed [43]. A decrease of the visual perception [44], of cautiousness [45], a higher number of mistakes during counting and writing [46], deteriorated ability to estimate time [47] and to drive motor vehicles [48], were also described. Carbon monoxide also affects peripheral nerves and its effects on the gastrointestinal tract, on the endocrine glands and on the spectrum of the blood serum proteins and fibrinolysis have also been reported [11].

In the popular literature, the cherry red colour of the skin is reported in individuals intoxicated with carbon monoxide. The colour of the skin is caused by carboxyhaemoglobin and it depends on the oxide concentration in the air, duration of the exposure and natural pigmentation of the skin and membranes. The distinct red colour of the skin and blood can be used to differentiate this poisoning from other forms of asphyxia. The extent of poisoning with carbon monoxide can be measured by determining the carboxyhaemoglobin concentration in the blood [20].

The normal concentration of carboxyhaemoglobin in the blood of nonsmokers is approximately 0.5%. This amount of carboxyhaemoglobin (COHb) is attributed to the endogenous production of carbon monoxide during the heme catabolism. The absorption of exogenous carbon monoxide increases the amount of the COHb in the blood. This increase is proportional to the oxide concentration in the air and to the duration of the exposure and rate of the subject oxygenation. A continuous exposure of man to 30 ppm of carbon monoxide resulted in the formation of 5% COHb. Roughly 80% of this amount was formed after four hours of exposure, the remaining portion of 20% COHb was formed slowly for further 8 hours. It is assumed that during continuous exposures to 20 and 10 ppm of carbon monoxide, 3.7 and 2% of COHb, respectively, are formed. The mentioned equilibrial COHb values are achieved in general after 8 or more hours of exposure. The time necessary for the equilibration can be reduced by the physical activity.

No effect on the human health was observed when the COHb level was less than 2%. In non-smokers, values greater than 2% of COHb (the mean value for smokers is 5% COHb) affected the central nervous system. At a 2.5% COHb level, which can result from about 90-minute exposure to 50 ppm of carbon monoxide, the ability to estimate time interval is reduced, and at about 5% of COHb reduced ability in the remaining psychomotor tests is observed. Cardiovascular changes occur at exposures leading to a formation of more than 5% COHb.

The therapy is based on the removal of carbon monoxide from the environment [20].

9.7.3 Solid particles in the air

Most materials transported with the air, which are of interest in toxicology, may be termed *aerosols* in general. This category includes particulate material in either solid or liquid form, however, it can also include gases and vapours, which are frequently absorbed or contained in particles or droplets transported with the air. Such substances are characterized by an extraordinary degree of dependence between physical characteristics and toxicity. Particles transported by the air may be divided into several wide groups. These are, for example, dust smoke, vapours, fog and a special group including, for instance, smog.

From the hygiene standpoint, particles of a size from 2.0 down to 0.1 μm are the most dangerous. The biological effect of the dust on the organism depends on its composition and physical properties. These characteristics affect the solubility in liquids, the toxicity, the electric charge, etc. The dust particles exert the following effects:

(a) mechanical — effects on the skin, conjunctival sac, damage to mucous membranes and lymphatic pathways in the lung,

(b) toxic — local and/or general changes in certain organs (e.g. perforation of the nasal septum after effects of dust containing chromium or lead),

(c) allergic — shown by an excess sensitivity of the skin or respiratory tract, or possibly by asthmatic manifestations,

(d) carcinogenic.

9.7.3.1 Silicon compounds

9.7.3.1.1 Silicosis

Knowledge concerning silicosis and the other lung diseases caused by dust (*pneumoconioses*) is already very extensive, forming almost an independent discipline. ***Silicosis*** is an irreversible, chronic lung disease connected with the inhalation of the dust of free crystalline ***silicon dioxide.*** The potential for its development is present in many industrial processes, e.g. in mines, quarries, building works, metallurgical works, and the ceramic industry. The earth's crust contains about 55 to 65% silicon, which is present in many crystalline as well as amorphous forms. Silicosis is induced by the crystalline form, based on a tetrahedron with silicon at the centre and four adjoining oxygen atoms.

During the inhalation of silica dust, silica particles are hydrated. The degree of silica solubility is directly proportional to its final toxicity. Particles smaller than 2 to 3 μm are assumed to be more soluble than larger particles. This solubility theory assumes a release of silicic acid, which may be combined with tissue components, thus increasing collagen production [49]. The course of this process is not quite clear under in vitro condition, so that different modifications of this theory may be encountered.

For the induction of silicosis, the effect of crystalline silicon dioxide on *macrophages* (histocytes), cells which belong to the reticuloendothelial system, is of the main importance. These cells are capable of considerable phagocytosis and they serve for removing from tissues foreign substances and residual components after a decay of tissue elements. Silica particles absorbed by macrophages cause their disintegration (autolysis) [50, 51]. During this, substances are released leading to the formation of a ***collagenic tissue*** (fibrosis) and to its ***hyaline conversion.*** This process results in an accumulation of macrophages, replacing ***autolysed elements*** (granulomas) and in the formation of ***fibrohyaline nodules.***

The change of a part of the lung tissue to the ***fibrous tissue*** (lung fibrosis) results in a reduction of the area used in the exchange of gases between the air and blood. The obliteration of bronchi, differences in the elasticity between fibrous and original tissues and requirements for filling the space result in emphysema between the nodules in the tissue, which further deteriorates the situation.

The disease is manifested by problems in breathing, at the outset only in the course of fatigue, but later on also under rest conditions. More advanced silicosis is frequently connected with bronchitis, which is manifested by coughing. Tuberculosis occurs as the most frequent complication in silicosis. Tuberculosis bacteria are able to grow and to multiply more actively in histiocytes that have phagocytized silica particles and thus, they are unable to destroy the bacteria as normal histiocytes. Thus, the combination of the two diseases (silicosis and tuberculosis) occurs frequently.

As mentioned above, the size of silica particles considerably affects the induction of the silicosis. The particle size is important for the following two reasons: (1) only particles of certain sizes (0.1–0.2 to 5–10 μm) can enter the lung with their subsequent deposition in this organ, (2) the particles act through their surface, so that small particles, with a large surface area to volume ratio, are more effective.

9.7.3.1.2 Asbestosis

Asbestos was used as early as 4000 years ago in the region of present-day Finland for strengthening clay vessels, and in the Middle Age as a resistant envelope for dead bodies of rich people. It has always been used for the production of wicks. The industrial use of asbestos dates back to the 1880's and it is very extensively developed today. Its mining continues to increase and a large fraction of the human population comes into contact with asbestos to a greater or lesser extent.

Asbetos is the general name for those silicates which occur in nature in fibrous forms. We can differentiate the following two types from each other: a fibrous species of serpentine (chrysolite) and five fibrous species of amphibole. Chrysolite is the most frequently occurring type of asbestos, characterized by the finest fibres. It forms about 90% of the asbestos used in the industry. Amosite has the longest and coarsest fibres, and crocidolite, which was the first form of asbestos to be suspected of carcinogenic action, and antophyllite are characterized by short fine fibres. The industrial importance of the remaining two forms (actinolite and tremolite) is low.

The disease named *asbestosis* is caused by the inhalation of asbestos fibres. It occurs after 5 to 10 years of working in an environment with high concentrations of the *asbestos dust*; in environments with lower concentrations its latency is longer. Asbestosis need not necessarily be only an occupational disease. It can also occur in persons who have never worked with asbestos and individuals very considerably in their sensitivity. The longer are the fibres, the more harmful is the material from the health standpoint.

Breathing problems and pain in the thoracic region are the initial manifestations, which do not include coughing. The vital capacity of the lung is reduced and the transport of gases is deteriorated without any obliteration of the bronchi. X-ray examination yields much more diverse patterns as compared to other pneumoconioses. The first changes usually occur at the base of the lung, where the normal pattern of vessels is obscured by *irregular shades*, which later become more intense with their extension into lung regions. Thickening of the pleura is characteristic of asbestosis, and this can also be the only X-ray finding. In the developed form of the disease, which can be seldomly observed earlier than 20 years after the exposure, particularly after the exposure to antophyllite, in the pleura, there are a considerable number of *calcifications* [52]. The *lung fibrosis* is diffuse, very different from that involved in silicosis [53]. Asbestos corpuscles were demonstrated in the sputum and lung. These are characteristic formations of asbestos fibres coated by a *brown protein layer* containing iron. They are frequently found in inhabitants of cities and they need not necessarily indicate the presence of asbestosis. Asbestos corpuscles in the lung are formed by a series of chemical reactions occurring along asbestos fibres. In the course of these reactions the fibres become gradually coated with proteins, which may sometimes contain iron, as mentioned above. The ends of fibres have a thick protein coating, so that the fibres are *dumb-bell shaped*. These corpuscles are about 7 μm long and 3 μm in diameter. Pure asbestos fibres situated free in the lung are approximately 50 μm long and 0.5 μm wide [54]. Asbestosis is a more serious disease than silicosis and it is set faster.

A connection has been well demonstrated between residence in an asbestos-containing environment and lung cancer [10]. The rate of occurrence of bronchogenic carcinomas is very high, particularly in a connection with simultaneous smoking and it is possible that these two oncogenic effects, asbestos and smoking, are not only summed, but also amplified. Besides the lung-fibrosis, foci on the pleura, calcification and cancer of the lung, further damage was manifested in workers exposed to asbestos dust — *mesothelioma*, a diffuse tumour, which is extended in the pleura and peritoneum and it is considered to be connected particularly with effects of an environment containing crocidolite. This disease is developed after 25 to 40 yeras after initial exposure and then its course is very rapid and fatal [55, 56].

The particular types of the cancer disease induced by different asbestos species are given in Table 9.10. The table shows that besides the most frequent cancer types, such as bronchial cancer, mesotheliomas of the pleura and peritoneum, it is also possible to observe gastrointestinal tumours and tumours of the larynx, pancreas and lymphatic nodes (lymphomas). The relation between these diseases and asbestos has still not been definitely established [57].

Table 9.10. Asbestos and cancers

Cancer sites	Types of asbestos
Bronchial	Chrysolite (95%)
Mesothelial	Amphiboles
Pleural	Amosite
Peritoneal	Crocidolite
	Anthophyllite
Gastrointestinal	?
Larynx	?
Others (pancreas, lymphatic nodes, etc.)	?

It is assumed that the mesothelioma can be induced only by fibres of lengths exceeding 10 μm and diameters up to 1 μm. Larger fibres with diameter exceeding 3 μm and spherical particles can induce the disease only very rarely. During the inhalation of fibres, their entrance to the lung periphery is controlled by their diameter rather than by their length. These results were obtained after intrapleural injections of different types of asbestos to rats and to other small laboratory animals [58].

It seems that the composition and chemical structure do not play a very important role during the development of the mesothelioma in the course of the intrapleural inoculation, since all the asbestos types and certain very fine glass and ceramic fibres induced the disease. The results of experiments on animals did not support the hypothesis that trace elements or absorbed hydrocarbons can be of importance in the development of pleural tumours [59]. However, recent observations are of interest, showing that following a complete leaching of magnesium from chrysolite, the fibres induced mesothelioma only in few cases in comparison with those containing magnesium.

There is a lack of data about the effect of the fibre size in the development of bronchial tumours.

Current observations have demonstrated asbestos to be a pollutant which is essentially present everywhere. It occurs in large amounts particularly in large cities.

9.7.3.2 Metals and their compounds

Metals and their compounds are a further group of substances with toxic effects on the lung. This is a relatively limited group including the following elements: ***aluminium, arsenic, beryllium, cadmium, chromium, cobalt, copper*** and ***nickel***. Effects on the lung induced by their compounds are mostly caused solely by the metal part of these substances. Only in a limited number of cases are the effects on the lungs attributed to the entire metal compound.

9.7.3.2.1 Aluminium

Aluminium is usually considered as relatively non-harmful metal. From the standpoint of industrial toxicology, the effect of the dust of aluminium and aluminium oxide on the lung are most important. In World War II a new disease was observed in Germany, resulting from the inhalation of fine aluminium dust during the production of incendiary bombs. The disease, which was named *aluminiosis* developed rather rapidly, within some months of the work. It was mainly manifested by dry coughing, and it showed X-ray patterns similar to those observed in silicosis, however, without involving lymphatic nodes. The course of the described disease was very heavy [60]. Some recent studies suggest that the development of lung fibrosis following inhalation of Al dust is connected with lubricants used in the process. According to certain authors, it is the inhalation of aluminium vapours during melting, which results in a damage to the lung; however, other authors completely reject the existence of the aluminiosis.

During the inhalation of the smoke in the production of grinding materials based on corundum, a lung disease occurs rarely, referred to as the "Shaver's disease". This is an interstitial pneumonia without nodules. The etiology of this disease is still unclear. According to certain authors, it is induced by silica and not by aluminium compounds, with a possible simultaneous action of iron oxides. Following dust inhalation, the perforation of the nasal septum can sometimes occur. The occurrence of a lung disease after bauxite inhalation identical with that after the inhalation of metallic aluminium has been only rarely reported. Aluminium oxide dust inhalation led to the induction of lung tumours in mice, which is rather surprising and calls for further attention [20].

9.7.3.2.2 Arsenic

From the standpoint of air hygiene, the high content of arsenic in certain types of coal, particularly the brown coal used in power engineering, is of the main importance. Chemical forms of arsenic occurring in the coal are not still completely known, and there are probably great differences, depending on the origin of the coal. In the ash, arsenic is present in the form of iron, copper and calcium arsenites and arsenates and there is a high probability that a large fraction of this element is bound to these metals in the coal. In certain cases, arsenic was involved in the growth of the original prehistoric plants, before the coal formation, and thus, a small fraction is also bound in organic compounds, which can serve as sources of gaseous emissions. The physico-chemical conditions of coal combustion in thermal power stations leads to the major portion of arsenic in emissions being bound in the form of arsenic pentaoxide adsorbed on the surface of the finest fractions of the fly ash.

Acute inhalation poisoning by arsenic (except for the inhalation of arsine gas) is rare in the general population or in industry. It is assumed that such cases of poisoning can occur only randomly or intentionally. A chronic poisoning from inhalation is much more common. The most frequently encountered symptoms are as follows: vague malaise, abdominal discomfort, pain in the joints and extremities, a gradual loss of strength and pleuritis. In the case of long-term exposures to arsenic, it is possible to observe diarrhoea or constipation, flushing of the skin and sometimes oedema [61].

The carcinogenic effect of arsenic is very important in industrial toxicology. On the basis of many observations it was definitely demonstrated that arsenic in different forms can induce tumours in spite of the fact that these results were not completely validated. Tumours occur of the skin, lung and nasal cavities and more rarely of other organs (gastrointestinal tract, urogenital system and endocrine glands). When attempting to explain the development of these tumours, there are a number of possibilities to consider such as effects of arsenic on various biochemical processes, connection with carcinogenic aromatic hydrocarbons, combined effects of cobalt, nickel and ionizing radiation, relationship between arsenic and selenium and the colchicine-like disturbing effect of arsenic on cell division. Friction effects, injuries and solar radiation are supporting factors in the development of skin tumours. The possible role of arsenic as a strong supporting factor (cocarcinogen) remains still unclear. It is not known which arsenic compounds and what types of exposure may be considered as the most dangerous ones. No justified conclusions can as yet be presented as upper limits for safe doses or concentrations of arsenic in the air.

Levels of arsenic measured in exposed areas also depend on the season of the year. In winter periods they are essentially higher than levels measured in the summer. In areas with increased amounts of emissions containing arsenic and its compounds, it is possible to observe a mass destruction of bees and of other insect species providing pollination. Arsenic falling on grass in these areas can induce stillbirth and a decrease in the milk yield in cattle. Other species of animals can also be involved. Warning changes of the blood count and haemoglobin levels in children were also observed in areas exposed. In a comparison with control children, an increased frequency of the occurrence of respiratory diseases and skin diseases was demonstrated.

9.7.3.2.3 Beryllium

A rapid development of certain specialized industries such as the production of computers, beryllium ceramics, nuclear power engineering, rocket techniques and other complex technologies give rise to the possibility of occupational exposure to beryllium effects. In the vicinity of works producing beryllium, its alloys or salts, and also in coal combustion (where as much as 100 g of beryllium may be present in one ton of certain types of coal), the atmosphere is polluted with this toxic element, which thus leads to the exposure of the population in these localities. The maximal permissible beryllium concentration is as low as 0.002 mg m^{-3}.

Beryllium usually enters the body through the lung, in which a certain fraction of the element is deposited, the remaining portion being distributed into the other tissues of the organism with proteins of the blood plasma. In the blood plasma beryllium forms a slightly soluble complex with phosphates [62–64]. This colloidal phosphates is captured by the reticuloendothelial system (RES) of the liver. This also corresponds to a reduced RES activity after administering beryllium [65]. Beryllium, which is coupled to certain proteins in the lung is also transported into the spleen and bone as well as to the liver. Variable amounts are retained in the lung. The beryllium toxicity is directly dependent on the surface area of particles inhaled [66, 67].

Irritating effects on the skin, eyes and respiratory pathways are observed for the dust of certain beryllium compounds and for a fog or solutions of its salts, particularly fluorides and sulphates. After inhalation, manifestations of the irritation of airways, inflammations of the nasal mucous membrane (sometimes also perforations of the nasal septum), of the pharynx and bronchi can be observed. The degree of irritation may vary, depending on the type of the compound and magnitude of the burden during the involvement of the breathing system. A continuous change in the berylliosis itself can be clearly observed.

Berylliosis is induced by the inhalation of metallic beryllium, of its oxide, fluoride or sulphate; both its acute and chronic forms need to be considered. The acute berylliosis is actually a pneumonia, which may be differentiated from other pneumonias after inhaling other irritating substances, only by the longer latency period and by its clinical manifestations. Chronic berylliosis occurs after several months to years of the exposure. The disease is probably induced by stimulation of the adrenal glands, however, pregnancy and lactation showed no contributions to the manifestations of chronic berylliosis in experimental animals [68]. In the initial stages X-ray examination reveals small shadows on the lung. These later become larger nodules. Similar changes can also be observed in other organs, e.g. in the liver, so that the berylliosis can be considered as a general disease and not only as a disease of the lung. It is probably of an allergic nature [69–72]. The frequency of occurrence of the disease in particular persons varies, for equal exposures, between 0.3 and 7.5% [73, 74].

In the study of the effect of beryllium on fibroblast and myoblast cultures, anomalous mitoses were observed and the cell division was stopped in the metaphase, which was greatly extended. Practically no telophase and anaphase were observed. Beryllium was demonstrated histochemically in the liver and particularly in chromosomes of dividing cells. In the case of fibroblasts, there was a remarkable inhibition of the synthesis of nucleoproteins. Damage to the mechanism of the RNA synthesis is assumed to occur by action of beryllium. Beryllium is bound to DNA in the same way as magnesium, however, its affinity is many times higher. The complex of magnesium with DNA can be easily hydrolysed, whereas the complex with beryllium is stable. It was thus demonstrated that beryllium modifies physico-chemical characteristics of DNA.

The specific effect of beryllium in DNA metabolism may be highly relevant in the elucidation of its experimentally demonstrated carcinogenic action. Primary tumours of the lung in rats typically occur 8 months after intratracheal application. Either a single tumour or multiple tumours may be formed. Histologically those are adenomas, less frequently epitheliomas. By the action on beryllium, certain enzymes were affected, as in other experiments on animals, where the cancer disease was induced by different chemical substances [75]. Beryllium oxide experimentally induced osteosarcoma [76]. The higher rate of the occurrence of tumours in exposed persons has not still been completely confirmed [10].

9.7.3.2.4 Boron

Boron hydrides are among the most dangerous toxins to the lung. They are dangerous on the one hand after their inhalation and, on the other hand, after the absorption through the skin or after ingestion.

Diborane is one of three most toxically efficient boron compounds. Its LD_{50} is 30 to 90 mg m^{-3} during a 4-hour exposure [77]. In the course of higher exposure, manifestations of the irritation of the central nervous system, damage to the kidneys, and lung oedema are observed. Concentrations exceeding 2 to 4 ppm [78] can be detected by the smell and a 15-minute exposure to 159 ppm is lethal [79].

Pentaborane is considered to be the most toxic boron hydride in the case of inhalation. Inhalation exposures of small laboratory animals showed values of LD_{50} of 9 to 46 mg m^{-3}. It exerts particularly a cumulative action on the central nervous system, accompanied by tremor and cramps. Chronic exposures (for 6 months) to vapours at a concentration of 2.5 mg m^{-3} resulted in an insufficient oxygen supply to tissues (anoxia), decreases in the body weight, apathy and tremor. Dissection demonstrated no serious pathological changes [77]. The chronic exposures of animals can lead to damage to the liver and kidneys [80].

The exposure of the human organism to low levels of pentaborane resulted in nausea and drowsiness, whereas exposures to higher levels led rapidly to cephalalgias, dizziness, excitation, pains and spasms of muscles.

Decaborane is a further frequently-occurring boron compound. After a 4-hours exposure, the LD_{50} is 120 to 230 mg m^{-3}. It involves particularly the central nervous system. During repeated exposures, it can also damage the kidneys, livers and vessels [81].

9.7.3.2.5 Cadmium

Cadmium is one of the extremely toxic substances, inducing damage to the lung after inhalation, manifested by an irritation of the respiratory tract, which starts several hours after the exposure. In the final stage, lung oedema occurs, which causes death in these cases. The estimate of the lethal concentration of CdO smoke for man is approximately 5 mg m^{-3} during an 8-hour exposure [82].

After exposure to low concentrations, either local changes (including the damage to the upper airways) or system changes leading to absorption of cadmium can occur. The system changes include damage to the kidneys with proteinuria, anaemia and an increased rate of sedimentation. The damage to the lung is manifested by emphysema. Damage to the upper airways is accompanied by vascular diseases. The material absorbed damages particularly the kidneys, tubular proteinuria [83, 84] being the main manifestation. Analysis of the protein excreted revealed the presence of low-molecular protein β-2-microglobulin [85–87], lysozyme and protein-binding retinol [88, 89].

The damage to the liver is manifested by cirrhosis in animals, but not, however, in the human organism. Prolonged exposures of animals to cadmiun result in a destruction of erythrocytes and in an iron deficiency in the bone marrow, which results in hyperchronic anaemia [90].

The earlierst reports of the carcinogenic effect of cadmium on man are from 1965 [91]. In workers exposed to the dust, carcinomas of the prostate and malignant processes in the gastrointestinal tract, kidneys, liver and lung were observed [92, 93]. Teratogenic effects are also reported for certain cadmium compounds (cadmium chloride, cadmium sulphate) [94].

9.7.3.2.6 Chromium

In the free air of cities, chromium concentration ranges between 10 and 50 mg m^{-3}; in exceptional cases, these values are even higher. In the working environment, the hazard of an excess exposure to chromium may be encountered in the production of dichromates, the use of chromates in chemical industry, and in the course of the production and use of alloys in electroplating or possibly in other technological procedures for metal finishing. Hexavalent chromium is definitely toxic for man, however, trivalent chromium is an important biogenic component necessary in the metabolism of glycides.

The perforation of the nasal septum at the site where the mucous membrane is attached to the nasal septum cartilage is a characteristic damage caused by exposures to chromium salts [95]. Indistinct or nodular changes were observed in the lung of exposed persons in the form of a pneumoconiosis with a pronounced opacity [96]. Since chromium occurs particularly in the form of Cr(VI), which is an efficient allergen, it is not surprising that an increased occurrence of bronchial asthma was observed in exposed persons [97].

Carcinogenic effects are among the most harmful effects of chromium. The adenocarcinoma of the nasal mucous membrane was observed as early as 1890 and today, the occurrence of malignant tumours of the lung in persons exposed to chromium is higher by a factor of 5 to 40 as compared to the normal population [98, 99]. A higher occurrence of malignant tumours was also observed in other organs [100, 101].

9.7.3.2.7 Cobalt

Following the inhalation of the dust of many *cobalt compounds* a considerable irritation of the upper airways was observed, which can lead even to lung oedema in experimental animals. As a consequence of the inhalation, a special form of pneumonia, interstitial pneumonitis with hyperglobulinaemia, and asthmatic reactions or involvement of lungs with the eosinophilia [102, 103], is frequently described.

The carcinogenicity of cobalt is also supported by some experiments on animals and by data on an increased rate of occurrence of tumours at sites of cobalt ore mining [11, 104].

9.7.4 The penetration of carcinogenic substances through the respiratory system

As much as 60% of the etiology of cancer is connected with carcinogenic substances in the environment [105] and thus, it is important to follow the penetration of carcinogenic air-borne substances into the respiratory system. As already mentioned in connection with the toxicity of inorganic substances, the penetration of gases and solid particles is determined particularly by their volatility, solubility and the size of particles, which limits the range of deposit of gaseous and solid aerosols in the respiratory tract.

In general it is reported that particles with diameters exceeding 10 μm are stopped in the nose and pharynx, whereas those with diameters of 0.5 to 5 μm are stopped only in the tracheobronchial tree and alveoli. Particles smaller than 0.5 μm penetrate into the alveoli via diffusion and Brownian movement.

Cigarette smoke and exhalates from motor vehicles, containing gases, liguid and solid aerosols are among the most frequently occurring aggressive components of the environment. Their most carcinogenic components are PAH, which occur in the air either dissolved in tar or sorbed on solid particles. Solid particles can contain metals, which are also frequently carcinogenic. The most frequently inhaled particles contain 99% of minerals and 1% of organic matter, where the PAH are present only in trace amounts.

The metabolism of *polycyclic aromatic hydrocarbons* has been studied intensively since 1933, when Cook et al. [106] isolated tumours induced by 3,4-benzopyrene from coal tar. Among the components of these carcinogenic polycyclic hydrocarbons [107, 108], there are many products of the metabolic transformations of benzo[*a*]pyrene. This compound is hydroxylated by the enzyme aryl hydrocarbon hydroxylase which may be induced in different tissues, one of which is the lung tissue [109]. The hydroxylation, which is the result of their action, is assumed to decrease the carcinogenic potential of PAH.

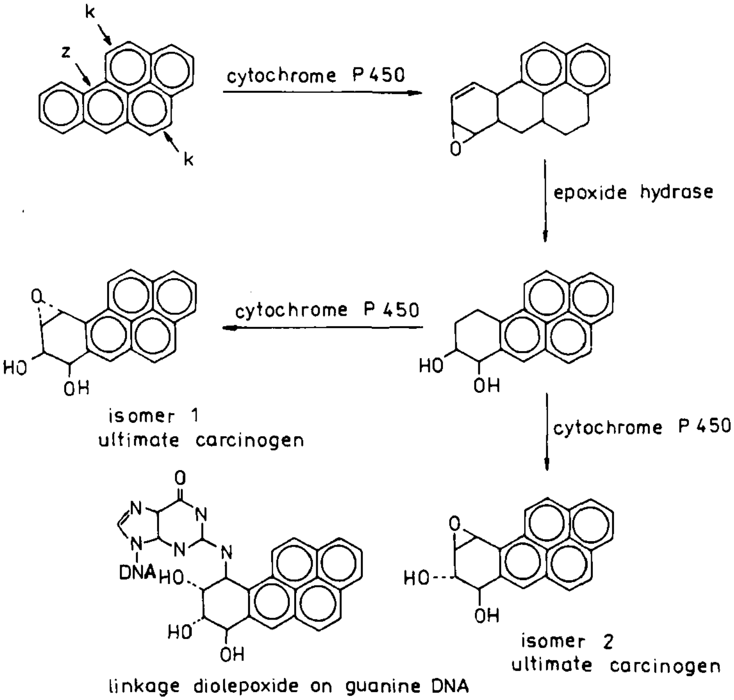


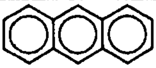
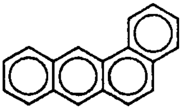
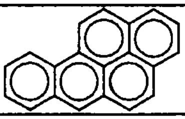
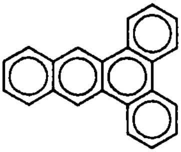
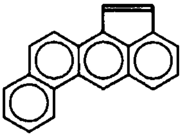
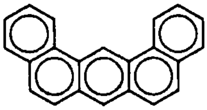
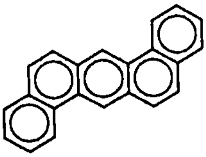
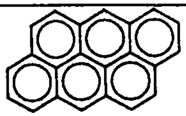
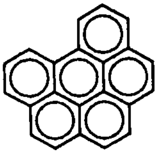
Fig. 9.6. Metabolic activation BaP and linkage of created aduct on DNA

It is also assumed that PAH in their original form are not carcinogenic. Through their activation, particularly during their metabolism, free radicals, epoxides and diolepoxides are formed, which are then bound, for example, to DNA (Fig. 9.6). A concept currently prevalent is that PAH are metabolized through several intermediate steps. Among the various metabolites, epoxides and diolepoxides are considered to be most dangerous from the standpoint of carcinogenicity. They are formed by the activity of microsomal polyfunctional oxidases. The enzyme system participating in PAH metabolism is referred to as aryl hydrocarbon hydrolase. The essential component of this system is cytochrome P450. The epoxidic ring may be formed at any part of the PAH molecule. This arrangement, however, occurs most frequently in the region K (Fig. 9.6). Epoxides formed are further modified by enzymes to dihydrodiols and diolepoxides. On the basis of quantum mechanical calculations and partial experimental results a theory was elaborated, according to which the ultimate carcinogens are diolepoxides where the epoxidic group is a part of the so-called Z ("bay region"). These are therefore PAH with at least one benzene ring angularly attached to the basic linear PAH molecule. The carcinogenicity in vivo was demonstrated in the following group of PAH: chrysene, benzo[*a*]pyrene, benzo[*j*]fluoranthene, dibenzo[*a*, *i*]pyrene, benzo[*a*]anthracene, indene[1,2,3-*cd*]pyrene, dibenzo[*a*, *h*]pyrene, benzo[*c*]-phenanthrene, dibenzo[*a*, *h*]anthracene, benzo[*b*]fluoranthene and 3-methylcholanthrene. The relations between carcinogenicity, mutagenicity and structure of certain PAH are set out in Table 9.11.

One of the basis current problems of PAH effects is that of their metabolic conversions. A knowledge of these processes would make it possible to consider, at least theoretically, potential methods of diminishing the origination of cancer processes by increasing the rate of detoxication of potential carcinogens or by using their electrophilic nature. In the case of PAH (or their metabolites), it is possible to employ their highly electrophilic character and to follow their effect by adding to the reaction system supercritical amounts of a nucleophilic agent, which could be bound preferably to the active electrophilic agent. In this way, it would be possible to prevent binding of PAH with other important cell macromolecules (DNA, proteins, etc.). Substances are known, which are able to block the activity of aryl hydrogenases. Elipticin and its derivatives were bound firmly to the reduced as well as to the oxidized form of cytochrome P450 in the liver microsomes and thus, it was possible to explain their role as strong inhibitors of the BaP-hydrolase. 7,8-Benzoflavene also exerts similar effects, also blocking the carcinogenic effect of 3-methylcholanthrene and 7,12-dimethylbenzo[*a*]anthracene. Indol derivatives also block the activity of BaP-hydrolase in addition to the inhibition of 7,12-dimethylbenzo[*a*]anthracene.

These considerations are, however, complicated by the fact that in the environment the interaction of PAH with other substances is also encountered. In the case of substances obtained in this way, mechanisms of effects of original PAH can occur and, in addition to these a new mechanism,

Table 9.11. Relations between the structure of PAH and their carcinogenic and mutagenic effects

Compound	Structure of basic hydrocarbon	Carcinogen	Mutagen
9,10-Dimethylanthracene		+	+
7,12-Dimethylbenzo[*a*]anthracene (BaA)		+	+
5,6-dihydrodimethyl(BaA)		+	−
8,9,10,11-tetrahydro(BaA)		+	−
Benzo[*a*]pyrene		+	+
Benzo[*e*]pyrene		−	+
Dibenzo[*a*, *c*]anthracene (BacA)		+	+
9,14-dihydro(BacA)		?	+
10,11,12,13-tetrahydro(BacA)		−	+
3-Methylcholanthrene (MCH)		+	+
11,12-dihydro(MCH)		+	+
6,7,8,8,10,12b-hexahydro(MCH)		+	+
Dibenzo[*a*]anthracene (DBA)		+	+
5,6-dihydro(DBA)		+	+
1,2,3,4,8,9-hexahydro(DBA)		−	+
Dibenzo[*a*, *h*]anthracene (DBahA)		+	+
1,2,7,8-tetrahydro(DBahA)		−	+
5,6-dihydro(DBahA)		+	+
7,14-dihydro(DBahA)		+	+
1,2,3,4,12,13-hexahydro(DBahA)		+	+
Anthracene (An)		+	+
4,5-dihydro(An)		−	+
1,2,3,7,8,9-hexahydro(An)		−	+
Benzo[*ghi*]perylene (BghiP)		−	+
5,6,7,8,9,10-hexahydro(BghiP)		−	+

dependent on new functional arrangements, may be encountered. For example, hydroxyderivates and quinones are formed by photooxidation, via interaction with SO_2 sulphonic acids of PAH are produced, and by the reaction with NO_2, nitroderivatives of PAH are obtained. Furthermore, after interactions with free radicals, it is possible to obtain various alkyl and alkoxy derivatives of PAH. PAH nitro derivatives were detected in exhaust gases from engines. In contrast to epoxides and diolepoxides of PAH, which are characterized by a short half-life, nitroderivatives reside in the air for a fairly long time and they act as a direct carcinogen not requiring activation.

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9.8 Ecotoxicology of soil

The soil is the product of very long-term biophysical processes of rocks under conditions which are not readily reproducible. The conversion of rock to fertile soil depends on climatic conditions, species and numbers of specimens of soil microorganisms, plants and human acitivity. The soil is formed at the boundary of the lithosphere, atmosphere and hydrosphere as a substrate, which may be categorized into certain genetic horizons. Physically speaking, *the soil* is a three-phase system, *consisting of solid, liquid and gaseous phases.* The solid phase is formed by inorganic and organic matter (humus and soil microorganisms), the liquid phase is water and aqueous solutions of nutrients, and the gaseous phase is represented by air (including CO_2, which is particularly important since, together with water, it is necessary for photosynthesis).

The importance of the soil in the biosphere lies not only in the production of plants as a source of foodstuffs and certain raw materials for industry; it also affects the composition of the atmosphere and of surface and groundwaters, accumulates solar radiation energy and makes possible the circulation of nutrients. It is thus a critical factor governing whether or not a given terrain can support life.

Typical soils exhibiting distinctive layers with increasing depth are called *horizons* (Fig. 9.7). The top layer, normally several centimetres in thickness, is known as the *A horizon*, or topsoil. This is the layer of maximum biological activity in the soil and it contains most of the soil organic matter. Metal ions and clay particles in the A horizon are subject to considerable leaching. The next layer is the *B horizon*, or subsoil. It receives material such as organic matter, salts, and clay particles leached from the topsoil. The *C horizon* is composed of weathered parent rocks from which the soil originated [1].

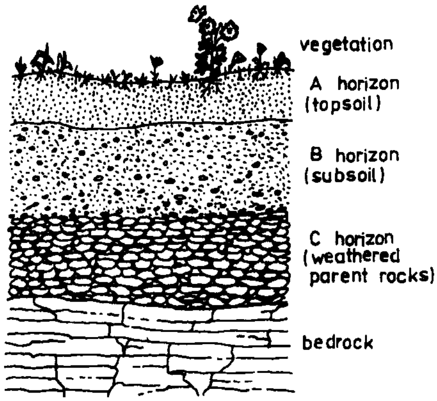


Fig. 9.7. Soil profile showing soil horizon

In order to cope with the demand for food by the rapidly increasing human population, considerable amounts of artificial fertilizers are supplied to cultivated soils, in order to increase plant production. This increase is also a condition for a more rapid growth of animal production. Due to the development of industry in general, large amounts of wastes and pollutants also come onto the soil surface or into the soil, which may negatively affect the natural, normal course of biochemical processes of soil cleaning. The change of the biocenosis and, as a result of this, also the course of biochemical processes in the soil can be affected particularly by the accumulation of chemical substances used for plant protection, which contain active compounds, differentiated by their toxic effects and times of residence in the environment.

9.8.1 Ecological aspects of soil pollution with heavy metals

With the development of modern technology, the consumption of metals and metalloids is rapidly increasing. This holds particularly for *non-ferrous metals*, which until fairly recently were produced only in relatively low amounts, frequently only on the pilot plant or laboratory scale (*beryllium, titanium, germanium, gallium, vanadium, selenium, molybdenum, tungsten*). The production of classic non-ferrous metals is also continually growing, as they gradually find new applications. This holds particularly for *aluminium, lead, nickel, copper, chromium, antimony* and *mercury* [2].

The increasing contamination of the human environment (air, water, soil and foodstuffs) by all these metals is an ever-growing hygiene problem.

Due to the activity of soil and aquatic bacteria and moulds, *organic substances* polluting the environment are chemically decomposed, in contrast to metals which are not chemically degraded and which are accumulated in surface layers of the soil. Soil microorganisms and the aquatic microflora even support binding of a fraction of toxic metals with organic substances, thus either increasing or greatly modifying their toxicity [3, 4]. With the rise of the content of toxic metals in the soil, their contents in foodstuffs of plant and animal origin is also frequently increased. This may bring undesirable consequences for man.

The content of elements in the nutritional chain is affected by chemical characteristics of the elements, soil composition, plant species, time of harvesting and many other factors. For example, changes of pH of soils after applications of calcium can be manifested in plants by an increased intake of molybdenum and reduced concentrations of copper, iron, manganese and zinc. An increased intake of phosphorus, nitrogen and potassium by plants is manifested by a reduction in the intake of sodium and magnesium by farm animals. Intense fertilization with nitrogen-containing compounds also induces a decrease of the content of copper and zinc in plants, which is manifested adversely in the intake of these elements by animals [5].

Trace elements and toxic metals are very important factors in the environment. In the organism, they can affect metabolic processes positively as well as negatively. Due to the pollution of particular components of the environment by a wide spectrum of elements as a result of human activity, these substances enter the human nutritional chain.

The increased use of *fertilizers* makes a large contribution to the penetration of elements into the nutritional chain. The fertilizers can contain, depending on their production and origin, high amounts of particular elements, including toxic ones. By the application of such fertilizers, the content of these elements in the soil is increased and they enter plants via their root system. Certain types of fertilizers, particularly natural superphosphates, contain more than 30 mg kg^{-1} of cadmium and lead. Depending on the soil pH, absorption of these metals and their accumulation in particular parts of plants is encountered. The increased global use of fertilizers fortified by certain microelements has considerably increased their contents in the soil and foodstuffs.

For the study of the entry of toxic elements into the nutritional chain, it is necessary to follow geochemical changes resulting from the development of industry and technologies, where wastes can contaminate particular components of the environment, involving relevant biocycles.

9.8.1.1 Arsenic

The arsenic content in the soil varies from trace amounts to about 40 mg kg^{-1}. In low concentrations it is present in volcanic gases, on land as well as in the oceans. For this reason, it is always present in negligible amounts in all animal and plant tissues and liquids [6, 7]. In nature it occurs most frequently in the form of sulphides, arsenopyrite being the most commonly occurring mineral containing arsenic. These sulphides usually accompany sulphides of other metals.

After several years applications of pesticides containing arsenic, and also in the vicinity of metallurgical works treating ores of non-ferrous metals, arsenic concentrations may commonly be as high as hundreds of mg kg^{-1}. A similar situation can also be encountered in the vicinity of thermal power stations burning coal with high arsenic contents.

With increasing arsenic concentrations, the content of nitrogen in the soil decreases, the population of *Escherichia coli* increases and the germination of mustard seeds is suppressed, in spite of the fact that in a range of concentration of 13 to 21 ppm, the germination was even improved as compared with controls. Arsenic is accumulated in surface layers of the soil and the soil may become gradually sterilized for the growth of certain plants, particularly of Papilionaceae. For a complete sterilization of the soil, very high concentrations are, however, necessary, which cannot occur in practice. The toxicity for plants is modified by the solubility of the preparation used, the iron content in the soil or possibly by the types of fertilizers used. On strongly polluted soils, plants adsorb higher amounts of arsenic, but these amounts do not acutely endanger human health. High contents of arsenic in the tobacco of American cigarettes was considered to be connected with the mass use of pesticide-containing preparations in the USA in comparison with low contents of this element in tobacco from Bulgaria, Turkey and other countries, where these preparations were not used in large amounts. The problem of the arsenic content in tobacco was considered particularly from the standpoint of its assumed carcinogenic effects in smokers [7].

One of the most efficient methods for removing arsenic from highly polluted soils is deep ploughing, which facilitates the transport of arsenic into the sorption substrate thus speeding its penetration into deeper layers. The use of more resistant cereals is also recommended (e.g. *Secale cereale*).

In certain fruit trees, where excess arsenic induced a zinc deficiency, the spraying of zinc sulphate or zinc chelates on leaves was shown to be a good approach. A simultaneous application of nitrogen into the soil was also advantageous [8].

The data available indicate that most cereals, vegetables and fruits contain 0.1 to 1 mg kg^{-1} of arsenic (related to dry matter). From the standpoint of the soil contamination, superphosphates containing arsenic may be the source. Feeding of cattle with hay containing high amounts of arsenic (10 mg kg^{-1}) resulted in manifestations of poisoning in the case of a daily intake of the hay of 1 to 2 kg per animal. It gave rise to anorexia, reduced weight increments, decrease or complete interruption of the milk production and particularly accumulation of arsenic in animal tissues and its increased excretion with the milk.

9.8.1.2 Chromium

In the earth's crust, there are about 125 mg kg^{-1} of chromium, and this element occupies the 20th position as regards its abundance. Its concentration in the soil ranges between trace amounts and 250 mg kg^{-1}, sometimes it can occur in even higher amounts. Cultivated plants can contain as much as 10 mg kg^{-1}. Chromium is present in the soil particularly in its trivalent form and thus, it is rather weakly absorbed by plants. For this reason it can barely threaten human health even when agricultural products are grown in areas burdened by an excess pollution with chromium [9]. Plants accumulating iron can usually also accept higher amounts of chromium [10]. The chromium content in the soil also increases with the use of phosphate fertilizers [11].

There is only scattered information about chromium concentrations in foodstuffs. In general, foodstuffs of plant origin contain only very low amounts of chromium, usually ten to several hundreds of micrograms per kilogram of dry matter. There are only few data about the content of chromium in foodstuffs of animal origin. Chromium is probably not accumulated in such materials (the contents are roughly 75 $\mu g\ kg^{-1}$, in the milk approximately only 10 $\mu g\ kg^{-1}$).

9.8.1.3 Copper

The mean concentration of copper in the earth's crust is about 50 $\mu g\ kg^{-1}$. The higher copper concentrations are found in ferromanganese minerals. Copper is concentrated in the mineral fraction of the soil; soils containing manganese oxides or those rich in organic substances also contain higher contents of copper. The copper content in soils is very variable. The largest range of values is in brown soils on chalk on terraces and slopes and in a gley soil on non-calcareous lowland deposits. More constant values can be observed in chernozem illimerized on loesses, in brown soil on orthogneisses and small layers and in meadow soil on calcareous lowland deposits.

Copper is an essential element. It is of a great importance in the metabolic processes of plants, its content in plant tissues being very low, much lower than those of zinc and manganese. Copper ions form complexes with proteins and with the other biopolymers in plant tissues. These complexes are more stable than those of the other metals. Binding to proteins enhances the catalytic activity of copper. Copper participates in many oxidation-reduction enzymatic systems, and it is thus of importance particularly in respiration and photosynthesis processes. In plants it is also essential in the nitrogen metabolism. Its concentration in plants ranges from 1 to 50 $\mu g\ g^{-1}$ of dry matter. Concentrations below 5 $\mu g\ g^{-1}$ probably represent a copper deficiency [12].

Toxic effects of copper on plants occur very rarely, coming into question only in the case of increased concentrations of copper in the soil after excess applications of fungicides containing this element. Whether a particular copper concentration in plants is insufficient or, on the other hand toxic, depends on the plant species as well as on the physico-chemical composition of the soil.

9.8.1.4 Molybdenum

Molybdenum is an essential element for plants. Amounts between 0.2 and 0.7 mg kg^{-1} in the soil are considered as normal, those below 0.2 mg kg^{-1} are insufficient and concentrations exceeding 0.7 mg kg^{-1} are considered as excess levels [13]. Fertilizers contain on average 2.0 to 5.9 mg molybdenum per kg [14].

Molybdenum occurs in the environment generally in fairly low concentrations.

9.8.1.5 Nickel

Nickel does not occur in large amounts in the earth's crust. As with arsenic, its occurrence in the environment is ubiquitous. The nickel content in the soil ranges between 3 and 1000 mg kg^{-1} [15].

A high content of nickel in the soil is toxic for plants [16]. In comparison with the biomass of soil bacteria and moulds, the ability of plants to absorb and metabolize this element is low. Thus, the soil bacteria and moulds are more important than plants for nickel removal, as is the case with some other metals [17].

9.8.1.6 Lead

The mean lead concentration in rocks and soils are approximately 20 μg g^{-1}. Most values are in the range 10 to 130 μg g^{-1}, depending on the thickness of the layer, locality and certain rock characteristics. In acid rocks the lead content is usually higher than in alkaline ones. It is normally present in rock simultaneously with zinc and copper. Its concentration in the soil is directly reflected by its concentration in groundwaters. For this reason, high concentrations of lead in the soil are very dangerous from the ecological standpoint. Besides natural sources, from which lead enters water on the one hand, on the other hand, into the atmosphere in the form of dust, smoke from forest fires and aerosols from sea water. The current most important sources of environmental pollution by this element are the mining and treatment of ores, production of accumulators and use of petrol containing tetraethyllead. The lead from exhaust gases is deposited in the form of lead oxide, chloride and bromide on the vegetation and soil in the vicinity of roads. Only a small portion enters into plants from the soil through the roots. Atmospheric pollution is the main source in the aboveground green parts of plants. The lead content in plant leaves shows a high correlation with the concentration of atmospheric lead and it is usually inversely proportional to the distance from the emisssion sources.

9.8.1.7 Vanadium

The natural vanadium concentration in the soil is 5 to 140 mg kg^{-1}. In areas with a considerable fallout of fly ash the values may be as high as 400 mg kg^{-1}. From the soil it is washed out into water in its pentavalent form [18].

Vanadium belongs to the group of ubiquitous elements and thus, it is not surprising that it can be found in all the components of foodstuffs. The following concentrations were determined: in potatoes 1 μg to 1.5 mg kg^{-1}, cow milk 0.2 to 10 μg kg^{-1}, and in cattle meat approximately 1 μg kg^{-1} fresh weight. In spite of this rather low content, food is the main source of this element for man. On the basis of different analyses the daily vanadium intake is assumed to be in the range of several tens of μg to 2 mg.

9.8.1.8 Zinc

The mean zinc concentration in the earth's crust is 40 mg kg^{-1}. In soils its concentration varies between 10 and 300 mg kg^{-1} of dry matter [19]. The content in the soil depends on the zinc content in parent rocks.

Zinc is an essential element for the growth of plants. An insufficient concentration in plant tissues is shown by growth disturbances. Its toxic effect is manifested only very rarely, in areas with a high soil pollution by this element. The zinc concentration in grasses and cereals is typically between 10 and 100 mg kg^{-1}.

The mean daily intake of zinc in different regions of the world is between 5 and 22 mg [20]. The foodstuffs rich in proteins usually contain sufficiently high zinc concentrations (10–50 mg kg^{-1} fresh weight). In contrast to this, fruits and vegetables contain only low zinc concentrations (6 and 2 mg kg^{-1}, respectively).

9.8.2 Nitrogen in the soil and its conversions

The beginning of great interest in the *conversions of nitrogen* in the soil may be dated back to the period when the extraordinary importance of this biogenic element for foodstuff production was realized, i.e. the second half of the last century. Methods for improving the supply of nitrogen to cultivated plants were rapidly found and the crop yield was improved by using nitrogen fertilizers.

In the early investigation of nitrogen conversions in the soil, pioneer work was performed by soil microbiologists, who demonstrated unambiguously by the discovery of azonitrification, mineralization, nitrification and also denitrification biological processes that the nitrogen conversions in the soil are primarily the results of the soil microflora activity. Physicochemical principles of nitrogen conversions in the soil were gradually also demonstrated and complicated relationships were revealed between particular partial processes. The conversions of nitrogen in the soil can be the main cause of many accompanying ecological, nutritional and also economic problems.

9.8.2.1 The abundance and representation of nitrogen in the soil

Nitrogen occupies the fourth position as regards its abundance in the solar system, after hydrogen, helium and oxygen. The total nitrogen amount on the Earth is about 2.17×10^{17} t [21] and it occupies the 20th position

Table 9.12. Nitrogen abundance in nature [21]

Environment	Total nitrogen amount (t)	% of the total N amount of the Earth
Atmosphere	0.425×10^{16}	1.96
Lithosphere	2.127×10^{17}	98.03
Biosphere	1.804×10^{11}	0.01

with respect to the content of elements of the Earth [22]. Its abundance in particular components of the Earth is given in Table 9.12.

From the table it follows that in comparison with nitrogen occurring in the rock of the lithosphere and in the atmosphere, its content in the biosphere (terrestrial humus, sea sediments and biological tissues) is essentially negligible.

A considerable portion of nitrogen has been accumulated in the pedosphere (the soil). The forms in which it now exists have been brought about by complicated and long-term processes. The decisive conditions considered in this connection are as follows:

— processes of forming the atmosphere with molecular nitrogen,

— non-biological processes yielding organic substances,

— biological processes of nitrogen conversion.

The total nitrogen content in the earth's pedosphere is estimated from a knowledge of carbon content. Considering the carbon and nitrogen ratio in the humus to be C:N = 10, the pedosphere was found to contain about 0.9×10^{11} t of nitrogen.

In the natural ecosystem, the nitrogen content in the soil is kept at a fairly steady level which depends on the climate, vegetation type, physicochemical characteristics of the soil, nature of the terrain, and microflora and microfauna activity [23]. The nitrogen–soil relationship is, however, simultaneously dynamic, and any change of characteristics of the environment can result in a change of the soil nitrogen level. As a result of this, there are different nitrogen contents in different soils, not only in the topsoil, but also in the profile.

The contribution of factors affecting the total amount of nitrogen in the soil can be arranged in the following sequence [24]: climate → vegetation → relief → soil-forming substrate → age.

9.8.2.2 The qualitative structure of the soil nitrogen

The major portion of nitrogen in the soil is found in organic compounds (95–98%) and thus, only a small portion involves inorganic nitrogen. The two forms are present in the soil, mutually interacting as a result of processes of the *mineralization of organic nitrogen* and *immobilization of mineral nitrogen*. The mineralization leads to a biological transformation of organic substances containing nitrogen to a mineral form, and the immobilization is the reverse conversion of mineral nitrogen to organic substances. Both processes are brought about particularly by living organisms.

9.8.2.3 Biological immobilization

The biological immobilization is a conversion of mineral nitrogen, in which it is bound into organic structures. It occurs as a result of the assimilation of mineral nitrogen by plants and by the rich microflora. The immobilization by plants is the most important form of nitrogen immobilization.

Mineral nitrogen in any form accepted by plants cannot be directly incorporated into proteins, however, it needs first to be transformed via keto acids into molecules of amino acids. All these processes are anabolic and endothermic and thus, they require energy, which is mainly released by the oxidation of organic substances produced during photosynthesis and CO_2 assimilation.

The reduction of nitrates to nitrites and ammonia occurs just after their entrance into plants, mainly in thin small roots. When the roots do not contain sufficient amounts of reducing substances, then the enzyme nitrate reductase is unable to reduce all the nitrogen accepted. It is then transported into aboveground organs of plants, where its reduction can continue. In the case of an uptake of excess nitrates only 30 to 50% is reduced in the roots and the remaining portion is transported into the stem and leaves. They can accumulate, polluting the plant mass if there is insufficient energy for the reduction.

Nitrogen accepted by plants is usually bound in the immobilized form for longer times than that bound by soil microorganisms. Its release usually occurs only after decay of the plants (after harvesting), i.e. only at the time when the plant body becomes a component of the soil organic matter. Not only the soil nitrogen, however, also nitrogen from fertilizers is immobilized with plants in the case of intense agriculture. The scale of the immobilization depends on soil-ecology and production conditions, on the type of the plant grown, on the crop yield and of course, also on the dose of fertilizers supplied.

The basic requirement for *nitrogen immobilization* by microorganisms is the presence and biological decomposition of organic matter with a low nitrogen content or with a high C:N ratio. Under these conditions, the microbial mineralizer does not find sufficient nitrogen in the organic matter to be decomposed, and it is forced to utilize and immobilize mineral nitrogen from the environment. Thus, the immobilization intensity depends essentially not on the content of easily degradable organic substances, but mainly on their qualitative structure.

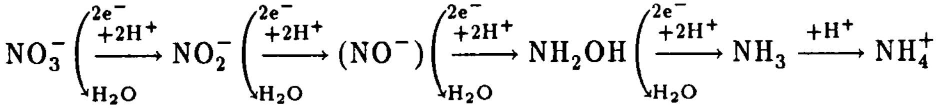
The nitrogen immobilization can be provided by decomposed organic substances from the humus, from residual parts of plants after harvesting and of course from dung supplied. Not only nitrogen released in the soil, but also nitrogen added in natural or anthropogenic ways can be immobilized. Mineral nitrogen can be immobilized very actively by decomposed straw of cereals, where cellulose is the efficient immobilization component. In this case, the immobilization function is fulfilled by a specialized physiological group of microorganisms decomposing the straw. The immobilization effects of plant residues after harvesting, particularly of the straw, are frequently considered to compete with the mineral (particularly nitrogen) nutrition of plants. It was shown that introduction of straw into soil by ploughing can reduce the extent of nitrogen nutrition of the plants with negative consequences for the crop yield.

At the present time, particularly in developed countries, the nitrogen supply to the soil is at a high level, so that even ploughing of all the straw into the soil need not result in any major decrease in the content of mineral nitrogen in the soil.

Factors affecting the immobilization of mineral nitrogen include essentially all the factors governing the general activity of the soil microflora. Particularly the aeration, which is closely related to the soil humidity, is of importance. Under aerobic conditions, mineral nitrogen may be immobilized more rapidly in comparison with conditions with insufficient air.

9.8.2.4 Nitrates in plants

Nitrate assimilation can occur in any plant organ in the presence of sufficient amounts of saccharides, which release during their oxidation the energy necessary for the reduction of nitrates. The entire reduction and assimilation process can be described by the following scheme:



$$NO_3^- \left(\overset{2e^-}{\underset{H_2O}{\xrightarrow{+2H^+}}} \right) NO_2^- \left(\overset{2e^-}{\underset{H_2O}{\xrightarrow{+2H^+}}} \right) (NO^-) \left(\overset{2e^-}{\underset{H_2O}{\xrightarrow{+2H^+}}} \right) NH_2OH \left(\overset{2e^-}{\underset{H_2O}{\xrightarrow{+2H^+}}} \right) NH_3 \xrightarrow{+H^+} NH_4^+$$

The enzyme starting the NO_3^- metabolism is nitrate reductase (flavoproteid containing molybdenum). A further reducing enzyme is nitrite reductase (flavoproteid containing bivalent iron and bivalent copper).

The nitrate reduction is an important process, since it facilitates the entrance of NO_3^- into the plant metabolism. The resorbed ammonia nitrogen, urea nitrogen and amino acids can be easily utilized by the plants. Nitrates accepted are used for the synthesis of nitrogen-containing organic substances only after their reduction to ammonia. This reduction is sensitive to the environmental conditions. In the case of a lack of saccharides as energy sources, or if the activity of the reductases is lessened, nitrate nitrogen can be accumulated in plant tissues.

Molecular mechanisms of nitrate accumulation depend not only on the nitrate reductase system, but also on the ability of roots to take from the soil, nitrate or ammonium ions, and on the plant's capacity for their conversion by assimilation processes to higher products. Besides this, the assimilation depends on the ability of a given genotype to transport substances necessary for the synthesis. It was shown that genotype differences of the nitrate reductase level do not depend on the nitrate content in tissues [25]. Nitrates are accumulated in plant organisms at high concentrations when all the nitrogen accepted cannot be utilized for the production of amino acids and for subsequent protein synthesis [26]. This occurs when the plant, in the course of its metabolism, is unable to reduce the accepted nitrates into the assimilable ammonia form.

Nitrate assimilation in the plant is the result of the following three sequential processes:

(a) intake and translocation of NO_3^- ions from the external environment into cells,

(b) reduction of NO_3^- ions to ammonia,

(c) incorporation of nitrogen in its reduced form through keto acids into amino acid molecules.

Thus, it can be said, with some simplification, that the nitrate concentration in the plant, or more precisely in its particular parts, follows on the one hand from the intensity of accepting NH_3^- ions and, on the other hand, from the intensity of nitrate reduction in the plant metabolism.

9.8.3 Ecological aspects of soil pollution by pesticides

Soil pollution by pesticides may arise from several sources. A high proportion of pesticides comes into contact with the soil either during their direct application to the soil against soil pests and weeds, or indirectly as a fallout when applying pesticides in the form of a spray or powder. Other mechanisms are: flooding, rain and dust, industrial and municipal wastes, and residues after harvesting of plants treated with pesticides during their vegetative period.

Pesticides in the soil environmnet exhibit essentially two types of the behaviour: either they can *persist in the soil* or they can *disappear from the soil*, depending on adsorption and desorption, leaching and diffusion, evaporation and decomposition. The movement of pesticide in the soil starts by the leaching and diffusion, and via evaporation they enter the atmosphere [27]. In these processes adsorption is a decisive factor, depending on the chemical and physical characteristics of the pesticide compounds (chemical structure of the molecule, its polarity, stability, solubility, and volatility), the type and composition of the soil (loamy fraction, content of organic and mineral substances, pH value, moisture, temperature), as well as on the nature of the pesticide applied.

9.8.3.1 The persistence of pesticides

Considerable research effort has been paid to the problems of the persistence of chemical means for the plant protection. Many of the studies have been aimed at the persistence of pesticides in the soil. *Insecticides* based on chlorinated hydrocarbons are particularly persistent, for instance DDT, BHC isomers and so-called polychlorinated cyclodiene compounds, aldrin, dieldrin, andrin, heptachlor. In many countries the use of these pesticides has been either restricted or even prohibited on account of their persistence in the environment. For chemical protection of plants they are gradually being replaced by organophosphate and carbamate substances, which are more toxic, but are less stable in the environment (e.g. parathion, dichlorvos, carbaryl, propoxur).

From the standpoint of their persistence in the soil, the pesticides can be categorized as follows:
— highly persistent — can be detected even after 18 months,
— persistent — occurring up to 18 months,
— medium persistent — detected up to 12 months,
— less persistent — detected up to 6 months,
— non-persistent — detected up to 3 months.

Pesticides containing metals and chlorinated hydrocarbons such as DDT and aldrin belong to the highly persistent substances; persistent ones are urea and triazin pesticides; medium persistent ones include amides and derivatives of benzoic acid; less persistent pesticides are based on phenoxyacetic acids, toluidine and nitriles; non-persistent ones include carbamates and organophosphates. This categorization is, however, not precise; depending on conditions, some pesticides can exhibit a persistence different from that following from this classification.

9.8.3.2 Physical, chemical and biological processes involved in the degradation of pesticides

In the soil, pesticides are exposed to different effects which bring about their degradation. The removal of pesticides from the soil may occur as a result of physical, biological and chemical processes, which have not yet been sufficiently investigated. Among the *physical processes*, light, evaporation, washing out and adsorption are especially important. The most important *biological processes* include metabolic processes in microorganisms and plants. Oxidation, reduction and hydrolysis are the basic *chemical reactions* involved [28].

Depending on the exact location of the pesticide (on the surface or below the surface of the soil) different processes will predominate in the degradation. On the soil surface, at the boundary between the gaseous phase (air) and solid phase (soil) the physico-chemical phenomena such as photochemical decomposition and oxidation are of great importance.

Agrochemical effects and washing out result in a *transport of pesticides* from top layers of the soil into deeper layers. During the deactivation and degradation of pesticides in the soil, biological processes are mainly involved together with adsorption, hydrolysis and reduction. The effect of soil microorganisms on pesticide persistence was studied by comparing sterile and non-sterile soils. In the sterile soil, pesticides resided for a very long time, whereas in the non-sterile soil they were degraded very rapidly. Phenoxyacetic compounds were found to be decomposed by the bacteria *Arthrobacter*; triazine compounds were decomposed by fungi, bacteria and protozoan. The bacteria *Pseudomonas* and *Bacillus* decompose organic substances containing phosphorus. Pesticides affect the enzymatic and antibiotic activity as well as multiplication of certain soil bacteria. In deeper soil layers, in the absence of oxygen a more rapid degradation of DDT and DDD was observed.

The soil moisture helps to speed the degradation of pesticides in two ways. On the one hand, it presents more favourable conditions for the activity of microorganisms and, on the other hand, it facilitates the transport of pesticides, increasing the rate of their evaporation. An exception are fumigants, which are degraded more slowly in moist soils in comparison with the degradation in dry soils.

The presence of organic substances and clay particles increases pesticide persistence in the soil. This is a result of an increased adsorption of these substances on humus and clay particles. As a result of this, pesticides become a suitable substrate for the activity of soil microorganisms. The rate of their evaporation and washing out is decreased.

Certain pesticides pass from the soil through the root system into plants and, as a result of this, their content in the soil is reduced in the vicinity of roots.

9.8.3.3 The penetration of pesticides from the soil into plants

Pesticides are usually applied directly onto plants or into the soil. Some of them penetrate into all the parts of the plant, independently of the method of their application. The residual amount is also affected by the dosage and number of applications, physico-chemical characteristics of the substance, the form of the preparation, type of plant and soil, and atmospheric conditions as well as the length of the period between the treatment and harvesting.

As already mentioned, residual amounts of pesticides in plants can also result from the presence of these substances in the soil. The degree of transfer of pesticides from the soil into the plant depends on the type and concentration of the compound and on the plant species and soil type.

The condition for uptake of the pesticide by the plant is given by its persistence or system characteristics. The most persistent pesticides are particularly organometallic (most of them organomercury) compounds or derivatives of chlorinated hydrocarbons. Depending on the concentration in the soil, they can be identified especially in root crops, carrot, radish, beet, potatoes and plants giving oil. The rate of uptake of these substances by plants are different even in the case of substances with a similar persistence [29, 30]. The uptake can also be different in the case of identical plants [31]. Solid pesticides penetrate more easily into agricultural products from sandy and clay soils [32].

Some pesticides can be found in the soil arising from its preceding pollution, whereas system compounds are applied into the soil intentionally. They are distributed from the soil by conductive tissues together with nutrients into the whole plant. The rate of the penetration, particularly in the case of granulated forms, is connected with the water content in the soil. The higher is the soil humidity, the more rapid the pesticide uptake by the plants. In the soil as well as in plants, pesticides are exposed to the action of microorganisms and enzymes in biotransformation processes. The metabolites produced are mostly not different from those detected in animal organisms; differences are of only quantitative rather than qualitative character.

Mutual interactions between different pesticides in the soil can also occur [33].

9.8.4 Biological aspects of soil pollution by petroleum substances and natural gas

It goes without saying that petroleum is a vital raw material for energy production, heat, and also as a raw material for the production of a great variety of refinery and petrochemical products. However, on soils polluted by petroleum and by most of its products, the plants are destroyed.

For the resolution of problems of the *microbiological degradation* of petroleum products in water-permeable soils under aerobic and anaerobic conditions, an understanding of the mutual relationships soil–microorganism–petroleum substances is of essential importance. The upper layers of the soil play an important role from the standpoint of physico-chemical sorption and as a medium where different polluting substances, including petroleum substances, are destroyed due to biological processes. Biocenoses in the soil are different from biocenoses of recipients and thus, the destruction of petroleum substances and in general of industrial wastes in the soil profile has a quite specific character.

The conversion of petroleum substances in the soil depends on:

(a) the type of petroleum hydrocarbons,
(b) the geological-pedological conditions,
(c) the hydrological conditions,
(d) microbial processes.

The escape of natural gas from the gas distribution networks also exerts a considerable effect on physical, chemical and biological processes in the soil. The extent of the gas zone depends greatly on the rate of its escape, depth of the groundwater level, type of pipeline, the nature and moisture of the soil, treatment of its surface, etc. The composition of the gaseous phase in the soil is affected by the microbiological oxidation of methane. The rate of this depends on the soil temperature, presence of oxygen and the content of nutrients. At low temperatures, this microbial process is restricted, which also restricts the anaerobic zone.

An escape of natural gas leads to the poisoning of trees. The damage to vegetation by such gas occurs for several reasons; decrease of the oxygen content in the soil as a result of displacing oxygen by the gas leads to the formation of a reducing medium, changes of the microbial biocenosis, secondary drying or moistening of the soil, excessive increase of nitrogen and carbon dioxide contents in the soil, etc.

9.8.4.1 Petroleum substances and microorganisms

There is a considerable understanding of the *relationships between microorganisms and petroleum substances.* The action of microorganisms on petroleum hydrocarbons can be considered from the standpoint of the human activity as both positive and negative. The positive effects are as follows:

(1) Locating deposits of bitumens on the basis of geomicrobiological methods — for example the occurrence of methane bacteria can indicate natural gas, propane bacteria indicate the presence of petroleum, and similarly for bacteria utilizing butane, pentane and hexane.

(2) The release of petroleum from collectors by the action of microorganisms — active cultures of bacteria increase the useful yield of petroleum deposits. After inoculating the deposit with the appropriate bacteria, microbial processes induce a decrease of the viscosity and density of petroleum. Due to the decomposition of heavy petroleum hydrocarbons, natural gas is released, thus increasing the pressure driving petroleum from porous spaces. Changes to phase boundaries in the system water – petroleum – collector also occur.

(3) Changes of physico-chemical characteristics of petroleum substances by action of microorganisms.

(4) Destruction of wastes containing petroleum substances — biodegradation of these substances in surface and wastewaters from the petrochemical industry and in the soil.

(5) The synthesis of organic compounds by microorganisms from petroleum substances — production of proteins from natural gas, salicylic acid from naphthalene, amino acids from light fractions of petroleum, and yeast nutrients from liquid n-alkanes.

The negative effects are as follows:

(a) microbial corrosion,

(b) the formation of sludge and deposits.

From the standpoint of environmental protection, the microbial oxidation of petroleum substances is most important. The microorganisms which can grow in petroleum substances, utilizing them as the only source of carbon, consist of bacteria and fungi in the soil. The fungi are certain genera such as *Penicillium, Aspergillus*, which oxidize alkanes fairly intesively; among the bacteria, these are certain species of the genera *Pseudomonas, Micromonospora, Vibrio, Bacillus, Nocardia* and some actinomycetes. The oxidation and mineralization processes in petroleum substances are of a great importance not only in the carbon circulation in nature but also for the cleansing of water and soil from these substances. The oxidation of saturated petroleum hydrocarbons by microorganisms is considered to occur according to the following sequence: saturated hydrocarbons → unsaturated hydrocarbons → higher alcohols → keto compounds → fatty acids → carbon dioxide and water.

The rate of the biological degradation of n-alkanes in the soil depends on the length of the substrate chain. In a mixture of n-alkanes with an admixture of aromatic hydrocarbons (4 to 10%) it was found that yeast cells utilize very intensively n-alkanes, independently of the amount of aromatic hydrocarbons in the substrate, whereas aromates and isoalkanes are oxidized much more slowly. Bacteria oxidize n-alkanes and aromates at essentially the same rate. Compounds containing hydroxy and carboxy groups are oxidized most readily. In the case of a good aeration they are rapidly converted to carbon dioxide and water. In the absence of oxygen, the oxidation of these compounds is possible only in the presence of hydrogen acceptors such as nitrates and sulphates. Besides n-alkanes, microorganisms are able to utilize aromatic hydrocarbons, which are decomposed intensively in concentrations up to 0.01%. Pure cultures of the *Bacterium bensoli* were separated from the soil, these were able to oxidize benzene, toluene, xylene, ethylbenzene, cumene, cymene and others. Similar effects were observed for the bacteria *Mycoplana bullata, Bacterium platichoma.*

In general, the utilization of aromatic hydrocarbons is more difficult for microorganisms. Non-utilized hydrocarbons are, however, also converted by microorganisms in the co-oxidation process. This process depends on the possibility of the oxidation of non-utilizable hydrocarbon occurring simultaneously with the oxidation of a readily utilizable hydrocarbon.

The presence of a certain amount of petroleum substances in the soil increases the number of microorganisms which are able to decompose them. Thus, in petroleum fields, on the sites of former refineries and of the current petrochemical industry, in the soil layer under the surface we can find large amounts of bacteria utilizing petroleum hydrocarbons.

The microbial population of the soil is mainly in a depth from 0 to 20 cm; this also holds for microorganisms utilizing petroleum substances. Their population declines mainly in the zone 0 to 10 cm. The amount of microorganisms oxidizing petroleum substances hence decreases with increasing depth, but with a uniform distribution of petroleum substances, their content relatively increases with the depth.

The vertical distribution of oxidizing bacteria in the soil profile during the degradation of petroleum substances is dependent on several factors: on the content of organic compounds, on the soil type, on the amount of hydrocarbons released in soil air and on the partial pressure of oxygen present in particular soil layers. The development of microorganisms in the soil is conditioned by the temperature, content of gases and pH of the soil. At a low temperature and pH, the formation of enzymes of soil bacteria is reduced.

9.8.4.2 Harmful effects of petroleum substances on organisms

An anomalous geochemical environment enriched in or oversaturated with the petroleum substances or natural gas is manifested in *anomalies of the vegetation.* The extent of changes is conditioned by the degree of the saturation of the environment with petroleum substances. By their action, quantitative and qualitative changes in the structure of different species occur. The changes are manifested by the decay of the most sensitive component of the vegetation — mosses and lichens and then by that of sensitive species of higher plants, with a considerable propagation of resistant species. According to the relationship between the plant species and polluting substances, it is possible to consider positive and negative phytoindicators.

The vegetation cover greatly affects the formation and protection of the environment and it participates in the removal of substances polluting the atmosphere. In this way circulation of water in nature and its quality are also affected. Thus, a knowledge of the concentration of harmful substances in relation to the vegetation is of considerable economic importance and it frequently facilitates the indication of different types of the pollution. The effect of natural gas and petroleum substances on vegetation is manifested in several ways. On polluted areas, the vegetation cover is remarkably reduced. Depending on the type and amount of the polluting substance, the aboveground vegetation may be even completely destroyed. The recovery of the vegetation is dependent particularly on the adaptation of plants to the new, unfavourable conditions. The original state may be recovered on surface polluted with petroleum substances only in the vegetation period of the second to fourth years after the contamination.

It is a matter of general agreement that plants preferring warm and dry conditions are more resistant to emissions than other species. However, in the case of pollution by petroleum substances and natural gas, xerothermic species are shown to be sensitive to the impact of petroleum substances. On all the polluted areas, the number of species is reduced. Certain sensitive plant species are suppressed or even completely destroyed and only tolerant species can survive.

The tolerant species undergo gradual propagation and thus, on most polluted areas a vegetation cover with only one species is obtained, similar in character to a monocoenosis. Examples are species of the ruderal vegetation such as *Melilotus alba, Bromus tectorum, Elytrigia repens, Daucus carota* and *Cirsium arvense.*

On the basis of the resistance and rate of occurrence of plant species on polluted areas, it is possible to divide plants into three groups depending on their resistance to petroleum substances or natural gas.

Resistant species are those resisting the effects of the petroleum substance. In this group, there are, besides the above-mentioned species forming the monocoenoses, weeds of universal character: *Artemisia vulgaris, Anthemis arvensis, Bromus sterilis, Conyza canadensis, Medicago lupulina, Reseda lutea, Rapistrum perenne, Tussilago farfara*, etc. The occurrence of resistant species on polluted areas is characterized by their distinct and predominant abundance, reflecting their easy adaptability to unfavourable conditions of the environment. The reason for their propagation and formation of extensive cover lies in their easy vegetative reproduction with a subsequent restriction of the presence of competing species of plants.

Tolerant species exhibit an adaptation to an environment polluted with petroleum substances. The main tolerant species are as follows: *Achillea millefolium, Anagallis arvensis, Carduus acanthoides, Echium vulgare, Tithymalus cyparissias, Linaria vulgaris, Plantago lanceolata, Poa annua, Taraxacum officinale, Trifolium pratense, Trifolium repens, Senecio vulgaris, Vicia villosa, Pastinaca sativa* and *Tragopogon orientalis.* The occurrence of tolerant species with a low abundance is also characterized by slight covering of the surface. Tolerant species can resist smaller amounts of petroleum substances and they are partially displaced to the margins of the polluted area.

Sensitive species are those, which are gradually eliminated from the polluted area, such as *Capsella bursa-pastoris, Cardaria draba, Cichorium intybus, Dactylis glomerata, Stellaria media, Veronica hederifolia, Hypericum perforatum, Plantago major, Papaver rhoeas, Viola tricolor, Melilotus officinalis, Onopordum acanthium, Symphytum officinale, Ranunculus arven-*

sis, Arrhenatherum elatius, Leontodon autumnalis. The adaptability of the sensitive species is remarkably restricted. Even if they start to grow on polluted area, they decay very rapidly.

Both inhibiting and stimulating effects of petroleum substances can be observed. In certain species a *shift* of their *development* was also observed. *Melilotus alba, Daucus carota, Reseda lutea, Achillea millefolium*, etc., bloom either earlier or more generally later in comparison with the same species on adjacent unpolluted areas, the period of blooming being shifted by ±14 days. Some of the above-mentioned species can even bloom twice in one vegetation period.

On areas polluted with petroleum substances, the vitality of the vegetation is investigated in addition to other factors. In the first stage after the pollution, necrosis and other pathological manifestations occur.

Even *some stimulating effects* of substances contained in petroleum and petroleum products can also be observed. On polluted areas, there is a violent and unusual growth of certain species, achieving its optimum limit most frequently in the second year after the pollution with petroleum substances. Giant forms were observed for example with *Melilotus alba, Daucus carota, Artemisia vulgaris*, etc. In the first year after the interaction, dwarf forms can also occur, with the species *Daucus carota, Anthemis arvense, Solidago gigantea*, etc. In certain species, at localities polluted with petroleum substances, lateral branching occurs with a lack of a terminal part.

In the escape of *natural gas* from gas lines and from distribution networks, it is also possible to observe different reactions to the presence of the gas in the rhizosphere. Soil pollution by natural gas results in changes in the vegetation cover, which can terminate by its complete destruction. Desiccation, nanism and sterility are prevalent; changes of the characteristic colour of leaves and their deformations are also observed. Only few species are resistant to a long-term action of natural gas.

The resistant species, characterized by an increased vitality, adaptability or even stimulation are *Dactylis glomerata, Junctus effusus, Rubus fructicosus*, etc. These species form a rapidly growing cover.

The sensitive species include *Anemone narcissiflora, Luzula sylvatica, Cerastium holosteoides, Scrophularia nodosa*, etc.

Tolerant species with nanism manifestations are *Anagallis arvensis, Trifolium repens, Elytrigia repens, Lathyrus latifolius, Chenopodium strictum, Chenopodium album, Sinapis alba*, etc. In agricultural crops nanism is observed, for example, in maize (e.g. 20 cm), lucerne, barley and wheat achieving a height of about 10 cm and being sterile. Changes of the colour (greyish-blue-green) and shape of needles or even desiccation may be observed for the pine and larch. Poplars, willows, birches and oaks are fairly resistant.

In the study of different effects of petroleum substances on the growth of plants it was found that the more viscous petroleum substances (oils, diesel fuel, etc.) exert strong and long-term effects. The limiting value dividing the amount of a petroleum substance with the positive effects from that with negative effects depends on many factors, which include particularly the soil group, type and composition of the petroleum substance, species of plants or the type of phytocenosis. Climatic conditions, character of the locality, effects of further pollutants in the soil and atmosphere are also of importance [34].

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