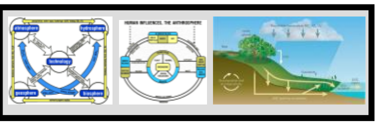
Chapter 1

Introduction to Environmental Chemistry



Dear student, this chapter deals with Introduction to Environmental Chemistry. It deals with definition of some basic terms and concept of Environmental Chemistry. You will also discuss further about the properties of chemicals in the environment, environmental transformation and degradation as well as matter and cycles of matter.

Learning objective of the unit

Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:-

- Define the terms such as Environment, Environmental Science and Environmental Chemistry
- Mention some properties of chemicals in the environment
- Compare and contrast environmental transformation and degradation
- Explain abiotic transformation and degradation
- Discuss biotransformation and degradation processes
- Describe matter and cycles of matter

1.0 Introduction to Environmental Chemistry

Dear student, under this main content you will learn about the basic concepts of environmental chemistry. Do you know what Environmental Chemistry is? Attempt the following activities by yourself.

Learning task 1.0

a) Define Environment, Environmental Science and Environmental Chemistry
b) Describe the various parts of the environment
c) Describe the environmental impacts of human activities on the environment and vice versa
d) Discuss influence of industrialization on environmental pollution

To understand Environmental Chemistry, it is important to have some appreciation of environmental science as a whole.

Environmental science in its broadest sense is the science of the complex interactions that occur among the terrestrial, atmospheric, aquatic, living, and anthropological environments. For our purpose, environmental science is defined as the study of the earth, air, water, and the living environments, and the effects of technology there on. It includes such disciplines, as chemistry, biology, ecology, sociology, & government that affect or describe these interactions.

The Environment

Everyone nowadays seems to be concerned about the environment, but what do we mean by the term?

It is

- The place where we live or work?
- The atmosphere which we breathe and water which we drink?
- Unspoilt areas of the world which could soon be ruined?
- Part of the atmosphere which shields us from harmful radiation?

The environment may include all these areas and any other area which could affect the well - being ness of living organisms. To understand the environment, we must realize that it is never static. For convenience it can be said that the *"environment"* consists of the biosphere, the atmosphere, the geosphere, the hydrosphere, the anthroposphere, and all the fauna and flora, with their interactions as a whole. This is illustrated as follows using the various compartments of the environment as "separate" entities.

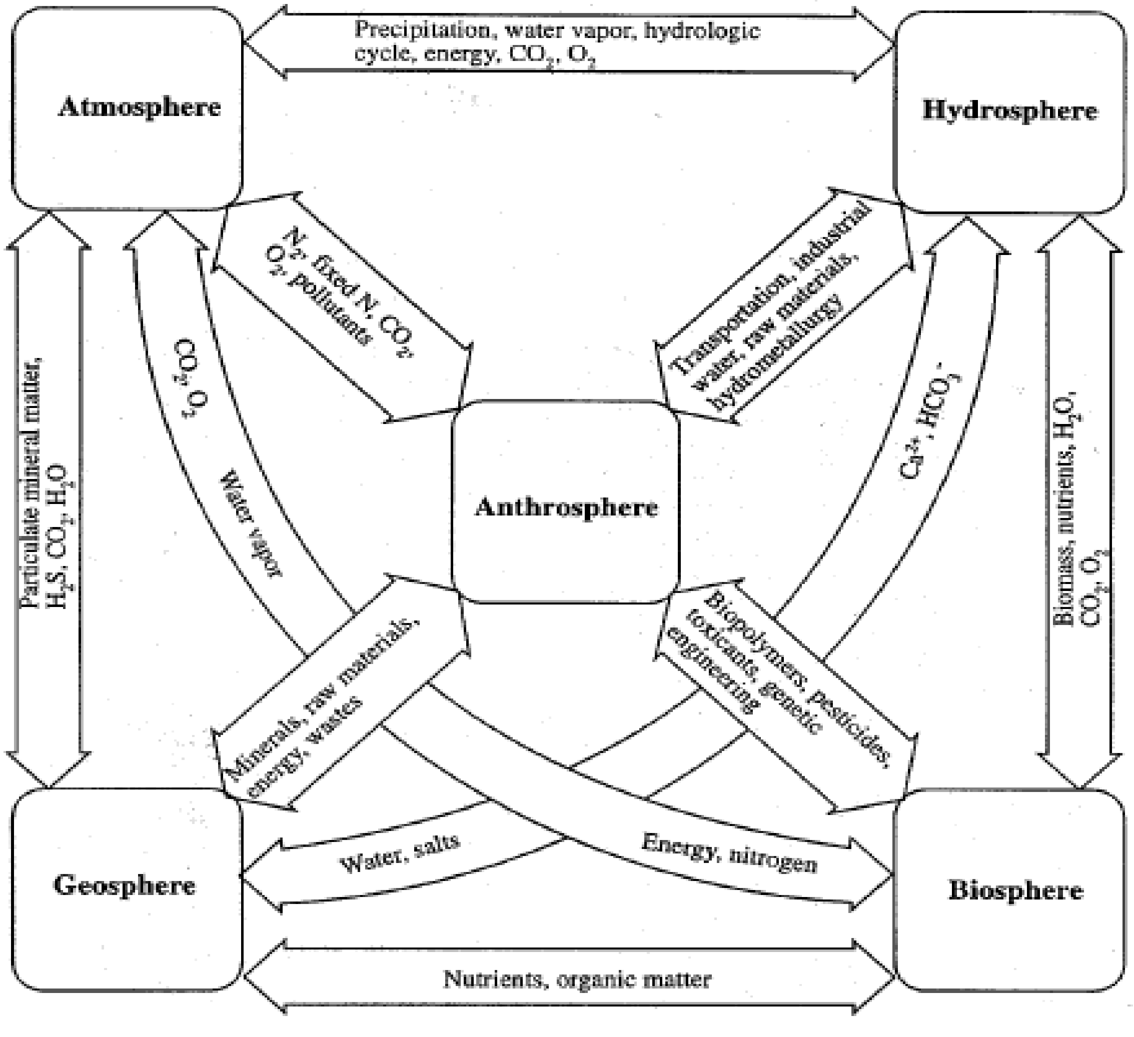


Figure 1.1 Illustration of the close relationship among the compartments of the Environment

i) The Atmosphere

A thin layer of gases that cover the earth's surface

Its roles are:

- ✓ reservoir of gases,
- ✓ moderate earth's temperature,
- ✓ absorbing energy & damaging Uv radiation from the sun,
- ✓ transport energy away form the equatorial regions, and
- ✓ pathway for vapor-phase movement of water in the hydrologic cycle

ii) The Hydrosphere

- ✓ Contains earth's water
- ✓ Over 97 % of earth's water is in oceans

Most of the remaining fresh water is in the form of ice. Therefore, only a relatively small percentage of the total water on earth is actually involved with terrestrial, atmospheric, & biological processes.

iii) The Geosphere

- ✓ Consists of the solid earth, including soil, which supports most plant life
- ✓ *Lithosphere* is solid part of the geosphere that is directly involved with environmental processes through contact with the atmosphere, the hydrosphere, & living things. The lithosphere varies from 50-100km in thickness.
- ✓ The most important part of the lithosphere is so far as interactions with the other spheres of the environment are concerned is its thin outer skin composted largely of lighter silicate-based minerals called the *crust*.

iv) The Biosphere

- ✓ All living entities on earth compose the *biosphere*. The biosphere is the name given to that part of the environment consisting of organisms & living biological material.
- ✓ Living organisms & the aspects of the environment pertaining directly to them are called *biotic* & other portions of the environment are *abiotic*.
- ✓ the biotic environment can be classified into three functional groups;
    i. **Producers** - the autotrophic (self - nourishing) organisms largely are green plants.

ii. **Consumers** - the heterotrophic (other - nourishing) organisms, chiefly all animal life, including mammals, fish, insects and bird; these ultimately depend upon consumption of producers to sustain life.

iii. **Decomposers -** heterotrophic organisms, chiefly the bacteria and fungi that break down complex compounds from waste materials - including dead producers and consumers - to again make the chemical components available to producers.

The biosphere strongly influences and in turn is strongly influenced by, the other parts of the environment

Organisms in the biosphere are involved in:

- ✓ Removing carbon dioxide, CO_2, - photosynthesis & reducing global warming
- ✓ Weathering processes
- ✓ Biomass production
- ✓ Respiration
- ✓ Anaerobic /aerobic degradation, & so on

Human & the biosphere

Humans depend upon the biosphere for food, fuel, & row materials. Bioengineering of organisms with recombinant DNA technology, older techniques of selection, hybridization & causing great changes in the characteristics of organisms & promise to result in even more striking alternations in the future. It is the responsibility of human kind to make such changes intelligently & to *protect* and *nurture* the biosphere. Virtually the entire *biosphere* is contained by the *geosphere and hydrosphere* in the very thin layer where these environmental spheres interface with the atmosphere. There are some sophisticated life forms at extreme depths in the oceans, but there are still relatively close to the atmospheric interface. To a large extent, the strong interactions among living organism and the various spheres of the biotic environment are best described by *cycles of matter* that involve biological, chemical, & geological processes & phenomena. Such cycles are called *biogeochemical cycles*.

v) The anthroposphere

The *anthroposphere* may be defined as the part of the environment "*made''* or modified by humans and used for their activities. Of course, there are some ambiguities associated with this definition. Clearly, a factory building used for manufacturing is part of the anthroposphere, as is an ocean going ship used to ship goods made in the factory. The ocean on which the ship moves belongs to the hydrosphere, but it is clearly used by humans.

Ecology and Ecosystem

Ecology is the science that deals with the relationships between living organisms with their physical environment & with each other. *An ecosystem* consists of an assembly of mutually interacting organisms and their environment in which materials are interchanged in a largely cyclical manner. An ecosystem has physical chemical & biological components along with energy sources & pathways of energy & materials interchange. The environment in which a particular organism lives is called habitat.

Dear student, the study of ecology is often done by dividing it into four broader categories:

- The terrestrial environment: land & its biomass
- The freshwater environment:
  - ✓ standing-water habitats (lakes, reservoirs)
  - ✓ running-water habitats (rivers, streams)
- The oceanic marine environment - characterized by saltwater
  - ✓ shallow water of continental shelf - neritic zone
  - ✓ deeper waters of ocean - Oceanic region
- Symbiotic environment – an environment in which two or more kinds of organisms exist together to their mutual benefits.

The impact of man upon the Environment

Humans alone have the ability to gather resources from beyond their immediate surroundings and process those resources into different, more versatile forms. These abilities have made it possible for human population to thrive and furnish beyond natural constraints. But the natural and manufactured wastes generated and released into the biosphere by these increased numbers of human beings have upset the natural equilibrium.

*Anthropogenic (*human induced) pollutants have overloaded the system. The overloading came relatively late in the course of human interaction with the environment, perhaps because early societies were primarily concerned with meeting natural needs, needs humans share in common with most of the higher mammals. These people had not yet begun to be concerned with meeting the acquired needs associated with more advanced civilization.

i) Satisfying natural needs

Early man used natural resources to satisfy their needs for air, water, food and shelter. These natural, unprocessed resources were readily available in the biosphere, and the residues generated by the use of such resources were generally compatible with, or readily assimilated by the environment. Primitive human beings ate plant and animal foods without even disturbing the atmosphere with the smoke from a campfire. Even when use of fire became common, the relatively small amounts of smoke generated and assimilated by the atmosphere.

ii) Satisfying acquired needs

With the dawn of the industrial revolution, humans were better able than ever to satisfy their age-old needs of air, water, food, & shelter. Increasingly they turned their attention to other needs beyond those associated with survival. By the late nineteenth & early twentieth centuries, automobiles, appliances, and processed foods and beverages had become so meeting these acquired needs had become a major thrust of modern industrial society.

Unlike the natural needs discussed earlier, acquired needs are usually met by items that must be processed or manufactured, or refined, and the production, distribution, and use of such items usually results in more complex residuals, many of which are not compatible with or readily assimilated by the environment.

Impact of the environment upon humans

Though rivers become stagnant, skies smoke shrouded, and dumping grounds odoriferous and unsightly, populations generally managed to ignore their impact on the environment until they begin to become aware of the ill-effects that a polluted environment can have up on their own health & well-being. Though stagnant rivers, smoky skies, and unsightly dumps were esthetically displeasing to the citizens of overcrowded cities of earlier centuries, no attempt was made to reverse the negative impact humans had on their environment until it became evident that heavily polluted water, air, & soil could exert an equally negative impact on the health, the aesthetic and cultural pleasures, and the economic opportunities of humans.

Concern must extend over any process which would affect the well-being of living organisms, whether it is physical (e.g. global warming), chemical (e.g. ozone layer depletion) or biological (e.g. destruction of rain forests).

Health concerns

Elements of the air, the water, and the land may host harmful biological and chemical agents that have impact on human’s health. A wide range of communicable diseases can be spread through elements of the environment by human and animal waste product. This is most certainly evidenced by the plagues of the middle ages when disease spread through rats that fed on contaminated solid and human waste.

Pollution of the atmosphere has also posed severe health problems that are of great concern to environmental chemists. People in crowded cities have likely suffered from ill effects (s) of air pollution for centuries, but it is only in this century that increasingly heavy pollution has caused health problems so dramatic as to be easily attributed to air pollution.

1.1 Basic concepts in Environmental Chemistry

It is difficult to precisely define Environmental Chemistry since the topic has not yet reached a stage where there is universal accord in the chemical community on its scope. However the above definition provides a reasonable and acceptable statement at this stage.

Environmental Chemistry is the study of the sources, reactions, transport, effects, and fates of the chemical species in the air, soil, water and living environments, and the effects of technology thereon. To understand this topic, it is important to have some appreciation of Environmental Science as a whole.

Environmental Science in its broadest sense is the science of the complex interactions that occur among the terrestrial, atmospheric, aquatic, living, and anthropological environments. It includes disciplines such as Chemistry, Biology, Ecology, Sociology and Government that affect or describe these interactions.

Environmental chemistry is probably the most interdisciplinary of the many branches of chemistry. It is closely related to the branches of chemistry (organic, inorganic, analytical & physical) as well as more diverse areas such as biology, toxicology, biochemistry, public health & epidemiology.

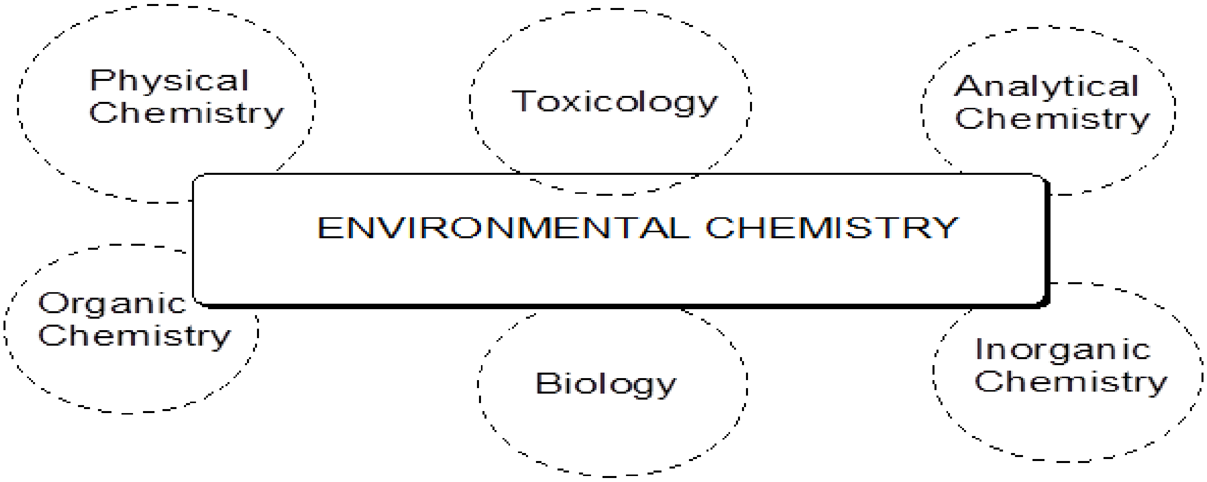


Figure 1.1 Diagrammatic illustrations of some of the relationships between Environmental chemistry and other areas of science.

1.2 Properties of Chemicals in the Environment

Dear student, in the previous session, you have been introduced about the basic concepts of Environmental Chemistry and the components of the Environment. Now you will learn about the basic properties of chemicals in the Environment. Do you know the properties of chemicals in the Environment? Attempt the following activities by yourself.

Learning task 1.2

a) List some of the chemicals found in the Environment
b) Explain the chemical and physical properties of substances in the Environment
c) Explain the partition behavior of substances

The behavior of chemicals in the environment is governed by their **physical** and **chemical** properties as well as **transformation** and **degradation** processes. For example, compounds with low boiling points evaporate rapidly into the atmosphere, whereas compounds that are highly soluble in water disperse rapidly in streams and rivers. Thus, an understanding of these properties would be expected to give a clearer perception of how compounds will behave in the environment. This means that the measurement of the physical and chemical properties of a compound could be soil, animals, etc. Properties of compounds are largely influenced by intermolecular and intramolecular forces.

Physical States

A cursory examination of the nature of our environment reveals that matter exists in three states: **solid, liquid** and **gas**. Solids are present as soil, rocks and so on whereas liquids are represented by the great water bodies of the oceans, lakes and rivers. The gaseous components of the environment are the atmosphere. These states exercise a basic influence on the nature and distribution of all substances, both natural and manmade in the environment.

Polarity of bonds and molecules

Bonds can be polar or non-polar based on the difference in electronegativities of the bonded atoms. The C-H bond, one of the most common bonds in organic compounds, is weakly polar for the ΔEN is 0.4. On the other hand, the bond between O-H is polar for $\Delta EN = 1.4$. The bond between two hydrogen atoms in hydrogen molecule is non - polar because the value of $\Delta EN = 0$.

Molecular polarity is dependent on bond polarity and resultant or net dipole moment. Dipole moment is a vector quantity, which is given by charge multiplied by charge separation. A variety of important chemicals widely distributed in the environment are weakly polar to non-polar. For example, Dichloro Diphenyl Trichloroethane (DDT) is weakly polar to non-polar since the weakly polar C-Cl bonds are distributed in such a manner as to reduce the overall polarity of the molecule to a very low level.

The PolyChlorinated Biphenyls (PCBs) and most of the chlorohydrocarbon pesticides are also weakly polar to non-polar. On the other hand, the herbicide 2, 4-dichlorophenoxy acetic acid (2, 4-D) is a polar molecule because the carboxylic (COOH) group is polar. One of the most important compounds in the environment is water since it is the major component of oceans, lakes and rivers and thus has a major impact on the distribution of chemicals.

The melting point

The melting point of a substance is the temperature at which the solid phase converts to the liquid phase under pressure of 1 atm. The melting point is one of the physical properties of a substance that is useful for characterizing (describing) and identifying the substance. To measure the melting point of a substance, it is necessary somehow to gradually heat a small sample of the substance while monitoring its temperature with a thermometer. The temperature at which liquid is first seen is the lower end of the melting point range. The temperature at which the last solid disappears is the upper end of the melting point range.

Although many substances melt cleanly and can be melted, crystallized, and remelted repeatedly without chemical decomposition, others chemically decompose before they melt, forming substances of lower molecular weight. The temperature of decomposition is just as useful as the melting point in physically characterizing a substance. Decomposition is usually signalled by a color change; for example, white substances invariably start to turn brown near the decomposition temperature. The temperature at which the color change is first observed signals that the substance is approaching the decomposition temperature at somewhat higher temperature, liquid may form. At this temperature or at an even somewhat higher temperature, gas bubbles may be seen if gaseous decomposition products are formed.

Boiling Point

When a liquid is heated, it eventually reaches a temperature at which the vapor pressure is large enough and equals to the atmospheric pressure(i.e.1atm). At this point bubbles rise form inside the body of the liquid. This temperature is called the **boiling point**. Once the liquid starts to boil, the temperature remains constant until all of the liquid has been converted to a gas.

The normal boiling point of water is 100^oC. But if you try to cook an egg in boiling water while camping in the Rocky Mountains at an elevation of 10,000 feet, you will find that it takes longer for the egg to cook because water boils at only 90^oC at this elevation.

The normal boiling point of water is 100°C because this is the temperature at which the vapor pressure of water is 760 mmHg, or 1 atm. Under normal conditions, when the pressure of the atmosphere is approximately 760 mmHg, water boils at 100°C.

Density

In chemistry, density is a physical property of matter that depends on both mass and volume. The equation below shows this. Density = mass/volume

Remember, mass is how much matter is in an object. Volume is the amount of space that an object occupies. Density can be calculated by taking the mass (usually measured in grams) and dividing it by the volume (usually measured in cm^3).

Water in its liquid form is called ice. A unique property of water is that solid water is less dense than liquid water. This means that ice floats. You have probably observed this when drinking a glass of ice water. The density of ice is very important to living things. During the winter lakes form layers of ice on the surface, but there is still liquid water (which is more dense) below. This allows fish and other animals to survive during the winter.

Solubility

An important environmental property of a substance is its solubility in water and other solvents, since this property influences its dispersal in the open environment, including the oceans and aquatic systems generally. In addition a range of important biological properties can be related to solubility in water and other solubility related properties. An understanding of this property can help to understand many of the most important environmental properties of compounds.

When a substance dissolves to form a solution, individual molecules of the solute are separated by molecules of the solvent. In simple terms, for a substance to dissolve, the solvent molecules must form a set of bonding with the solute molecules which are, in total, stronger than the solute to solute bonds. If this does not occur, the solvent molecules will move together due to mutual attraction and the substance will come out of solution and thus be insoluble.

The “Like dissolves like” principle is a useful tool to predict whether a solute dissolved by a particular solvent. For example most ionic compounds are soluble in polar solvents. This is because the ions in solution are each surrounded by water molecules with the oppositely charged ends attracted to the ion. The forces of attraction between the water molecules and the ions are greater than the attraction between the ions. In this way, a stable solution is formed and so generally ionic compounds are dissolved by polar and ionic solvents.

If a non-polar solvent was used with an ionic or polar solute, the bonds between the non-polar solvent molecules and the ions or polar substances would be very weak and generally insufficient to form a stable solution. Thus, non-polar solvents, such as hexane would not be expected to dissolve polar and ionic compounds to any significant extent. Many chemicals of environmental importance are weakly polar to non-polar and includes dioxins, PCBs and chlorohydrocarbon pesticides. These compounds show very little solubility in water. In common non-polar or weakly polar solvents such as n-hexane and n-octanol they are soluble.

In the environment, an important non-polar to weakly polar solvent is biota lipid. Biota lipid is a complex-mixture in all organisms but always contains large numbers of non-polar groups, leading to overall non polarity or weak polarity for the lipid in general. A substance must have a reasonable solubility in lipid to penetrate membranes and enter the internal system of biota.

Substances that are soluble in lipid are called lipophilic or lipid loving. The major components of lipids are fats, which are high molecular weight, non-polar to weakly polar esters. Compounds that are lipophilic are likely to have biological effects, such as a tendency to accumulate in organisms to higher concentrations than occur in the external environment and a general toxicity to all biota. In addition these substances are often also persistent in the environment and exhibit resistance to transformation and degradation. In addition to having the property of lipid solubility, lipophilic compounds usually exhibit relatively low solubility in water. For this reason they are often called as hydrophobic compounds, which mean that they are water hating.

i) Partition Behavior

Dear student can you explain the partition behavior of substances?

The principle of solubility is based on polarity: like dissolves like. However, we have many situations that are not clear-cut, and the compounds have both polar & non polar properties.

Example, butyric acid $CH_3(CH_2)_2COOH$ has polarity and in fact partially forms ions (depending on the pH of the solvent) but also has a non-polar part, as shown below:

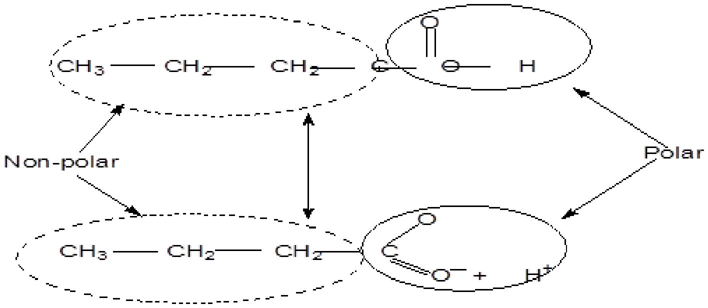


Figure1. 2 The butyric acid molecule, indicating polar and non-polar sections

If placed in water, which is a polar solvent, some of the butyric acid will dissolve in the water because it is moderately soluble in water. However, if it is placed in a non-polar solvent such as hexane or ethyl ether, some of it will also dissolve in these non-polar solvents. This means that it is moderately soluble in both polar and non-polar solvents. If one places sufficient diethyl ether and water together, they will form a two phase system with ether forming a separate layer floating above the water. The ether is a weakly polar to non- polar liquid that has limited solubility in the polar water.

If one place butyric acid in this system and shakes it thoroughly, one finds that the butyric acid has partitioned (or distributed) between the two liquids. In fact, at equilibrium the ether contains a conc. of three units per volume & the water contains a conc. of one unit per volume. This partitioning can be quantitatively measured as the part ion coefficient. The partition coefficient for butyric acid in an ether-water system is 3. The partition coefficient is constant for a given substance in two specific liquids under constant environmental conditions such as temperature and pressure.

The partition coefficient is dependent on:

- Polarity of the substance
- Molecular weight
- Relationship of the polarity of the solvent used.

One of the most widely used physico-chemical characteristics of compounds applied in environmental chemistry is the n-octanol/water partition coefficient. This partition coefficient is important because it imitates the biota lipid /water partition process. Octanol is in many ways similar to biota lipid since it is fat-like in many of its physical properties. The n-octanol/ water partition coefficient (K_{ow}) is defined as:

$$K_{ow} = \frac{C_o}{C_w}$$

Where Co - the concentration of the substance in octanol and

Cw - is the concentration of the substance in water at equilibrium at constant temperature

Kow values can be measured in a shake flask system, similar to diethyl ether/ water system. The K_{ow} values are dimensionless since both Cw and Co are measured in the same units. Values have been measured for a wide variety of compounds of environmental importance and these ranges from about 0.001 to over 10,000,000. Some typical illustrative values are indicated below.

Table 1.2 Some octanol/water partition coefficient (Kow) values for various compounds

Compound	**Kow**	**log Kow**
Ethanol	0.49	-0.31
2,4,5- T	3.98	0.60
2,4, - D	37.20	1.57
Benzene	134.90	2.13
1,4 – Dichlorobenzene	3310.0	3.52
DDT	2.29×10^6	6.36

The K_{ow} values are constant for a given compound and reflect the lipophilicity of a compound. As K_{ow} increases, the solubility in lipid increases relative to water. Thus, increasing Kow values reflect increase lipophilicity. An increasing Kow value also usually reflects a decline in the solubility in water. A compound such as ethanol with $K_{ow} = 0.49$ actually has greater solubility in water than in octanol and is not a lipophilic compound. Compounds are usually considered lipophilic at values of $K_{ow} > 100$. As a general rule, lipophilic compounds have Kow values in the range from 100 to 3,000,000; i.e., log K_{ow} = 2 - 6.5.

ii) Solubilities of gases

The Solubility of gases in water is described by Henry's law, which states that "at constant temperature the solubility of a gas in liquid is proportional to the partial pressure of the gas in contact with the liquid". For a gas, X, this law applies to equilibria of the type

$$X\,(g) \rightleftharpoons X\,(aq)$$

Mathematically, Henry's law is expressed as:

$$[X\,(aq)] = KP_x$$

Where [X (aq] is the aqueous concentration of the gas, P_x is the partial pressure of the gas, and K is the Henry's law constant applicable to a particular gas at a specified temperature.

Henry's law constant (H) can also define as:

$$H = \frac{P}{C_w}$$

Where P - partial pressure of the compound in air

Cw - is the corresponding concentration in water

This characteristic quantifies the relationship between a contaminant in a water body (such as a lake or an ocean) and the atmosphere at equilibrium. The environment can be considered to be made up of phases, such as air, water, soil, atmosphere and biota. A chemical enters to the environment and partitions between these phases as basic mechanism governing distribution. For gas concentrations in units of moles per liter and gas pressures in atmospheres, the units of K are mol L^{-1} atm^{-1}. Some values of K for dissolved gases that are significant (relatively found) in water are given below.

Table 1.3 Henry's law constants for some gases in water at 25^0C

Gases	**K, Mol x L^{-1} x atm^{-1}**
O_2	1.28×10^{-3}
CO_2	3.38×10^{-2}
H_2	7.90×10^{-4}
CH_4	1.34×10^{-3}
N_2	6.48×10^{-4}
NO	2.0×10^{-4}

In calculating the solubility of a gas in water, a correction must be made for partial pressure of water by subtracting it from the total pressure of the gas. At 25^0C the partial pressure of water is 0.0313 atm; values at other temperatures are readily obtained from standard handbooks. The concentration of oxygen in water saturated with air at 1.00 atm and 25^0C may be calculated as an example of a simple gas solubility calculation. Considering that dry air is 20.95% by volume oxygen, factoring in the partial pressure of water gives the following:

$$\mathbf{P_T = P_{gas} + P}\ H_2O$$

Where, $P\ H_2O$ = Vapor pressure of H_2O from $P_{gas} = P_T - P\ H_2O$

Therefore, $PO_2 = P_T - P\ H_2O$

$PO_2 = (1.0000\ atm - 0.0313 atm) = 0.9687 atm$

$PO_2 = (0.9687 atm) \times 0.2095 = 0.2029$ atm (since dry air is 20.95% by volume oxygen)

$[O_2\ (aq)] = K \times PO_2 = 1.28 \times 10^{-3}\ mol\ L^{-1} \times atm^{-1}\ X\ 0.2029 atm$

$= 2.60 \times 10^{-4}\ mol\ L^{-1}$

Since the molecular weight of oxygen is 32, the concentration of dissolved oxygen in water in equilibrium with air under the conditions given above is 8.32mg/L, or 8.32ppm.

The Solubilities of gases decrease with increasing temperature. Account is taken of this factor with the **Clausius -Clapeyron** equation,

$$\text{Log}\ {C2}/{C1} = \triangle H/{2.303R}\ [1/T_1 - 1/T_2]$$

Where C_1 and C_2 denote the gas concentrations in water at absolute temperatures of T_1 and T_2, respectively; $\triangle$H is the heat of solution; and R is the gas constant. The value of R is 1.987 cal x $degree^{-1}$ x mol^{-1}, which gives $\triangle$H in units of cal/mol.

1.3. Environmental Transformation and Degradation processes

Dear student, under this main content you will learn about the Environmental Transformation and Degradation processes. Do you know the processes of the Environmental Transformation and Degradation? Attempt the following activities by yourself.

Learning task 1.3

a) Define Environmental transformation and Environmental degradation
b) Explain factors that causes Environmental transformation and degradation
c) Compare and contrast Environmental Transformation and Degradation processes

Dear student, do you know how transformation and degradation occurred in the Environment?
The environment contains many chemicals. These chemicals may undergo **transformation**, which can be defined as any change in the molecular structure of the substance. This could be a rearrangement of the molecule into another form. Alternatively, it could be the addition or loss of chemical groups by environmental processes. **Degradation** usually refers to the breakdown of the original molecule by the loss of the various component parts or by the fragmentation of the molecule into smaller substances.

Transformation and **degradation** may occur through interactions with other chemicals in the environment. This can be facilitated by the input of energy in the form of radiation or heat. Alternatively, biota may be involved, leading to the transformation and degradation of compounds through biological processes. With these processes, the organic compounds are chemically acted upon by other substances in the external environment or within the biota. Both oxygen and water are substances that are reactive and available in large quantities in the environment for the transformation of compounds.

1.3.1. Abiotic Transformation and Degradation

Dear student, under this main content you will learn about the Abiotic Transformation and Degradation processes. Do you know the processes of the Abiotic Transformation and Degradation? Attempt the following activities by yourself.

Learning task 1.3.1

a) Define the following terms : transformation, degradation and accumulation
b) Mention factors that causes Abiotic transformation and degradation
c) Compare and contrast Abiotic transformation and degradation

1.3.1.1 Oxidation Through Combustion

Dear student can you explain how oxidation through combustion undergoes abiotic transformation degradation in the environment?

Oxygen reacts with organic compounds by oxidation processes that often involve the addition of oxygen to the molecule. This can result in the formation of a molecule that is increased in size by the addition of oxygen or it may result in splitting the molecule into smaller oxygen-containing fragments.

The oxidative degradation of an organic compound to the ultimate level results in the formation of CO_2, H_2O, NH_3, NO_3^-, NO_2^-, PO_4^{3-} (orthophosphate), H_2S, SO_4^{2-} and so on, depending on the conditions involved and the nature of the original compound.

A simple example is the oxidation of methane by combustion. $\mathbf{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}$
Often spectacular oxidation of organic molecule by atmospheric oxygen occurs by combustion. Many organic compounds can exist in the environment in the presence of the 20% of O_2 in the atmosphere without combustion. However, ignition by a spark or flame initiates the occurrence of combustion.

1.3.1.2 Hydrolysis

Dear student can you explain how Hydrolysis is responsible for abiotic transformation and degradation?

Water is present in large quantities in the environment in oceans, rivers, and streams. It is also available in substantial quantities within all biota and in the vapor form in the atmosphere. In biota, it is the basic fluid used for the transfer of substances in biological processes.

The chemical reaction of a compound with water is known as **Hydrolysis**. Hydrolysis is one of the most important chemical processes that can act upon the many types of organic compounds occurring in the environment arising from both natural and manmade sources. It often results in the fragmentation of the molecules into smaller parts that may contain additional hydrogen and oxygen. The general reaction below defines the hydrolysis process.

$$\mathbf{R\text{-}X \quad + \quad H_2O \quad \longrightarrow \quad R\text{-}OH \quad + \quad HX \quad or\ (H^+ + X^-)}$$

Where R-X represent organic compound

A wide variety of functional groups and compounds are potentially susceptible to hydrolysis, including peptides, ester groups in fats etc. Hydrolysis also occurs with a wide range of synthetic compounds, including many pesticides and other substances. These reactions can be mediated by biota or can occur without the need for biological assistance. However, when they occur idiotically, the rates of reaction can be very slow. Some chemical structures and groups tend to be resistant to hydrolysis, including alkanes, polycyclic aromatic hydrocarbon (PAH), alcohols, aldehydes and ketones.

The importance of hydrolysis from an environmental point of view is that the reaction introduces an -OH group into the parent molecule and may fragment the molecule into smaller groups. The –OH group is a polar group and usually tends to increase the polarity of the molecule, but this depends on the nature of the group that is removed. The products of hydrolysis are usually more susceptible to biotransformation and the –OH group makes the chemical more water soluble, as does the smaller size of molecular fragments that may be produced.

With compounds having high Kow values, the Kow values of the products will be less and the biological activity altered. Furthermore, the product is usually less toxic than the initial starting material but there are some exceptions to this. Hydrolysis reactions are commonly catalyzed by H^+/OH^- ions. This results in a strong dependence of the rate of hydrolysis on the pH of the water in which the reaction occurs.

In general, oxidation and hydrolysis may result in the production of smaller fragments that contain additional oxygen alone or both oxygen and hydrogen. Both oxidation and hydrolysis can occur when substances come in contact with oxygen and/or water under the appropriate conditions in air, water, soil and biota. These processes may occur without the intervention of biota as a result of abiotic processes.

On the other hand, oxidation and hydrolysis can also occur through the facilitation of biota. Reactions facilitated by animals or plants are described as biotic reactions. Both types of reactions are influenced by the prevailing temperature, the presence of oxygen and water, light and a variety of other factors.

1.3.1.3 Photochemical Transformation

Dear student, under this main content you will learn about the Abiotic Transformation and Degradation processes. Do you know the processes of the Abiotic Transformation and Degradation? Attempt the following activities by yourself.

Learning task 1.3.1.3

a) Define photochemical transformation.
b) Mention factors that causes photochemical transformation and degradation.
c) List the stages of photochemical reaction.

Many organic chemicals are introduced into the environment and can absorb radiation and, as a result, undergo chemical transformation. All chemical processes require the reacting substances to have attained certain energy. This energy can be obtained either from thermal (heat) energy, as with combustion or by absorption of radiation. Thermal energy in a molecule results from being "jostled" by its neighbors and it is manifested as translation, rotation, and vibration of the molecules. Absorption of electromagnetic radiation (EMR) in the IR range causes increased molecular rotation and vibration. Absorption of Ultra-violet (UV) radiation brings about electronic energy state changes.

Molecules activated by radiation absorption are described as photochemically activated molecules and they differ in a number of important aspects from those that are thermally activated. Radiation absorption that will cause a change in the electronic state of a molecule is only possible if the energy of an incident photon corresponds to the energy difference between two internal electronic energy states of the molecule.

To initiate a photochemical transformation, the photon energy must be relatively large, which corresponds to radiation in the UV-Vis region of the electromagnetic spectrum (EMS). If the light absorbed is of sufficient energy, the excited molecule produced can undergo various transformations that would essentially not occur under normal conditions.

The basic characteristics of radiation can be described by the relatively simple equations. The two important equations that relate energy, frequency and wavelength of radiation are:

$E = h\upsilon$

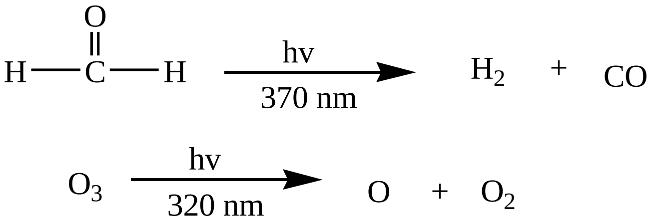
Where, E is the energy

h is Planck's constant (6.63×10^{-34}J and υ is frequency of light

and

$C = \upsilon\,\lambda$; where C is speed of light, υ is frequency of light & λ is wavelength

Reactions induced by UV-Vis include fragmentation, oxidation and polymerization. It is also possible that an excited molecule can return to its original state and in the process emits radiation at a different wavelength.



$$H-\overset{\overset{O}{\|}}{C}-H \xrightarrow[370\ nm]{hv} H_2 + CO$$

$$O_3 \xrightarrow[320\ nm]{hv} O + O_2$$

Examples of photo-transformation reactions

Photochemical reactions can be divided into three stages:

- **Absorption**: the stage in which the absorption of photons of light gives excited molecules
- **Primary photochemical process** (primary photoreaction): in this case, any elementary chemical process undergoes by an electronically excited molecular entity and yielding a primary photoproduct.
- **Secondary photochemical processes**: these processes follow primary photochemical processes.

Phototransformation in the environment can only occur if the UV-Vis absorption spectrum of the compound and the solar admission spectrum overlap. Solar radiation contains a substantial amount of UV-Vis radiation when it reaches the earth's surface. Some structures or functional groups are poor absorbers of solar radiation and these include alcohol (-OH), ethers (R-O-R') and amines ($R-NH_2$). For such groups, or chemicals containing only these functional groups, phototransformation is likely to be unimportant. In addition phototransformation can only occur when the chemical is likely to be exposed to solar radiation. For example, the atmosphere, upper layers of water bodies and the surface of soil are likely locations in which chemicals would be exposed to solar radiation.

1.3.2 Biotransformation and Biodegradation

Dear student, under this main content you will learn about the Biotransformation and Biodegradation processes. Do you know the processes of the Biotransformation and Biodegradation? Attempt the following activities by yourself.

Learning task 1.3.2

a) Explain Biotransformation and Biodegradation

b) Lists factors that cause Biotransformation and Biodegradation

c) Explain the typical pattern of growth of a microbial population

Biotransformation and biodegradation of chemicals are performed by the action of living organism is one of the major processes that determine the fate of chemicals in environment. These processes can be divided into two broader categories. These are microbial transformation and transformation by higher organisms.

1.3.2.1 Microbial Transformation

Microorganisms are ubiquitous in the environment. Distribution of microbial community in different water bodies are given below:

- Clear mountain lake ~ 50-300 /ml
- Turbid, nutrient – rich lake ~ 2000 – 12,000 /ml
- Lake sediments ~ $8x10^9$ - 5×10^{10} /ml
- Stream sediments ~ 10^7 - 10^{10} /ml

Generally, as the amount of organic matter increases in a water body, the microbial population also increases. Microorganisms play a major role in the biogeochemical cycles of various elements that occur in the environment. Frequently, microbial transformation is the most important and possibly the only significant process that can decompose an organic xenobiotic in the environment.

A **xenobiotic** is a chemical which is found in an organism but which is not normally produced or expected to be present in it. The term is very often used in the context of pollutants such as dioxins and polychlorinated biphenyls and their effect on the biota, because xenobiotics are understood as substances foreign to an entire biological system, i.e. artificial substances.

Microorganisms include Bacteria, Fungi, Algae, Protozoa and Virus. Most bacteria in aquatic environments are nutritionally heterotrophic. Fungi are aerobic which can be uni-or multicultural and generally can thrive in more acidic media than bacteria. The most important function of fungi in the environment is to breakdown cellulose in wood and other materials.

Although fungi don’t grow well in water, they play an important role in determining the composition of natural water because of the large amounts of their decomposition products that enter natural water bodies. A particularly important example of these decomposition products are the humic substances that occur in soil and run off water entering natural water bodies. Algae are photosynthetic and are abundant in both fresh & saline waters, soils, and other sectors of the environment.

1.3.2.2 Microbial degradation

The rate at which compounds bio-transformed and biodegraded by microbes depends upon its role in microbial metabolism and a variety of other factors. Heterotrophic bacteria, which are capable of using complex carbon as their principle source of energy, can degrade organic compounds to provide the energy and carbon required for growth. This is known as metabolism of growth substances, these substances are identifiable by their ability to serve as the sole carbon force for a bacterial culture.

Many toxic and synthetic substances function as growth substrates for bacteria in a manner similar to naturally occurring organic compounds. Metabolism of growth substances usually results in relatively complete degradation or mineralization to carbon dioxide, water & inorganic salts.

Growth Patterns of microorganisms

Before the degradation of a compound begins, the microbial community must adapt itself to the chemical, in many cases, which results in a lag phase initially when little growth occurs. With growth substances, both laboratory and field investigations have shown that this adoption results in a lag time of 2-50 days before the microbial community adjusts.

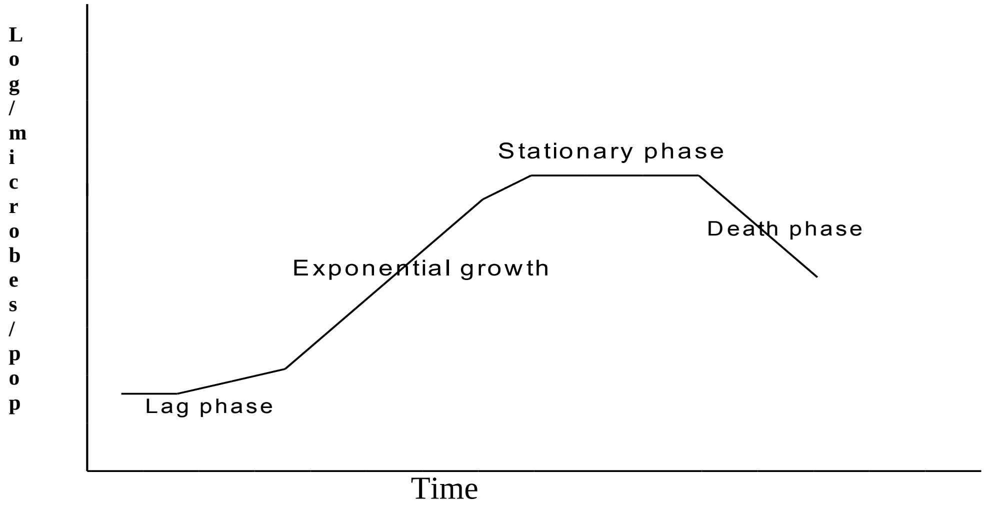


Figure 1.3.2 typical pattern of growth of a microbial population

Frequently, specific organisms within a community with specific enzymes are required for degradation to occur. The adjustment period can involve species selection and numbers increase as well as the production of specific enzymes systems to match the substrate. This production of enzymes is referred to as **enzyme induction**. These factors are outlined below:

i) **Prior exposure to organic compound**

Prior exposure to the organic compound substrate reduces the adaptation or lag time. Thus lag times in pristine environments should generally be much longer than in locations which have been previously exposed.

ii) **Initial numbers of suitable species**

Areas with larger microbial communities should require relatively short lag times to develop a viable population of degrading microorganisms.

i) **The presence of more easily degraded carbon sources**

The presence of more easily degraded carbon sources may delay the adaptation of the microbial community to more persistent contaminants. For example, it has been found that microorganisms degraded added glucose completely before degrading hydrocarbons in lake water.

ii) **Concentration of organic compound**

There may be concentration thresholds below which adaptation doesn't occur. On the other hand, too high a concentration of the organic compound may be toxic to the organisms.

When the lag phase is completed, population growth occurs rapidly and usually increases at an exponential rate. At the completion of this phase, the microorganism population effectively establishes equilibrium with growth substances available and a stationary phase in terms of population occurs. Finally, the growths substances are exhausted and wasted accumulate, leading to a decline in the population number.

Co-metabolism

Compounds that co-metabolize usually degrade only in the presence of another carbon source. This is in contrast to growth substances that are able to serve as the sole carbon source for microbial community. Microorganisms can degrade compounds that they apparently can't use for growth or energy via co-metabolism. Co-metabolism is believed to occur when enzymes of low specificity alter or degrade a compound to form products that other enzymes in the organism can't degrade. Substances that undergo co-metabolism are usually similar in structure to natural substrates, but are altered or degraded without necessarily providing significant amounts of energy to the microorganism. Often, this is an important mechanism for the degradation of pesticides in soil.

The kinetics of co-metabolism differs significantly from that of growth substances. Often, no lag period occurs before co-metabolism begins, and accumulation of intermediate products resulting from partial degradation is likely. Generally, slower raters of degradation are observed composed to metabolism of growth substances.

Transport of Pollutants in the Environment

The fate a chemical in the environment depends both on the nature (physical & chemical) of the chemical and the environment (not static) into which the chemical is released. A chemical can disperse, reconcentrate or degrade in the environment. Knowing this helps to select areas where high concentrations are likely to be found which will provide suitable sampling location.

Materials are constantly being transported between the atmosphere, the hydrosphere, the lithosphere and the biosphere. At each stage of the transportation, the concentration of the compounds will be altered either by phase transfer, dilution or surprisingly, re-concentration.

1.4 Matters and Cycles of Matter

Dear student, under this main content you will learn about Matters and Cycles of Matter in the Environment. Do you know the processes of Matters and Cycles of Matter? Attempt the following activities by yourself.

Learning task 1.4

a) Describe how matter cycles occur between the living nonliving parts of an ecosystem
b) Explain why nutrients are important in living systems
c) Describe how the availability of nutrients affects the productivity of ecosystems
d) Describe some of the nutrients cycle in the environment

Matter is anything that occupies space and has rest mass (or invariant mass). It is a general term for the substance of which all physical objects consist. Typically, matter includes atoms and other articles which have mass. Mass is said by some to be the amount of matter in an object and volume is the amount of space occupied by an object, but this definition confuses mass and matter, which are not the same.

In general, massless particles such as photons and gluons are not considered forms of matter, even though when these particles are trapped in systems at rest, they contribute energy and mass to them. For example, almost 99% of the mass of ordinary atomic matter consists of mass associated with the energy contributed by the gluons and the kinetic energy of the quarks which make up nucleons. In this view, most of the mass of ordinary "matter" consists of mass which is not contributed by matter particles.

1.4.1 Cycles of matter

Cycles are sequences of reoccurring events. Cycles of matter, often based on elemental cycles, are utmost importance in the environment. Cycle's material and energy flow (back and forth) among and within the earth's sub-systems. These cycles have the name natural biogeochemical cycles. Organisms participate in biogeochemical cycles, which describe the circulation of matter, particularly plant and animal nutrients, through ecosystems. ***The flow are delicately and naturally balanced (no excess-no deficiency)***

Biogeochemical cycles are ultimately powered by solar energy. These cycles interchange matter among the atmosphere, biosphere, anthroposphere, geosphere, and hydrosphere.

The following are common properties of cycles

- All natural cycles are governed by the law of conservation of mass.
- Earthly materials are repeatedly recycled. The cycles can take place in global scale or local scale.
- Cycles could be completed in fractions of seconds or millions of years.

Fundamental terms

1. Flow/Flux- rate at which material(s) pass a given point.
2. Reservoir (Sink/stock) - natural dominant storage place. For example atmosphere is a reservoir for N_2, CO_2, O_2 and etc, Ocean is a reservoir for water
3. Path- route of movement
4. Residence time- average length of time a substance remains in a particular reservoir.
5. Equilibrium- a system which is balanced (input = output)

Cycles can be divided as Endogenic and Exogenic. Endogenic cycles are types of cycles, which predominantly involve subsurface rocks of various kinds, and exogenic cycles, which occur largely on Earth’s surface and usually have an atmospheric component. In general, sediment and soil can be viewed as being shared between the two cycles and constitute the predominant interface between them.

Most biogeochemical cycles can be described as elemental cycles involving nutrient elements such as carbon, nitrogen, oxygen, phosphorus, and sulfur.

Dear student why is Matter Recycled on Earth?

The matter in your body has been on Earth since the planet formed billions of years ago. Matter on Earth is limited, so it must be used over and over again. Each kind of matter has its own cycles. In these cycles, matter moves between the environment and living things.

In the past decades humans have been the cause of extensive environmental pollution. Pollution is not a one-sided term; all kinds of matter have been applied by humans, resulting in a disturbance in natural processes. Disturbances of natural processes are clearly shown, when you take a look at human interference in matter cycles. This has caused various environmental problems, which are important issues today.

Hydrological or Water Cycle

Dear student, what is hydrological or Cycle?

Without water there would be no life on Earth. All living things are made mostly of water. Water carries other nutrients to cells and carries wastes away from them. It also helps living things regulate their temperatures. Like all matter, water is limited on Earth. The water cycle let’s living things use water over and over.

There are three ways in which humans cause environmental problems by interfering with the hydrological cycle. Firstly, we remove large quantities of freshwater from rivers, lakes and groundwater supplies. In areas where great amounts of people use the water from groundwater supplies, groundwater may be fully depleted. This effect is enhanced by vegetation removal to create new farmland or underground mines, or to build roads. Secondly, because of vegetation removal, rainwater washes away and it no longer infiltrates, so that the groundwater supplies are not restored.

In many cases groundwater supplies will be filled up with salt water from rivers and lakes. When groundwater is salinated the entire area is influenced. Other effects also occur because of vegetation removal; the risk of flooding is enhanced, and soil erosion and land sliding increase. Finally, people change the quality of water, by adding nutrients and contaminants. This causes the ecological processes that usually purify the water to be disturbed.

Nitrogen Cycle

What is nitrogen cycle?

Humans cause environmental problems, by interfering with the nitrogen cycle in several ways. During fuel combustion various compounds are released, among which nitrogen oxides (NO_x). Nitrogen oxides react with oxygen in air, so that nitrous oxide gas (N_2O) is formed. Nitrous oxide is a greenhouse gas, which enhances the earth's temperature when it is present in the atmosphere too extensively. It can also react with ozone in the atmosphere, so that the ozone layer is broken down. The ozone layer is a kind of shell around the earth that consists entirely of ozone. This layer protects the earth and all its life from damaging UV-radiation. When the ozone layer is broken down, humans and animals can experience serious sunburns and skin cancer.

Nitrogen dioxide may also react with hydrogen in the atmosphere; to form nitric acid (HNO_3), which causes acid deposition that damage trees and marine ecosystems, due to increases in the pH of soil and water. Humans are also responsible for shortages of nitrogen on certain locations. The shortages consist when humans remove nitrogen, to create fertilizers to apply on farmland. As a result, farmland becomes too rich in nutrients and other areas will suffer nitrogen shortages. Vegetation in this area depletes. When people want to create new farmland they often burn parts of forests, because the ground underneath these forests is very fertile. While the wood is burned more nitrogen dioxide escapes into air and nutrients are removed from the ground.

Nitrogen fixation

About 78% of Earth's atmosphere is nitrogen gas. Most organisms cannot use nitrogen gas directly. Bacteria in soil can change nitrogen gas into forms that plants can use. This is called **nitrogen fixation**. Other organisms can get the nitrogen they need by eating plants or organisms that eat plants.

Phosphorus cycle

What is phosphorous cycle?

Humans also cause environmental problems by interfering with the phosphorus cycle. We remove phosphates on certain locations, to apply it on farmland as fertilizers. On these locations the phosphate supply is moving, causing phosphate levels of surrounding land-soils and groundwater to become too high. On farmland where phosphates are applied as fertilizers, plants do not absorb all phosphate. The phosphates end up in water and stream towards lakes and reservoirs, where they cause a phenomenon called eutrophication.

Eutrophication means that the water is so rich in nutrients that it causes certain water plants, such as green algae, to grow extensively. As a result the oxygen supply in the water depletes, causing fish and other oxygen-dependent organisms to die and bacteria that are not oxygen dependent (anaerobic) to take over. When people practice extensive wood chopping in forest areas, such as the tropical rain forest, phosphate supplies deplete, because most of the phosphate can be found in the ground under the trees in such areas. When the trees are removed the rain washes phosphates away, causing the ground to become unproductive. Phosphate supplies are restored very slowly, because most phosphate in soils and water comes from weathering rocks and oceanic sediments.

Sulphur cycle

What is Sulphur cycle?

Today, humans are responsible for the consistence of 90% of the Sulphur salts that are found on earth. These salts are mainly formed during industrial processes, such as coal combustion processes, petroleum refining processes and melting processes. Sulphur compounds, such as sulphuric acid, sulfur dioxide and hydrogen sulphide can cause acid deposition on water and soil. This phenomenon causes the pH of water and soil to fall, which can influence life in the soil and water and disturb natural processes.

Carbon cycle

What is carbon cycle?

Humans cause environmental problems by influencing the carbon cycle in two ways. Firstly, the removal of forests has caused depletion in plants and trees that absorb carbon dioxide. Humans cause great carbon emissions to the atmosphere, which take place during industrial processes, such as coal and oil combustion. These processes serve the generation of energy. As a result of these effects the carbon dioxide levels in the atmosphere have greatly increased. Between 1870 and 1990 the carbon dioxide emissions to air have increased 25%.

The carbon dioxide levels in air are now so high, that the uptake by plants and oceans is not fast enough. Carbon dioxide is a greenhouse gas. This means that increasing carbon dioxide levels in air support the greenhouse effect. The greenhouse effect is a term that is used for climate change on earth, caused by greenhouse gases in the atmosphere. Too much carbon dioxide in the atmosphere can cause the earth to warm up. This will in time cause all kinds of negative effects, such as melting of ice from the Arctic causing floods on other continents.

Secondly, during the industrial revolution humans have used fossil fuels extensively for energy generation, as has been mentioned before. Because fossil fuels consist of dead organic matter it takes a very long time to restore the supplies. Because humans have been burning fossil fuels extensively over the past decades fossil fuel supplies are in danger of being exhausted.

Photosynthesis and respiration

Plants are producers. This means they make their own food. They use water, carbon dioxide, and sunlight to make sugar. This process is called photosynthesis.

Photosynthesis is the basis of the carbon cycle. Animals are consumers. This means they have to consume other organisms to get energy. Most animals get the carbon and energy they need by eating plants.

How does this carbon return to the environment?

It returns when cells break down sugar molecules to release energy. This process is called respiration.

Decomposition and combustion

Fungi and some bacteria get their energy by breaking down wastes and dead organisms. This process is called **decomposition**. When organisms decompose organic matter, they return carbon dioxide and water to the environment. When organic molecules, such as those in wood or fossil fuels, are burned, it is called **combustion**. Combustion releases the carbon stored in these organic molecules back into the atmosphere.

Chapter Summary

- **Environment** is the place where we live or work, the atmosphere which we breathe and water which we drink, unspoilt areas of the world which could soon be ruined, and part of the atmosphere which shields us from harmful radiation
- **Environmental Chemistry** is the study of the sources, reactions, transport, effects, and fates of the chemical species in the air, soil, water and living environments, and the effects of technology thereon.
- **Transformation** is any change in the molecular structure of the substance.
- **Degradation** refers to the breakdown of the original molecule by the loss of the various component parts or by the fragmentation of the molecule into smaller substances
- **Accumulation** is a process of a substance accumulating in specific site with or without any change
- **Combustion** is the reaction of organic compounds with oxygen
- **Hydrolysis** is the chemical reaction of a compound with water
- **Photochemical transformation** is the process of chemical transformation of organic chemicals in the environment by absorbing radiation.
- The three stages of photochemical reactions are absorption, primary photochemical process (primary photoreaction and secondary photochemical processes.
- **Biotransformation** and **biodegradation** of chemicals are performed by the action of living organism that determines the fate of chemicals in environment.

Self test exercises

1. Define terms such as: Environment, Environmental science and Environmental Chemistry
2. Describe the interactions between the components of environment
3. List the most important impacts of man on the environment and the vice-versa
4. Discuss the history of environmental chemistry, its definition, and roles in the study of environmental science
5. What factors affect the fate of a chemical in the environment?
6. Explain the chemical and physical properties of chemicals in the Environment
7. Compare and contrast Environmental transformation and degradation
8. Compare and contrast abiotic transformation and degradation and biotic transformation and degradation
9. Explain factors that cause Environmental transformation and degradation
10. Explain the possible consequences of the overuse of natural resources to foster an appreciation of the catastrophic consequences of negligent human act.
11. List some of the chemicals found in the Environment that can be transformed or degraded by Environmental factors
12. Define photochemical transformation and explain the three stages of photochemical reaction.
13. Describe matter and cycles of matter in the environment
14. Describe how matter cycles between the living and nonliving parts of an ecosystem.
15. Explain why nutrients are important in living systems.
16. Describe how the availability of nutrients affects the productivity of ecosystems
17. Describe some of the nutrients cycle in the Environment

Chapter 2

Fundamentals of Aquatic Chemistry

Unit Introduction

Dear student, this chapter deals with Fundamentals of Aquatic Chemistry. It deals with definition of some basic terms, sources and uses of water, the hydrologic cycle, the Properties of water, characteristics of water bodies, chemical phenomena in water bodies, gases in water (O_2, CO_2,), water acidity, water alkalinity, calcium in water, complexation reaction in water, redox reaction in water, water quality, water quality parameters (physical, chemical and biological), water quality requirements, nature and types of water pollutants and classes of pollutants.

Learning objective of the unit

Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:-

- Define important terms like hydrology, limnology, alkalinity, water quality,
- Explain the effects and significance of a water to have unique properties
- Describe the major characteristics of water
- Explain the major Chemical phenomena in water bodies
- Mention some of the major gases in water bodies
- Explain the significance and effects of major gases in water bodies
- Explain the source of acidity in water bodies
- Describe the source of alkalinity in water bodies
- Mention the significance of different chemical reactions in water bodies
- Explain the major water quality parameters and Water quality requirements
- Explain the nature and types of water pollutants

2.1. Fundamentals of Aquatic Chemistry

Dear student, under this main content you learn about the fundamentals of aquatic Chemistry. Do you know some of fundamentals of aquatic chemistry, sources and uses of water? Let warm up your self with the following activities.

Learning task 2.1

a. Define hydrology, limnology and Oceanography
b. Explain fundamentals of aquatic chemistry
c. List the major sources and uses of water

Throughout history, the quality and quantity of water available to humans have been vital factors in determining their well-being. Whole civilizations have disappeared because of water shortages resulting from changes in climate. Even in temperate climates, fluctuations in precipitation cause problems. For example, devastating droughts in Africa during the 1980s resulted in catastrophic crop failures and starvation and in 1997 an unprecedented flood struck huge sections of North Dakota inundating most of the City of Grand Forks, and in 1998 floods produced by torrential rains from Hurricane Mitch killed thousands in Central America.

Waterborne diseases such as cholera and typhoid killed millions of people in the past and still cause great misery in less developed countries. Ambitious programs of dam and dike construction have reduced flood damage, but they have had a number of undesirable side effects in some areas, such as inundation of farmland by reservoirs and failure of unsafe dams. Globally, problems with quantity and quality of water supply remain and in some respects are becoming more serious. These problems include increased water use due to population growth, contamination of drinking water by improperly discarded hazardous wastes , and destruction of wildlife by water pollution.

Aquatic chemistry, the subject of this chapter, must consider water in rivers, lakes, estuaries, oceans, and underground, as well as the phenomena that determine the distribution and circulation of chemical species in natural waters. Its study requires some understanding of the sources, transport, characteristics, and composition of water. The chemical reactions that occur in water and the chemical species found in it are strongly influenced by the environment in which the water is found. The chemistry of water exposed to the atmosphere is quite different from that of water at the bottom of a lake. Microorganisms play an essential role in determining the chemical composition of water. Thus, in discussing water chemistry, it is necessary to consider the many general factors that influence this chemistry.

The study of water is known as **hydrology** and is divided into a number of subcategories. **Limnology** is the branch of the science dealing with the characteristics of fresh water including biological properties, as well as chemical and physical properties. **Oceanography** is the science of the ocean and its physical and chemical characteristics. The chemistry and biology of the Earth's vast oceans are unique because of the ocean's high salt content, great depth, and other factors.

2.1.1 Sources and uses of water: The Hydrologic Cycle

The world's water supply is found in the five parts of the **hydrologic cycle.** About 97% of Earth's water is found in the oceans. Another fraction is present as water vapor in the atmosphere (clouds). Some water is contained in the solid state as ice and snow in snowpacks, glaciers, and the polar ice caps. Surface water is found in lakes, streams, and reservoirs. Groundwater is located in aquifers

There is a strong connection between the *hydrosphere*, where water is found, and the *lithosphere*, which is that part of the geosphere accessible to water. Human activities affect both. For example, disturbance of land by conversion of grasslands or forests to agricultural land or intensification of agricultural production may reduce vegetation cover, decreasing **transpiration** (loss of water vapor by plants) and affecting the microclimate. The result is increased rain runoff, erosion, and accumulation of silt in bodies of water.

The nutrient cycles may be accelerated, leading to nutrient enrichment of surface waters. This, in turn, can profoundly affect the chemical and biological characteristics of bodies of water. The water that humans use is primarily fresh surface water and groundwater, the sources of which may differ from each other significantly. In arid regions, a small fraction of the water supply comes from the ocean, a source that is likely to become more important as the world's supply of fresh water dwindles relative to demand. Saline or brackish groundwater may also be utilized in some areas.

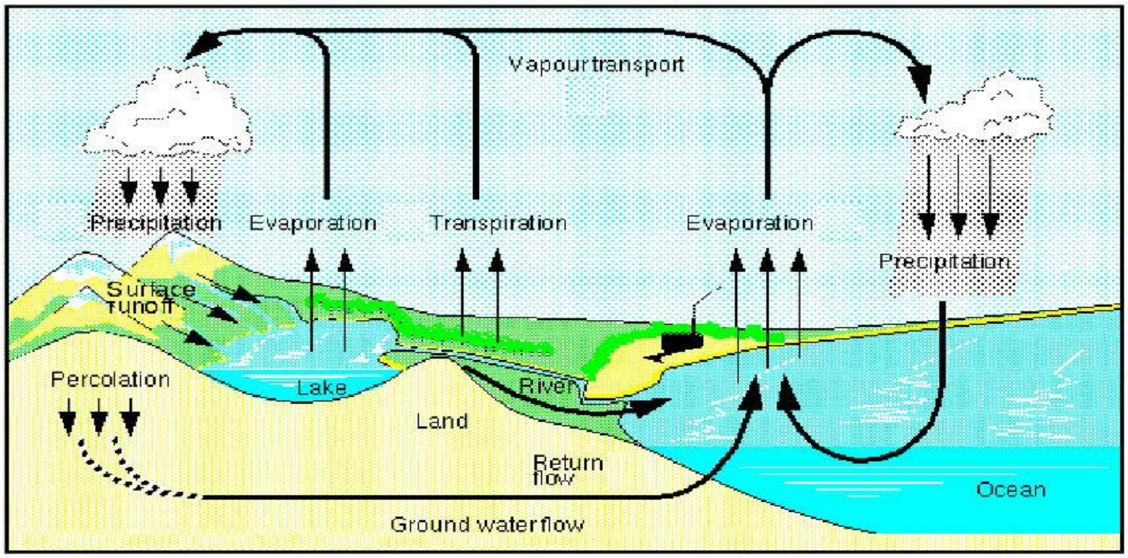


Figure 2.1.1 The hydrologic cycle

2.2. The Properties of water, a unique substance

Dear student, under this main content you learn about the unique properties of water. Can you mention some of the unique properties of water? Let warm up yourself with the following activities

Learning task 2.2

a) List some of the unique properties of water
b) Explain the effects and significance of a water to have unique property
c) Explain why water is unique from the rest liquids

Water has a number of unique properties that are essential to life. Some of the special characteristics of water include its polar character, tendency to form hydrogen bonds, and ability to hydrate metal ions. Some of important properties of water are summarized in table below.

Table 2.2 Important properties of water

Property	**Effects and significance**
Excellent solvent	Transport of nutrients and waste products, making biological processes possible in an aqueous medium
Highest dielectric constant of any common 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 ultraviolent light	Colorless, 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 of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

2.3 Characteristics of bodies of water

Dear student, under this main content you learn about the Characteristics of bodies of water. Can you mention some of the characteristics of bodies of water. Let warm up your self with the following points.

Learning task 2.3

a) Explain the difference among surface water, wetlands and estuaries
b) Describe the stratification of a lake
c) Mention some of the aquatic life
d) Define the following terms: Dissolved oxygen, Biochemical oxygen Demand, Eutrification
e) Explain the significance and effects of Dissolved oxygen, Biochemical oxygen Demand, Eutrification in water bodies

The physical condition of a body of water strongly influences the chemical and biological processes that occur in water. **Surface water** occurs primarily in streams, lakes, and reservoirs. **Wetlands** are flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants. **Estuaries** are arms of the ocean into which streams flow. The mixing of fresh and salt water gives estuaries unique chemical and biological properties. Estuaries are the breeding grounds of much marine life, which makes their preservation very important.

Water’s unique temperature-density relationship results in the formation of distinct layers within nonflowing bodies of water, as shown in Figure 2.3. During the summer a surface layer (**epilimnion**) is heated by solar radiation and, because of its lower density, floats upon the bottom layer, or **hypolimnion**. This phenomenon is called **thermal stratification.** When an appreciable temperature difference exists between the two layers, they do not mix but behave independently and have very different chemical and biological properties.

The epilimnion, which is exposed to light, may have a heavy growth of algae. As a result of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic. In the hypolimnion, bacterial action on biodegradable organic material may cause the water to become anaerobic (lacking dissolved oxygen). As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion.

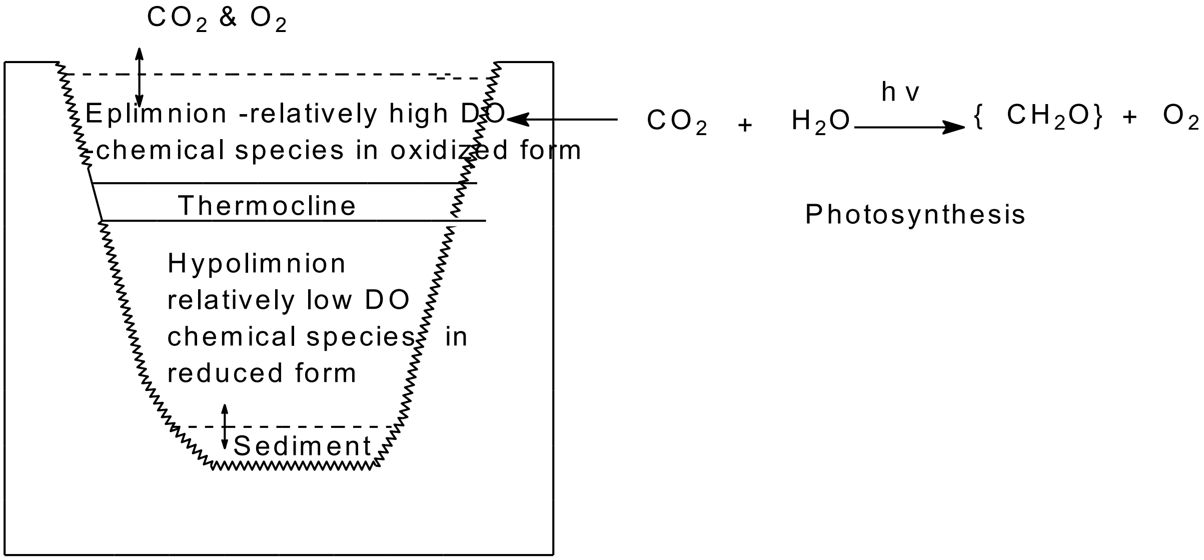


Figure 2.3 Stratification of lake

The shear-plane, or layer between epilimnion and hypolimnion, is called the **thermocline**. During the autumn, when the epilimnion cools, a point is reached at which the temperatures of the epilimnion and hypolimnion are equal. This disappearance of thermal stratification causes the entire body of water to behave as a hydrological unit, and the resultant mixing is known as **overturn**. An overturn also generally occurs in the spring. During the overturn, the chemical and physical characteristics of the body of water become much more uniform, and a number of chemical, physical, and biological changes may result. Biological activity may increase from the mixing of nutrients. Changes in water composition during overturn may cause disruption in water-treatment processes.

2.3.1 Aquatic life

Dear student can you mention some of the aquatic life?

The living organisms (**biota**) in an aquatic ecosystem may be classified as either autotrophic or heterotrophic. **Autotrophic** organisms utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. Algae are the most important autotrophic aquatic organisms because they are **producers** that utilize solar energy to generate biomass from CO_2 and other simple inorganic species.

Heterotrophic organisms utilize the organic substances produced by autotrophic organisms as energy sources and as the raw materials for the synthesis of their own biomass. **Decomposers** (or **reducers**) are a subclass of the heterotrophic organisms and consist of chiefly bacteria and fungi, which ultimately break down material of biological origin to the simple compounds originally fixed by the autotrophic organisms. The ability of a body of water to produce living material is known as its **productivity.** Productivity results from a combination of physical and chemical factors.

High productivity requires an adequate supply of carbon (CO_2), nitrogen (nitrate), phosphorus (orthophosphate), and trace elements such as iron. For example, water of low productivity generally is desirable for water supply or for swimming. Relatively high productivity is required for the support of fish and to serve as the basis of the food chain in an aquatic ecosystem. Excessive productivity results in decay of the biomass produced, consumption of dissolved oxygen, and odor production, a condition called **eutrophication**.

The influence of higher life forms upon aquatic chemistry is minimal. However, aquatic life is strongly influenced by the physical and chemical properties of the body of water in which it lives. ***Temperature, transparency,*** and ***turbulence*** are the three main physical properties affecting aquatic life. Very low water temperatures result in very slow biological processes, whereas very high temperatures are fatal to most organisms. The transparency of water is particularly important in determining the growth of algae.

Turbulence is an important factor in mixing processes and transport of nutrients and waste products in water. Some small organisms (**plankton**) depend upon water currents for their own mobility. **Dissolved oxygen** (**DO**) frequently is the key substance in determining the extent and kinds of life in a body of water. Oxygen deficiency is fatal to many aquatic animals such as fish. The presence of oxygen can be equally fatal to many kinds of anaerobic bacteria. **Biochemical oxygen demand, BOD** is the amount of oxygen utilized when the organic matter in a given volume of water is degraded biologically.

Carbon dioxide is produced by respiratory processes in water and sediments and can also enter water from the atmosphere. Carbon dioxide is required for the photosynthetic production of biomass by algae and in some cases is a limiting factor. High levels of carbon dioxide produced by the degradation of organic matter in water can cause excessive algal growth and productivity. The salinity of water also determines the kinds of life forms present. For example, irrigation waters may pick up harmful levels of salt. Marine life obviously requires or tolerates salt water, whereas many freshwater organisms are intolerant of salt.

2.4 Chemical phenomena in water bodies

Dear student, under this main content you learn about the major chemical phenomena in water bodies. Can you mention some of the chemical phenomena in water bodies. Let warm up yourself with the following activities.

Learning task 2.4

a) Mention the major chemical phenomena in water bodies
b) Explain the significance of chemical phenomena in water bodies
c) Explain the source of chemical phenomena in water bodies

To understand water pollution, it is first necessary to have an appreciation of chemical phenomena that occur in water. The remaining sections of this chapter discuss aquatic acid-base and complexation phenomena, Oxidation-reduction reactions and equilibria, solubility calculations and interactions between liquid water are discussed . The main categories of aquatic chemical phenomena are illustrated in Figure 2.4 . Aquatic environmental chemical phenomena involve processes familiar to chemists, including acid-base, solubility, oxidation-reduction, and complexation reactions.

Although most aquatic chemical phenomena are discussed here from the thermodynamic (equilibrium) viewpoint, it is important to keep in mind that kinetics—rates of reactions—are very important in aquatic chemistry. Biological processes also play a key role.

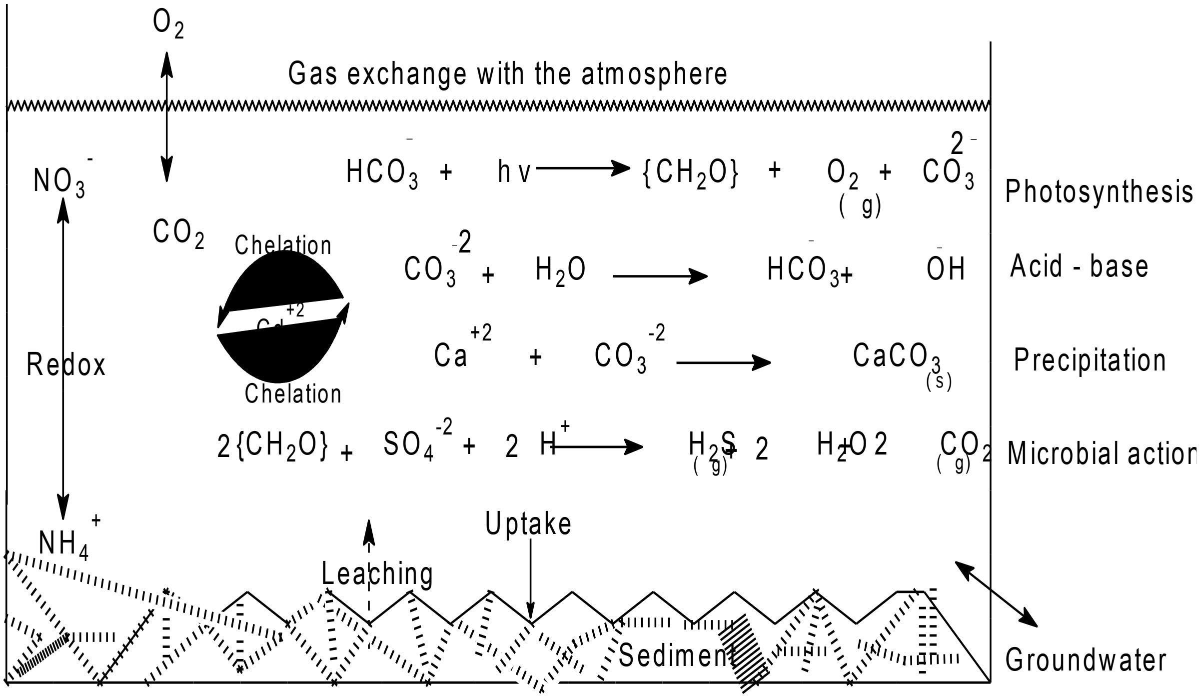


Figure 2.4 Major aquatic chemical processes.

Compared to the carefully controlled conditions of the laboratory, it is much more difficult to describe chemical phenomena in natural water systems. Such systems are very complex and a description of their chemistry must take many variables into consideration. In addition to water, these systems contain mineral phases, gas phases, and organisms. As open, dynamic systems, they have variable inputs and outputs of energy and mass. Therefore, except under unusual circumstances, a true equilibrium condition is not obtained, although an approximately steady-state aquatic system frequently exists. Most metals found in natural waters do not exist as simple hydrated cations in the water, and oxyanions often are found as polynuclear species, rather than as simple monomers.

The nature of chemical species in water containing bacteria or algae is strongly influenced by the action of these organisms. Thus, an exact description of the chemistry of a natural water system based upon acid-base, solubility, and complexation equilibrium constants, redox potential, pH, and other chemical parameters is not possible. Therefore, the systems must be described by simplified **models**, often based around equilibrium chemical concepts. Though not exact, nor entirely realistic, such models can yield useful generalizations and insights pertaining to the nature of aquatic chemical processes, and provide guidelines for the description and measurement of natural water systems. Though greatly simplified, such models are very helpful in visualizing the conditions that determine chemical species and their reactions in natural waters and wastewaters.

2.4.1. Gases in water

Dear student, under this main content you learn about gases in water bodies. Can you mention some of the gases that can be found in water. Let warm up yourself with the following

Learning task 2.4.1

a) Mention some of the major gases in water
b) Describe the source of gases in water
c) Explain the significance of gases in water bodies
d) Explain the effects of dissolved gases in water bodies
e) Describe the relationship between the solubility of gases with temperature

Dissolved gases; O_2 for fish and CO_2 for photosynthetic algae—are crucial to the welfare of living species in water. Some gases in water can also cause problems, such as the death of fish from bubbles of nitrogen formed in the blood caused by exposure to water supersaturated with N_2. For example; volcanic carbon dioxide evolved from the waters of Lake Nyos in the African country of Cameroon suffocated 1,700 people in 1986.

The solubilities of gases in water are calculated with **Henry's Law**, which states that ***the solubility of a gas in a liquid is proportional to the partial pressure of that gas in contact with the liquid.*** Mathematically it can be expressed as: $\mathbf{[X_{(aq)}] = KP_X}$ **;** where $[X_{(aq)}]$ is the solubility of a gas in a liquid, K is proportionality constant and P_X is partial pressure of that gas

<u>Example</u> : Calculate the concentration of O_2 in water saturated with air at 1.00 atm & 25^0C? At $25\ ^0$C, $P_{H2O} = 0.0313$ atm;

Solution: Dry air is 20.95% oxygen by volume

i) $PO_2 = (1.00\text{atm} - 0.0313\text{atm}) \times 0.2095$
$= 0.2029$ atm

$[O_2(aq)] = K \times PO_2$

$= 1.28 \times 10^{-3}$ mol x L x atm^{-1} x 0.2029 atm

$=\underline{2.60 \times 10^{-4} \text{ mol x L}^{-1}}$

ii) What is the concentration of DO at the specified condition?

Since the molecular weight of O_2 is 32 g/mol,

[$\mathbf{O_2}$] = 2.60×10^{-4} mol x L^{-1} x 32 g/mol x 1000mg/g

= $\underline{8.32 \text{ mg/L}}$

= $\underline{8.32 \text{ ppm}}$

Solubility of a gas decreases as temperature increases can be verified by Clausius - Clapeyron equation

$$\log \frac{C_2}{C_1} = \frac{\triangle H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Where C_1 and C_2 denote the gas concentration in water at absolute temperatures of T_1 and T_2 respectively; ΔH is the heat of solution; and R is the gas constant

2.4.1.1 Oxygen in Water

Without an appreciable level of dissolved oxygen, many kinds of aquatic organisms cannot exist in water. Dissolved oxygen is consumed by the degradation of organic matter in water. Many fish kills are caused not from the direct toxicity of pollutants but from a deficiency of oxygen because of its consumption in the biodegradation of pollutants. Most elemental oxygen comes from the atmosphere, which is 20.95% oxygen by volume of dry air. Therefore, the ability of a body of water to reoxygenate itself by contact with the atmosphere is an important characteristic. Oxygen is produced by the photosynthetic action of algae, but this process is really not an efficient means of oxygenating water because some of the oxygen formed by photosynthesis during the daylight hours is lost at night when the algae consume oxygen as part of their metabolic processes. When the algae die, the degradation of their biomass also consumes oxygen.

The solubility of oxygen in water depends upon water temperature, the partial pressure of oxygen in the atmosphere, and the salt content of the water. It is important to distinguish between ***oxygen solubility***, which is the maximum dissolved oxygen concentration at equilibrium, and ***dissolved oxygen concentration***, which is generally not the equilibrium concentration and is limited by the rate at which oxygen dissolves. The calculation of oxygen solubility as a function of partial pressure as discussed before is shown that the concentration of oxygen in water at 25°C in equilibrium with air at atmospheric pressure is only 8.32 mg/L.

Thus, water in equilibrium with air cannot contain a high level of dissolved oxygen compared to many other solute species. If oxygen-consuming processes are occurring in the water, the dissolved oxygen level may rapidly approach zero unless some efficient mechanism for the reaeration of water is operative, such as turbulent flow in a shallow stream or air pumped into the aeration tank of an activated sludge secondary waste treatment facility. The problem becomes largely one of kinetics, in which there is a limit to the rate at which oxygen is transferred across the air-water interface. This rate depends upon turbulence, air bubble size, temperature, and other factors.

If organic matter of biological origin is represented by the formula $\{CH_2O\}$, the consumption of oxygen in water by the degradation of organic matter may be expressed by the following biochemical reaction:

$$\{\mathbf{CH_2O}\} + \mathbf{O_2} \rightarrow \mathbf{CO_2} + \mathbf{H_2O}$$

The temperature effect on the solubility of gases in water is especially important in the case of oxygen. The solubility of oxygen in water decreases from 14.74 mg/L at 0°C to 7.03 mg/L at 35°C. At higher temperatures, the decreased solubility of oxygen, combined with the increased respiration rate of aquatic organisms, frequently causes a condition in which a higher demand for oxygen accompanied by lower solubility of the gas in water results in severe oxygen depletion.

2.4.2 CO_2 and Water acidity in water

Dear student, under this main content you learn about the Chemical phenomena in water bodies. Can you mention some of the Chemical phenomena in water bodies? Let warm up yourself with the following points.

Learning task 2.4.2

a) Explain the source of acidity in water bodies
b) Describe the significance and the effects of acidity in water bodies
c) Explain the distribution of species diagram for the CO_2–HCO_3^-—CO_3^{2-} system in water
d) Calculate the fraction of carbon dioxide, bicarbonate and carbonate system in water
e) Explain the relationship between the pH and the CO_2–HCO_3^-—CO_3^{2-} system in water

Acid-base phenomena in water involve loss and acceptance of H^+ ion. Many species act as **acids** in water by releasing H^+ ion, others act as **bases** by accepting H^+, and the water molecule itself does both. An important species in the acid-base chemistry of water is bicarbonate ion, HCO_3^-, which may act as either an acid or a base:

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

$$HCO_3^- + H^+ \rightleftharpoons CO_2(aq) + H_2O \quad .$$

Acidity as applied to natural water and wastewater is the capacity of the water to neutralize OH^- ; it is analogous to alkalinity, the capacity to neutralize H^+, which is discussed in the next section. Although virtually all water has some alkalinity acidic water is not frequently encountered, except in cases of severe pollution. Acidity generally results from the presence of weak acids, particularly CO_2, but sometimes includes others such as $H_2PO_4^-$, H_2S, proteins, and fatty acids. Acidic metal ions, particularly Fe^{3+} , may also contribute to acidity.

From the pollution standpoint, strong acids are the most important contributors to acidity. The term free mineral acid is applied to strong acids such as H_2SO_4 and HCl in water. Acid mine water is a common water pollutant that contains an appreciable concentration of free mineral acid. Whereas total acidity is determined by titration with base to the phenolphthalein endpoint (pH 8.2), free mineral acid is determined by titration with base to the methyl orange endpoint (pH 4.3). Some industrial wastes, such as spent steel pickling liquor, contain acidic metal ions and often some excess strong acid. The acidity of such wastes must be measured in calculating the amount of lime or other chemicals required to neutralize the acid.

Carbon Dioxide in Water

The most important weak acid in water is carbon dioxide, CO_2. Because of the presence of carbon dioxide in air and its production from microbial decay of organic matter, dissolved CO_2 is present in virtually all natural waters and wastewaters. Rainfall from even an absolutely unpolluted atmosphere is slightly acidic due to the presence of dissolved CO_2. Carbon dioxide, and its ionization products, bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}) have an extremely important influence upon the chemistry of water. Many minerals are deposited as salts of the carbonate ion. Algae in water utilize dissolved CO_2 in the synthesis of biomass. The equilibrium of dissolved CO_2 with gaseous carbon dioxide in the atmosphere, and equilibrium of CO_3^{2-} ion between aquatic solution and solid carbonate minerals, have a strong buffering effect upon the pH of water.

$$CO_2(\text{water}) \rightleftharpoons CO_2(\text{atmosphere})$$

$$MCO_3 \text{ (slightly soluble carbonate salt)} \rightleftharpoons M^{2+} + CO_3^{2-}$$

Carbon dioxide is only about 0.037% by volume of normal dry air. As a consequence of the low level of atmospheric CO_2, water totally lacking in alkalinity in equilibrium with the atmosphere contains only a very low level of carbon dioxide. However, the formation of HCO_3^- and CO_3^{2-} greatly increases the solubility of carbon dioxide. High concentrations of free carbon dioxide in water may adversely affect respiration and gas exchange of aquatic animals. It may even cause death and should not exceed levels of 25 mg/L in water.

A large share of the carbon dioxide found in water is a product of the breakdown of organic matter by bacteria. Even algae, which utilize CO_2 in photosynthesis, produce it through their metabolic processes in the absence of light. As water seeps through layers of decaying organic matter while infiltrating the ground, it may dissolve a great deal of CO_2 produced by the respiration of organisms in the soil. Later, as water goes through limestone formations, it dissolves calcium carbonate because of the presence of the dissolved CO_2:

$$CaCO_3\,(S) + CO_2 + H_2O \rightleftharpoons Ca^{+} + HCO_3^{-}.$$

This process is the one by which limestone caves are formed. The concentration of gaseous CO_2 in the atmosphere varies with location and season; it is increasing by about one part per million (ppm) by volume per year. For purposes of calculation here, the concentration of atmospheric CO_2 will be taken as 350 ppm (0.0350%) in dry air. At 25°C, water in equilibrium with unpolluted air containing 350 ppm carbon dioxide has a $CO_2(aq)$ concentration of 1.146×10^{-5} M. Although CO_2 in water is often represented as H_2CO_3, the equilibrium constant for the reaction: $CO_2(aq) + H_2O \rightarrow H_2CO_3$ is only around 2×10^{-3} at 25°C, so just a small fraction of the dissolved carbon dioxide is actually present as H_2CO_3. In this text, nonionized carbon dioxide in water will be designated simply as CO_2, which in subsequent discussions will stand for the total of dissolved molecular CO_2 and undissociated H_2CO_3.

The CO_2-HCO_3^--CO_3^{2-} system in water may be described by the equations,

$$CO_2 + H_2O \rightleftharpoons HCO_3^{-} + H^{+}, \quad Ka_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7}.$$

$$HCO_3 \rightleftharpoons CO_3^{2} + H^{+}, \quad Ka_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}.$$

The predominant species formed by CO_2 dissolved in water depends upon pH. This is best shown by a **distribution of species diagram** with pH; which is described in figure 2.4.2 below.

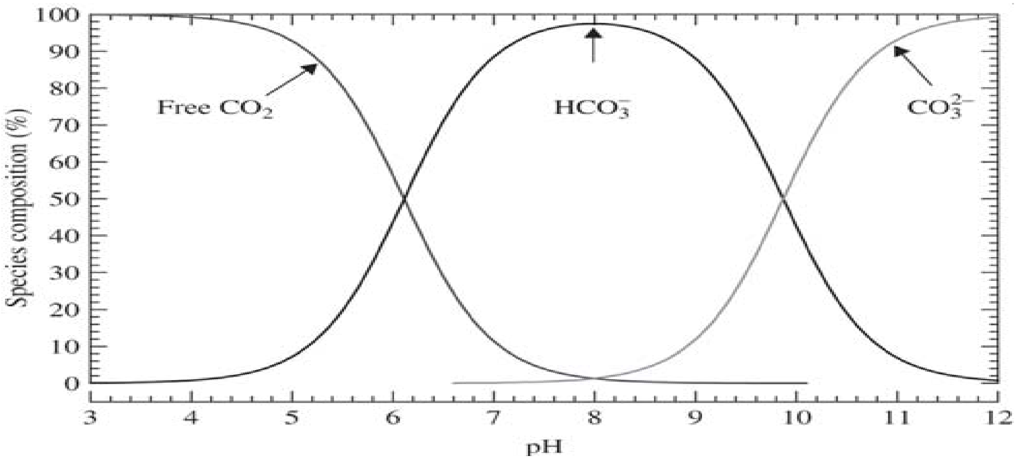


Figure 2.4.2 Distribution of species diagram for the CO_2–HCO_3^-–CO_3^{2-} system in water.

$$\alpha CO_2 \text{ (fraction of } CO_2\text{)} = \text{fraction of } CO_2 = \frac{[CO_2]}{[CO_2] + [HCO_3^-] + [CO_3^{2-}]}$$

$$= \frac{[H^+]^2}{[H^+]^2 + Ka_1\,[H^+]^2 + Ka_1Ka_2}$$

Exercise

- Do the same for the fraction of bicarbonate and carbonate?

Calculations from these expressions show the following:

- ✓ For pH significantly below pKa_1, α CO_2 is essentially =1
- ✓ When pH = pKa_1(6.35), α CO_2 = α HCO_3^-
- ✓ When pH = ½(pKa_1 + pKa_2), ½(6.35+10.33)=8.34
- ✓ α HCO_3^- is at its maximum value of 0.98
- ✓ When pH = pKa_2, α HCO_3^- = αCO_3^{-2}
- ✓ For pH significantly above pKa_2, α CO_3^{-2} is essentially 1

Generally; HCO_3^- is the predominant species in the pH range found in most natural waters, while CO_2 predominates in more acidic waters

2.4.3 Alkalinity in water

Dear student, under this main content you learn about alkalinity in water bodies. Can you mention some of the sources of alkalinity in water bodies? Let warm up yourself with the following activities.

Learning task 2.4.3

a) Define alkalinity
b) Mention the major source of alkalinity in water bodies
c) Explain the effects and significance of alkalinity in water bodies
d) Mention the major contributors to alkalinity at different pH Values
e) Explain the difference between alkalinity and basicity

The capacity of water to accept H^+ ions (protons) is called **alkalinity**. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Frequently, the alkalinity of water must be known to calculate the quantities of chemicals to be added in treating the water. Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids. These characteristics may be detrimental for water to be used in boilers, food processing, and municipal water systems. Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of a water to support algal growth and other aquatic life, so it can be used as a measure of water fertility.

Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

$$OH^- + H^+ \rightarrow H_2O$$

Other, usually minor, contributors to alkalinity are ammonia and the conjugate bases of phosphoric, silicic, boric, and organic acids. At pH values below 7, $[H^+]$ in water detracts significantly from alkalinity, and its concentration must be subtracted in computing the total alkalinity. Alkalinity generally is expressed as *phenolphthalein alkalinity*, corresponding to titration with acid to the pH at which HCO_3^- is the predominant carbonate species (pH 8.3), or *total alkalinity*, corresponding to titration with acid to the methyl orange endpoint (pH 4.3), where both bicarbonate and carbonate species have been converted to CO_2.

It is important to distinguish between high *basicity*, manifested by an elevated pH, and high *alkalinity*, the capacity to accept H^+. Whereas pH is an *intensity* factor, alkalinity is a *capacity* factor. This may be illustrated by comparing a solution of 1.00×10^{-3} M NaOH with a solution of 0.100 M HCO_3^-. The sodium hydroxide solution is quite basic, with a pH of 11, but a liter of it will neutralize only 1.00×10^{-3} mole of acid. The pH of the sodium bicarbonate solution is 8.34, much lower than that of the NaOH. However, a liter of the sodium bicarbonate solution will neutralize 0.100 mole of acid; therefore, its alkalinity is 100 times that of the more basic NaOH solution.

In engineering terms, alkalinity frequently is expressed in units of mg/L of $CaCO_3$, based upon the following acid-neutralizing reaction: $\mathbf{CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O}$
The equivalent weight of calcium carbonate is one-half its formula weight. Expressing alkalinity in terms of mg/L of $CaCO_3$ can, however, lead to confusion, and the preferable notation for the chemist is equivalents/L, the number of moles of H^+ neutralized by the alkalinity in a liter of solution.

2.4.3.1 Contributors to Alkalinity at different pH values

Natural water typically has an alkalinity, designated here as "[alk]," of 1.00 x 10^{-3} equivalents per liter (eq/L), meaning that the alkaline solutes in 1 liter of the water will neutralize 1.00 x 10^{-3} moles of acid. The contributions made by different species to alkalinity depend upon pH. This is shown here by calculation of the relative contributions to alkalinity of HCO_3^-, CO_3^{2-} , and OH^- at pH 7.00 and pH 10.00.

First, for water at pH 7.00, $[OH^-]$ is too low; in which $[HCO_3^-] >> [CO_3^{2-}]$ to make any significant contribution to the alkalinity. Therefore, the alkalinity is due to HCO_3^- and $[HCO_3^-]$ = 1.00 x 10^{-3} M. Substitution into the expression for Ka_1 shows that at pH 7.00 and $[HCO_3^-]$ = 1.00 x 10^{-3} M, the value of $[CO_2(aq)]$ is 2.25 x 10^{-4} M, somewhat higher than the value that arises from water in equilibrium with atmospheric air, but readily reached due to the presence of carbon dioxide from bacterial decay in water and sediments.

Consider next the case of water with the same alkalinity, 1.00 x 10-3 eq/L that has a pH of 10.00. At this higher pH both OH^- and CO_3^{2-} are present at significant concentrations compared to HCO_3^- and the following may be calculated: Therefore, the following equation is the complete equation for alkalinity in a medium where the only contributors to it are HCO_3^-,CO_3^{2-} and OH^-: $\mathbf{[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]}$; the concentration of CO_3^{2-} is multiplied by 2 because each CO_3^{2-} ion can neutralize $2H^+$ ions.

2.4.3.2 Dissolved Inorganic Carbon and Alkalinity

The values given above can be used to show that at the same alkalinity value the concentration of total dissolved inorganic carbon, [C], $[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$ varies with pH. At pH 7.00, [C] pH 7 = 2.25 x 10^{-4} + 1.00 x 10^{-3} + 0 = 1.22 x 10^{-3} whereas at pH 10.00, [C] pH 10 = 0 +

$4.64 \times 10^{-4} + 2.18 \times 10^{-4} = 6.82 \times 10^{-4}$. The calculation above shows that the dissolved inorganic carbon concentration at pH 10.00 is only about half that at pH 7.00. This is because at pH 10 major contributions to alkalinity are made by CO_3^{2-} ion, each of which has twice the alkalinity of each HCO_3^- ion, and by OH^-, which does not contain any carbon.

The lower inorganic carbon concentration at pH 10 shows that the aquatic system can donate dissolved inorganic carbon for use in photosynthesis with a change in pH but none in alkalinity. This pH-dependent difference in dissolved inorganic carbon concentration represents a significant potential source of carbon for algae growing in water which fix carbon by the overall reactions. As dissolved inorganic carbon is used up to synthesize biomass, $\{CH_2O\}$, the water becomes more basic. The amount of inorganic carbon that can be consumed before the water becomes too basic to allow algal reproduction is proportional to the alkalinity.

2.4.4 Calcium and other metals in water

Dear student, under this main content you learn about the source and significance of calcium and other metals in water bodies. Can you mention the source and significance of calcium and other metals in water bodies? Let warm up yourself with the following activities.

Learning task 2.4.4

a) Explain the source of calcium in water
b) Mention some of the significance and effects of calcium in water
c) Explain the significance and effects of dissolved carbon dioxide and calcium carbonate minerals
d) Describe carbon dioxide-calcium carbonate equilibria in water bodies

Metal ions in water, commonly denoted Mn^+, exist in numerous forms. A bare metal ion, Ca^{2+} for example, cannot exist as a separate entity in water. In order to secure the highest stability of their outer electron shells, metal ions in water are bonded, or coordinated, to other species. These may be water molecules or other stronger bases (electron-donor partners) that might be present. Therefore, metal ions in water solution are present in forms such as the hydrated metal cation

$M(H_2O)_x^{n+}$. Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including acid-base, precipitation, and oxidation-reduction reactions:

$$Fe(H_2O)_6^{3+} \rightarrow FeOH(H_2O)_5^{2+} + H^+$$

$$Fe(H_2O)_6^{3+} \rightarrow Fe(OH)_3(s) + 3H_2O + 3H^+$$

$$Fe(H_2O)_6^{2+} \rightarrow Fe(OH)_3(s) + 3H_2O + e- + 3H^+$$

These all provide means through which metal ions in water are transformed to more stable forms. Because of reactions such as these and the formation of dimeric species, such as $Fe_2(OH)_2^{4+}$, the concentration of simple hydrated $Fe(H_2O)_6^{3+}$ ion in water is vanishingly small; the same holds true for many other hydrated metal ions dissolved in water.

2.4.4.1 Calcium in Water

Of the cations found in most fresh-water systems, calcium generally has the highest concentration. The chemistry of calcium, although complicated enough, is simpler than that of the transition metal ions found in water. Calcium is a key element in many geochemical processes, and minerals constitute the primary sources of calcium ion in waters. Among the primary contributing minerals are gypsum, $CaSO_4 \bullet 2H_2O$; anhydrite, $CaSO_4$; dolomite, $CaMg(CO_3)_2$; and calcite and aragonite, which are different mineral forms of $CaCO_3$.

Calcium ion, along with magnesium and sometimes iron(II) ion, accounts for **water hardness**. The most common manifestation of water hardness is the curdy precipitate formed by soap in hard water. *Temporary hardness* is due to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water. Increased temperature may force this reaction to the right by evolving CO_2 gas, and a white precipitate of calcium carbonate may form in boiling water having temporary hardness.

$$\mathbf{Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(aq) + H_2O}$$

Water containing a high level of carbon dioxide readily dissolves calcium from its carbonate minerals: $\mathbf{CaCO_3(s) + CO_2(aq) + H_2O \rightarrow Ca^{2+} + 2HCO_3^-}$

When this reaction is reversed and CO_2 is lost from the water, calcium carbonate deposits are formed. The concentration of CO_2 in water determines the extent of dissolution of calcium carbonate. The carbon dioxide that water may gain by equilibration with the atmosphere is not sufficient to account for the levels of calcium dissolved in natural waters, especially groundwater. Rather, the respiration of microorganisms degrading organic matter in water, sediments, and soil, accounts for the very high levels of CO_2 and HCO_3^- observed in water and is very important in aquatic chemical processes and geochemical transformations.

$$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$$

2.4.4.2 Dissolved Carbon Dioxide and Calcium Carbonate Minerals

The equilibrium between dissolved carbon dioxide and calcium carbonate minerals is important in determining several natural water chemistry parameters such as alkalinity, pH, and dissolved calcium concentration (Figure 2.4.4.2). For fresh water, the typical figures quoted for the concentrations of both HCO_3^- and Ca^{2+} are 1.00×10^{-3} M.

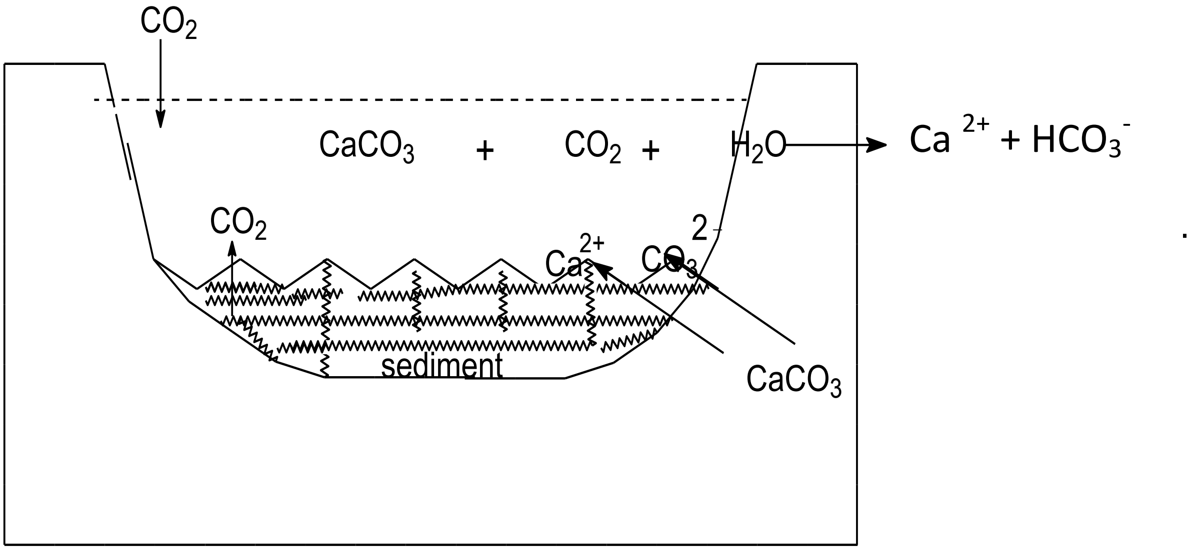


Figure 2.4.4.2 Carbon dioxide-calcium carbonates equilibria.

It may be shown that these are reasonable values when the water is in equilibrium with limestone, $CaCO_3$, and with atmospheric CO_2. The concentration of CO_2 in water in equilibrium with air has already been calculated as 1.146×10^{-5} M. The other constants needed to calculate $[HCO_3^-]$ and $[Ca^{2+}]$ are the acid dissociation constant for CO_2:

2.4.5 Complexation reaction in water

Dear student, under this main content you learn about the complexation reaction in water bodies. Can you mention some of the complexation reaction in water bodies. Let warm up yourself with the following Points.

Learning task 2.4.5

a) Define the following terms: Complex, Speciation, metal complexes, ligand, chelation and coordination compound
b) Explain the source of complexation reaction in water bodies
c) Explain the significance and effects of complexation reaction in water bodies
d) Describe the effect of Complexation upon oxidation-reduction equilibria

The properties of metals dissolved in water depend largely upon the nature of metal species dissolved in the water. Therefore, **speciation** of metals plays a crucial role in their environmental chemistry in natural waters and wastewaters. In addition to the hydrated metal ions, for example, $Fe(H_2O)_6^{3+}$ and hydroxy species such as $FeOH(H_2O)_5^{2+}$ discussed in the preceding section, metals may exist in water reversibly bound to inorganic anions or to organic compounds as **metal complexes**. For example, a cyanide ion can bond to dissolved iron(II): $Fe(H_2O)_6^{2+} + CN^- \rightarrow FeCN(H_2O)_5^+ + H_2O$

Additional cyanide ions may bond to the iron to form $Fe(CN)_2$, $Fe(CN)_3^-$, $Fe(CN)_4^{2-}$,$Fe(CN)_5^{3-}$, and $Fe(CN)_6^{4-}$,where the water molecules still bound to the iron(II) are omitted for simplicity. This phenomenon is called **complexation**; the species that binds with the metal ion, CN^- in the example above, is called a **ligand**, and the product in which the ligand is bound with the metal ion is a **complex**, **complex ion**, or **coordination compound**. A special case of complexation in which a ligand bonds in two or more places to a metal ion is called **chelation**. In addition to being present as metal complexes, metals may occur in water as **organometallic** compounds containing carbon-to-metal bonds. The solubilities, transport properties, and biological effects of such species are often vastly different from those of the metal ions themselves.

2.4.5.1 Complexation processes

Complexation may have a strong effect upon oxidation-reduction equilibria by shifting reactions, such as that for the oxidation of lead, Pb → $Pb^{2+} + 2e^-$ strongly to the right by binding to the product ion, thus cutting its concentration down to very low levels. Perhaps more important is the fact that upon oxidation, $M + 1/2O_2 \rightarrow MO$; many metals form self-protective coatings of oxides, carbonates, or other insoluble species which prevent further chemical reaction.

Copper and aluminum roofing and structural iron are examples of materials which are thus self-protecting. A chelating agent in contact with such metals can result in continual dissolution of the protective coating so that the exposed metal corrodes readily. For example, chelating agents in wastewater may increase the corrosion of metal plumbing, thus adding heavy metals to effluents. Solutions of chelating agents employed to clean metal surfaces in metal plating operations have a similar effect.

2.4.6 Redox reaction in water

2.4.6.1 The significance of Oxidation-reduction in water

Dear student, under this main content you learn about the Redox reaction in water. Can you mention some of the Redox reaction in water? Let warm up yourself with the following

Learning task 2.4.6

a) Define redox reaction
b) Explain the source of redox reaction in water bodies
c) Explain the significance and effects of redox reaction in water bodies

Oxidation-reduction (**redox**) reactions are those involving changes of oxidation states of reactants. Such reactions are easiest to visualize as the transfer of electrons from one species to another. For example, soluble cadmium ion, Cd^{2+}, is removed from wastewater by reaction with metallic iron. The overall reaction is $Cd^{2+} + Fe \rightarrow Cd + Fe^{2+}$

This reaction is the sum of two **half-reactions**, a reduction half-reaction in which cadmium ion accepts two electrons and is reduced, $Cd^{2+} + 2e- \rightarrow Cd$ and an oxidation half-reaction in which elemental iron is oxidized: $Fe \rightarrow Fe^{2+} + 2e-$. Oxidation-reduction phenomena are highly significant in the environmental chemistry of natural waters and wastewaters.

In a lake, for example, the reduction of oxygen (O_2) by organic matter (represented by $\{CH_2O\}$), $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$ results in oxygen depletion which can be fatal to fish. The rate at which sewage is oxidized is crucial to the operation of a waste treatment plant. Reduction of insoluble iron (III) to soluble iron (II), in a reservoir contaminates the water with dissolved iron, which is hard to remove in the water treatment plant.

$$Fe(OH)_3(s) + 3H^+ + e- \rightarrow Fe^{2+} + 3H_2O$$

Oxidation of NH_4^+ to NO_3^- in water, converts ammonium nitrogen to nitrate, a form more assimilable by algae in the water. Many other examples can be cited of the ways in which the types, rates, and equilibria of redox reactions largely determine the nature of important solute species in water.

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

This content discusses redox processes and equilibria in water. In so doing, it emphasizes the concept of pE, analogous to pH and defined as the negative log of electron activity. Low pE values are indicative of reducing conditions and high pE values reflect oxidizing conditions. Two important points should be stressed regarding redox reactions in natural waters and wastewaters. As it is known, many of the most important redox reactions are catalyzed by microorganisms. Bacteria are the catalysts by which molecular oxygen reacts with organic matter, iron (III) is reduced to iron (II), and ammonia is oxidized to nitrate ion. The second important point regarding redox reactions in the hydrosphere is their close relationship to acid-base reactions. Whereas the activity of the H^+ ion is used to express the extent to which water is acidic or basic, the activity of the electron, e-, is used to express the degree to which an aquatic medium is oxidizing or reducing.

Water with a high hydrogen ion activity, such as runoff from “acid rain”, is *acidic*. By analogy, water with a high *electron* activity, such as that in the anaerobic digester of a sewage treatment plant, is said to be *reducing.* Water with a low H^+ ion activity (high concentration of OH^-) such as landfill leachate contaminated with waste sodium hydroxide is *basic*, whereas water with a low electron activity highly chlorinated water, for example is said to be *oxidizing*. Actually, neither free electrons nor free H^+ ions as such are found dissolved in aquatic solution; they are always strongly associated with solvent or solute species. However, the concept of electron activity, like that of hydrogen ion activity, remains a very useful one to the aquatic chemist. Redox reactions in aquatic environments are catalyzed by microorganisms. Redox in hydrosphere is related with acid-base reactions.

Many species in water undergo exchange of both electrons and H^+ ions. For example, acid mine water contains the hydrated iron(III) ion, $Fe(H_2O)_6^{3+,}$ which readily loses H^+ ion to contribute acidity to the medium : $Fe(H_2O)_6^{3+} \rightarrow Fe(H_2O)_5OH^{2+} + H^+$ .The same ion accepts an electron to give iron(II) : $Fe(H_2O)_6^{3+} + e- \rightarrow Fe(H_2O)_6^{2+}$

Generally, the transfer of electrons in a redox reaction is accompanied by H^+ ion transfer, and there is a close relationship between redox and acid-base processes. For example, if iron(II) loses an electron at pH 7, three hydrogen ions are also lost to form highly insoluble iron(II) hydroxide, an insoluble, gelatinous solid. $Fe(H_2O)_6^{2+} \rightarrow e- + Fe(OH)_3(s) + 3H_2O + 3H^+$

The stratified body of water shown in Figure 2.4.6 can be used to illustrate redox phenomena and relationships in an aquatic system. The anaerobic sediment layer is so reducing that carbon can be reduced to its lowest possible oxidation state, -4 in CH_4. If the lake becomes anaerobic, the hypolimnion may contain elements in their reduced states: NH_4^+ for nitrogen, H_2S for sulfur, and soluble $Fe(H_2O)_6^{2+}$ for iron. Saturation with atmospheric oxygen makes the surface layer a relatively oxidizing medium. If allowed to reach thermodynamic equilibrium, it is characterized by the more oxidized forms of the elements present: CO_2 for carbon, NO_3^- for nitrogen, iron as insoluble $Fe(OH)_3$, and sulfur as SO_4^{2-} ,substantial changes in the distribution of chemical species in water resulting from redox reactions are vitally important to aquatic organisms and have tremendous influence on water quality.

As it is shown in figure 2.4.6, predominance of various chemical species in a stratified body of water that has a high oxygen concentration (oxidizing, high pE) near the surface and a low oxygen concentration (reducing, low pE) near the bottom. It should be pointed out that the systems presented in this content are assumed to be at equilibrium, a state almost never achieved in any real natural water or wastewater system. Most real aquatic systems are dynamic systems that may approach a steady-state, rather than true equilibrium. Nevertheless, the picture of a system at equilibrium is very useful in visualizing trends in natural water and wastewater systems, yet the model is still simple enough to comprehend. It is important to realize the limitations of such a model, however, especially in trying to make measurements of the redox status of water.

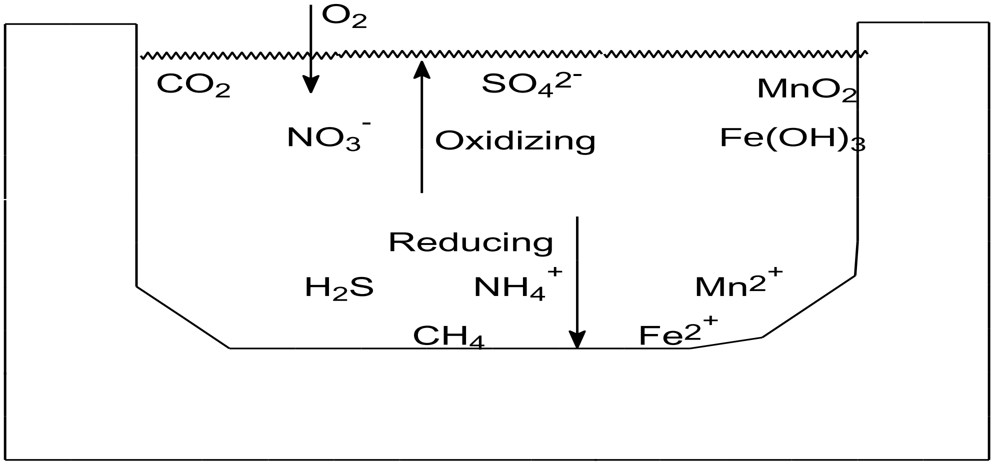


Figure 2.4.6 Redox phenomena and relationships in an aquatic system

2.4.6.2 Corrosion

Dear student, under this main content you learn about the corrosion in water. Can you mention some of the causes of corrosion in water? Let warm up yourself with the following

Learning task 2.4.6.2

a) Define corrosion
b) Explain the source of corrosion
c) Describe whether corrosion is redox reaction or not
d) Explain whether corrosion has advantage or disadvantage
e) Describe how corrosion can be minimized from water bodies

One of the most damaging redox phenomena is **corrosion**, defined as the destructive alteration of metal through interactions with its surroundings. In addition to its multibillion dollar annual costs due to destruction of equipment and structures, corrosion introduces metals into water systems and destroys pollution control equipment and waste disposal pipes; it is aggravated by water and air pollutants and some kinds of hazardous wastes.

Thermodynamically, all commonly-used metals are unstable relative to their environments. Elemental metals tend to undergo chemical changes to produce the more stable forms of ions, salts, oxides, and hydroxides. Fortunately, the rates of corrosion are normally slow, so that metals exposed to air and water may endure for long periods of time. However, protective measures are necessary. Sometimes these measures fail; for example, witness the gaping holes in automobile bodies exposed to salt used to control road ice.

Corrosion normally occurs when an electrochemical cell is set up on a metal surface. The area corroded is the anode, where the following oxidation reaction occurs, illustrated for the formation of a divalent metal ion from a metal, M: $M \rightarrow M^{2+} + 2e^-$.

Several cathodic reactions are possible. One of the most common of these is the reduction of H^+ ion: $2H^+ + 2e^- \rightarrow H_2$; Oxygen may also be involved in cathodic reactions, including reduction to hydroxide, reduction to water, and reduction to hydrogen peroxide:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$O_2 + 2H_2O + 2e^- \rightarrow 2OH^- + H_2O_2$$

Oxygen may either accelerate corrosion processes by participating in reactions such as these, or retard them by forming protective oxide films.

2.5 Water quality

Dear student, under this main content you learn about the water quality and water quality requirements. Can you mention some of the water quality and water quality requirements. Let warm up yourself with the following

Learning task 2.5

a) Define water quality
b) Mention the common water quality requirements
c) Explain the physical, chemical and biological water quality parameters
d) Explain the source, impacts, uses, and measurement of water quality parameters

Water quality should be assessed based on the characteristics of the water relative to the beneficial uses of the water. Water quality is not, as frequently used, a list of chemical constituent concentrations. In order to reliably assess whether the concentration of a constituent impairs the water quality - beneficial uses of a water body, it is necessary to evaluate on a site-specific basis whether the constituent is present in toxic/available forms at a critical concentration for a sufficient duration to be significantly adverse to aquatic life that is important to the beneficial uses of the water body.

Water Quality Assessment is an evaluation of the beneficial use impairment that is occurring, or could potentially occur, due to the presence of a particular chemical(s) or other constituent. It is not an assessment of the frequency of exceedance of a water quality standard.

Water Quality Standard Compliance is based on an assessment of the frequency of exceedance of a water quality standard in ambient waters receiving the discharge/runoff. Such compliance does not ensure that the beneficial uses of the water body are being protected or that significant over-regulation is not occurring.

2.5.1 Water quality requirements

Water quality criteria are based on variables that characterize the quality of water and/or the quality of the suspended particulate matter, the bottom sediment and the biota. Many water quality criteria set a maximum level for the concentration of a substance in a particular medium (i.e. water, sediment or biota) which will not be harmful when the specific medium is used continuously for a single, specific purpose. For some other water quality variables, such as dissolved oxygen, water quality criteria are set at the minimum acceptable concentration to ensure the maintenance of biological functions. Generally the water quality requirement can be assessed by physical, chemical and biological water quality parameters.

2.5.2 Water quality parameters

2.5.2.1 Physical Water quality parameters

Physical parameters define those characteristics of water that respond to the sense of sight, touch, taste or smell, suspended solids, turbidity, color, taste, odor and temperature

a) Suspended solids

Solids can be dispersed in water in both suspended and dissolved forms. Although some dissolved solids may be perceived by the physical sense, they fall more approximately under the category of chemical parameters.

Sources of suspended solids

Solids suspended in water may consist of ***inorganic or organic particles or of immiscible liquids***. Inorganic solids such as clay, silt and other soil constituents are common in surface water. Organic material such as plant fibers and biological solids (algal cell, bacteria, etc) are also common constituents of surface waters. These materials are often common natural contaminants resulting from the erosive action of water flowing over surfaces. Because of the filtering capacity of the soil, suspended material is seldom a constituent of ground water. Other suspended material may result from human use of the water.

Impacts of suspended solids

Suspended material may be objectionable in water for several reasons. It is aesthetically displeasing and provides adsorption sites for chemical and biological agents. Suspended organic solids may be degraded biologically, resulting in objectionable by-products. Biologically active (live) suspended solids may include disease causing organisms as well as organisms such as toxin-producing strains of algae.

Measurement of suspended solids

There are several tests available for measuring solids. Most are gravimetric tests involving the mass of residues. The total solids test quantifies all the solids in the water, suspended and dissolved, organic and inorganic. This parameter is measured by evaporating a sample to dryness and weighing the residue. The total quantity of residue is expressed as milligrams per liter, on a dry-mass-of-solids basis. A drying temperature slightly above boiling point (104^0C) is sufficient to dry off the liquid and the water adsorbed to the surface of the particles, while a temperature of about 180^0C is necessary to evaporate the occluded water.

Uses of suspended solids

Suspended solids, where such material is likely to be organic and /or biological in nature, are an important parameter of wastewater. ***The suspended-solids parameter is used to measure the quality of the wastewater influent, to monitor several treatment processes, and to measure the quality of the effluent***. EPA has set a maximum suspended-solids standard of 30 mg/L for most treated wastewater discharges.

b) Turbidity

A direct measurement of suspended solids is not usually performed on a sample from natural bodies of water or on potable water supplies. The nature of the solids in these waters and the secondary effects they produce are more important than the actual quantity. For such waters a test for turbidity is commonly used.

Turbidity is the measure of the extent to which light is either absorbed or scattered by suspended particles in water. Absorption and scattering are influenced by both size and surface characteristics of the suspended material, turbidity is not a direct quantitative measurement of suspended solids. For example, a small pebble in a glass of water would produce virtually no turbidity. If this pebble were crushed into thousands of particles of colloidal size, a measurable turbidity would result, even though the mass of solids had not changed.

Sources of Turbidity

Most turbidity in surface waters results from the erosion of colloidal material such as clay, silt, rock fragments, and metal oxides from the soil. Vegetable fibers and micro-organisms may also contribute to turbidity. Household and industrial wastewaters may contain a wide variety of turbidity-producing materials. Soaps, detergents and emulsifying agents produce stable colloids that result in turbidity. Although turbidity measurements are not commonly run in wastewater, discharges of wastewaters may increase the turbidity of natural waters.

Impacts of Turbidity

When turbid water in a small, transparent container, such as a drinking glass, is held up to the light, an aesthetically displeasing opaqueness or "milky" coloration is apparent. The colloidal material associated with turbidity provides adsorption sites for chemicals that may be harmful or cause undesirable tastes and odors and for biological organisms that may be harmful. Disinfection of turbid waters is difficult because of the adsorptive characteristics of some colloids and because the solids may partially shield organisms from the disinfectant.

In natural water bodies, turbidity may impart a brown or other color to water, depending on the light-absorbing properties of the solids, and may interfere with light penetration and photosynthetic reactions in streams and lakes. Accumulation of turbidity-causing particles in porous streambeds results in sediment deposits that can adversely affect the flora and fauna of the stream.

Measurement of Turbidity

Turbidity is measured photometrically by determining the percentage of light of given intensity that is either absorbed or scattered. The original measuring apparatus, called ***a Jackson turbidimeter***, was based on light absorption and employed a long tube and standardized candle.

In recent years this Jackson turbidimeter has been replaced by a turbidity meter in which a standardized electric bulb produces a light that is then directed through a small sample vial. In the absorption mode, a photometer measures the light intensity on the side of the vial opposite from the light source, while in the scattering mode; a photometer measures the light intensity at a 90^0 angle from light source. Although most turbidity meters in use today work on the scattering principle, turbidity caused by dark substances that absorb rather than reflect light should be measured by the absorption technique. Formazin, a chemical compound, provides more reproducible standards than SiO_2 and has replaced it as a reference. Turbidity meter readings are now expressed as *formazin turbidity units,* or FTUs. The term nephelometry turbidity unit, NTU, is often used to indicate that the test was run according to the scattering principle.

Uses of Turbidity measurement

Turbidity measurements are normally made on "clean" waters as opposed to wastewaters. Natural waters may have turbidities ranging from a few FTUs to several hundred. EPA drinking water standards specify a maximum of 1 FTU, while the American Water Works Association has set 0.1 FTU as its goal for drinking water.

c) Color

Pure water is colorless, but water in nature is often colored by foreign substances. Water whose color is partly due to suspended matter is said to have *apparent color*. Color contributed by dissolved solids that remain after removal of suspended matter is known as ***true color***.

Sources of color

After contact with organic debris such as leaves, conifer needles, weeds, or wood, water picks up tannins, humic acid, and humatels and takes on yellowish-brown hues. Iron oxides cause reddish water. Industrial wastes from textile and dyeing operations, pulp and paper production, food processing, chemical production, and mining, refining, and slaughter-house operations may add substantial coloration to water in receiving streams.

Impacts of color

Colored water is not aesthetically acceptable to the general public. In fact, given a choice, consumers tend to choose clear, non-colored water of otherwise poorer quality over treated potable water supplies in an objectionable color. Highly colored water is unsuitable for laundering, dyeing papermaking, beverage manufacturing, and dairy production. Thus, the color of water affects its marketability for both domestic and industrial use.

While true color is not usually considered unsanitary or unsafe, organic compounds causing true color may exert a chlorine demand and thereby seriously reduce the effectiveness of chlorine in a disinfectant

Measurement of color

Although several methods of color measurement are available, methods involving comparison with standardized colored materials are most often used. Color-comparison tubes containing a series of standards may be used for direct comparison of water samples that have been filtered to remove apparent color. Results are expressed in true color units (TCUs) where one unit is equivalent to the color produced by 1 mg/L of platinum in the form of chlorplatinate ions. For colors other than yellowish-brown hues, especially for colored waters originating from industrial waste effluents, especially spectrophotometer techniques are usually employed.

Uses of color

Color is not a parameter usually included in wastewater analysis. In potable water analysis, the common practice is to measure only the true color produced by organic acid resulting from decaying vegetation in the water. The resulting value can be taken as an indirect measurement of humic substances in the water.

Although several methods of color measurement are available, methods involving comparison with standardized colored materials are most often used. Color-comparison tubes containing a series of standards may be used for direct comparison of water samples that have been filtered to remove apparent color. Results are expressed in true color units (TCUs) where one unit is equivalent to the color produced by 1 mg/L of platinum in the form of chlorplatinate ions. For colors other than yellowish-brown hues, especially for colored waters originating from industrial waste effluents, especially spectrophotometer techniques are usually employed.

d) Taste and odor

The terms taste and odor are themselves definitive of this parameter. Because the sensation of taste and smell are closely related and often confused, a wide variety of tastes and odors may be attributed to water by consumers. Substances that produce an odor in water will almost invariably impart a taste as well. The converse is not true, as there are many mineral substances that produce taste but no odor.

Sources of taste and odor

Many substances with which water comes into contact in nature or during human use may impart perceptible taste and odor. These include minerals, metals, and salts from the soil, end products from biological reactions, and constituents of wastewater. Inorganic substances are more likely to produce tastes unaccompanied by odor. Alkaline mineral imparts a bitter taste to water, while metallic salts may give a salty or bitter taste. Organic material, on the other hand, is likely to produce both taste and odor problems in water with petroleum-based products being prime offenders. Biological decomposition of organics may also result in taste- and odor- producing liquids and gases in water. Principal among these are the reduced products of sulfur that imparts a "rotten egg" odor and taste.

Impacts of taste and odor

Constituents find taste and odor aesthetically displeasing for obvious reasons. Because water is thought of tasteless and odorless, the container associated taste and odor with contamination and may prefer to use tasteless and odorless water that might actually pose more of a health threat. Odors produced by organic substances may pose more that a problem of simple aesthetic, since some of those substances may be carcinogenic.

Measurement of taste and odor

Direct measurement of materials that produce taste and odor can be made if the causative agents are known. Several types of analysis are available for measuring taste-producing inorganics. Measurement of taste- and odor- causing organics can be made using gas or liquid chromatography. Because chromatographic analysis is time consuming and requires expensive equipment, it is not routinely performed with water samples, but should be done if problem organics are suspected. However, because of the synergism noted earlier, quantifying the sources does not necessarily quantify the nature or intensity of taste and odor.

Uses of taste and odor

Although odors can be a problem with wastewater, the taste and odor parameter is only associated with potable water.

e) Temperature

Temperature is not used to evaluate directly either potable water or wastewater. It is however, one of the most important parameters in natural surface - water systems. The temperature of surface waters governs to a large extent the biological species present and their rates of activity. Temperature has an effect on most chemical reactions that occur in natural water system. Temperature also has a pronounced effect on the solubility of gases in water.

Sources of temperature

The temperature of natural water systems responds to many factors, the ambient temperature (temperature of the surrounding atmosphere) being the most universal. Generally, shallow bodies of water are more affected by ambient temperatures than are deeper bodies.

Impacts of temperature

Cooler waters usually have a wider diversity of biological species. At lower temperatures, the rate of biological activity, i.e., utilization of food supplies, growth, reproduction, etc. is slower. If the temperature is increased, biological activity increases. An increase of 10^0C is usually sufficient to double the biological activity, if essential nutrients are present. Higher-order species, such as fish, are affected dramatically by temperature and by dissolved levels, which are a function of temperature.

2.5.2.2 Chemical water quality parameters

Dissolved materials and ions occur naturally in water because of mineral dissolution from weathered rocks and soils. The most common positively charged chemicals found in natural waters are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+). Several other chemicals are present and essential to sustaining life in aquatic systems. Nutrients such as nitrogen (N) and phosphorus (P) are needed by aquatic organisms, but at high concentrations can degrade ecosystems through eutrophication. Metal ions, similarly, are essential to biological processes at low concentrations but can be toxic at higher concentrations.

The most important negatively charged ions, called anions, found in natural waters are chloride ($Cl^–$), fluoride(F^-), sulphate ($SO_4^{2–}$), bicarbonate ($HCO_3^–$) and carbonate ($CO_3^{2–}$), which also originate from dissolution of rock and soil minerals. These anions play an important role in buffering water and also impact the solubility of many cations. The ability to neutralize acids is termed alkalinity and is mainly due to the presence of bicarbonate and carbonate. Industrial discharge from base metal mines (copper, lead and zinc) and other industrial activities can impair the chemical water characteristics if they are not regulated.

2.5.2.3 Biological water quality parameters

Biological water characteristics are used to describe the presence of microbiological organisms and water-borne pathogens. Many organisms can cause illness when consumed by humans and animals. Micro-organisms and waterborne pathogens enter rivers and lakes either naturally or via the release of untreated or partially treated sewage.

Achieving a water quality standard that will not harm aquatic organisms, and is safe for human consumption is a challenge throughout much of the basin. This is especially true for rural and peri-urban areas. Water borne diseases such as dysentery, cholera, typhoid, gastroenteritis and hepatitis are the primary cause of disease and poor health in developing countries. Bilharzia and malaria are other waterborne diseases that persist in the developing countries. Drinking and bathing water polluted with Escherichia coli and coli form bacteria can easily cause infections.

2.6 Nature and types of Water pollutants

Dear student, under this main content you learn about the nature and types of water pollutants. Can you mention some of the nature and types of water pollutants. Let warm up yourself with the following activities.

Learning task 2. 6

a) Define water pollution
b) Explain the major types of water pollutants
c) Describe the major classes of water pollutants
d) Explain the effects of water pollutants to aquatic life
e) Explain the relationship between oxygen sag curve and microbial growth

Throughout history, the quality of drinking water has been a factor in determining human welfare. Fecal pollution of drinking water has frequently caused waterborne diseases that have decimated the populations of whole cities. Unpleasant water polluted by natural sources has caused great hardship for people forced to drink it or use it for irrigation. Although there are still occasional epidemics of bacterial and viral diseases caused by infectious agents carried in drinking water, waterborne diseases have in general been well controlled, and drinking water in technologically advanced countries is now remarkably free of the disease-causing agents that were very common water contaminants only a few decades earlier.

Currently, waterborne toxic chemicals pose the greatest threat to the safety of water supplies in industrialized nations. There are many possible sources of chemical contamination. These include wastes from industrial chemical production, metal plating operations, and pesticide runoff from agricultural lands. Some specific pollutants include industrial chemicals such as chlorinated hydrocarbons; heavy metals, including cadmium, lead, and mercury; saline water; bacteria, particularly coliforms; and general municipal and industrial wastes.

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans, aquifers and groundwater). Water pollution occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. Water pollution affects plants and organisms living in these bodies of water. In almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities. Understanding the sources, interactions, and effects of water pollutants is essential for controlling pollutants in an environmentally safe and economically acceptable manner.

2.6.1 Types of water pollutants

There are different types of pollutants in water bodies.

i) **Pollutants can be: Non-conservative or conservative**

De*gradable (non-conservative) pollutants* are pollutants (impurities) which eventually decompose into harmless substances or which may be removed by treatment methods; that is, certain organic materials and chemicals, domestic sewage, heat, plant nutrients, most bacteria and viruses, certain sediments.**No*n-degradable (conservative) pollutants*** are pollutants (impurities) which persist in the water environment and do not reduce in concentration unless diluted or removed through treatment; that is, certain organic and inorganic chemicals, salts, colloidal suspensions

ii) Pollutants can be Hazardous waterborne pollutants or Radionuclide pollutants

H*azardous waterborne pollutants*: complex forms of deleterious wastes including toxic trace metals, certain inorganic and organic compounds. **R*adionuclide pollutants***: materials which have been subjected to a radioactive source.

iii) Based on constituents; pollutants can be toxic compounds, or can affect oxygen balance of water or can be inert suspended or dissolved solids.

iv) Based on the source pollutants can be point sources and non-point sources

2.6.2 Classes of water pollutants

There are different classes of pollutants. The main ones are Oxygen –Demanding Wastes, Pathogens, Nutrients, salts, thermal pollution, heavy metals, pesticides, Volatile Organic Compounds, Oxygen, oxidants, and reductants, organic pollutants, Soaps, Detergents, and Detergent Builders, polychlorinated biphenyls.

i. Oxygen –Demanding Wastes

One of the most important water quality parameters is the amount of dissolved oxygen (DO) present. Oxygen demanding wastes are substances that oxidize in the receiving body of water, reducing the amount of DO available. As DO drops, fish and other aquatic life are threatened and, in the extreme case, killed. In addition, as dissolved oxygen levels fall, undesirable odors, tastes, & colors reduce the acceptability of the water as a domestic supply and reduce its attractiveness for recreational uses.

Oxygen–demanding wastes are usually biodegradable organic substances contained in municipal wastewaters or in effluents from certain industries, such as food processing and paper production. In addition, the oxidation of certain inorganic compounds may also contribute to the oxygen demand. Even naturally occurring organic matter, such as leaves and animal droppings, that find their way into surface water add to the DO depletion.

There are several measures of oxygen demand commonly used. The chemical oxygen demand, COD, is the amount of oxygen needed to chemically oxidize the wastes, while the biochemical oxygen demand, BOD, is the amount of oxygen required by microorganisms to biologically degrade the waster. BOD has traditionally been the most important measure of the strength of organic pollution, and the amount of BOD reduction in a wastewater treatment plant is a key indicator of process performance.

ii. Pathogens

It has long been known that contaminated water is responsible for the spread of many communicable diseases. Pathogens are disease – producing organisms that grow & multiply within the host. Examples of pathogens associated with water include bacteria responsible for cholera, basically dysentery, typhoid, & paratyphoid fever; viruses responsible for infections hepatitis and poliomyelitis; protozoa, which cause amebic dysentery & giardiasis, & helminthes, or parasitic worms, which cause diseases such as schistosomiasis and dracontiasis (guinea worm). The intestinal discharges of an infected individual, a carrier, may contain billions of these pathogens, which, if allowed to enter the water supply, can cause epidemics of their disease, which makes it even more important to carefully protect all water supplies from any human waste contamination.

iii. Nutrients

Nutrients are chemicals, such as nitrogen, phosphorous, carbon, sulfur, calcium, potassium, ion, manganese, boron, & cobalt, which are essential to the growth of living things. In terms of water quality, nutrients can be considered as pollutants when their concentrations are sufficient to allow excessive growth of aquatic plants, particularly algal. When nutrients stimulate the growth of algae, the attractiveness of the body of water for recreational uses, as a drinking water supply, & as a viable habitat for other living things can be adversely affected.

Nutrient enrichment can lead to blooms of algae which eventually die and decompose. Their decomposition removes oxygen from the water, potentially leading to levels of DO that are insufficient to sustain normal life forms. Algae & decaying organic matter add color, turbidity, odors, and objectionable tastes to water that are difficult to remove & that may greatly reduce its acceptability as a domestic water source. The process of nutrient enrichment is called ***eutrophication.***

Aquatic species require a long list of nutrients for growth and reproduction, but from a water quality perspective; the three most important ones are carbon, nitrogen, & phosphorous. Major sources of both nitrogen & phosphorous include municipal wastewater discharges, run off from animal feedlots, & chemical fertilizers. In addition certain bacteria & blue green algae can obtain nitrogen directly from the atmosphere. These life forms are usually abundant in lakes that have high rates of biological productivity, making the control of nitrogen in such lakes extremely difficult. Certain forms of acid rain can also contribute nitrogen to lakes. While there are several special sources of nitrogen, the only unusual source of phosphorous is from detergents.

When phosphorous is the limiting nutrient in a lake that is experiencing an algal problem, it is especially important to limit the nearby use of phosphate in detergents.

iv. Salts

Water naturally accumulates a variety of dissolved solids, or salts, as it passes through soils and rocks on its way to the sea. These salts typically include such actions as sodium, calcium, magnesium, & potassium, & anions such as chloride, sulfate, & bicarbonate. While a careful analysis of salinity would result in a list of the concentrations of the primary cations & anions, a simpler, more commonly used measure of salinity is the concentration of total dissolved solid, TDS. As a rough approximation, fresh water can be considered to be water with less than 1500mg/L TDS; brackish waters may have TDS values up to 5000mg/L and, saline waters are those with concentrations above 5000mg/L. Sea water contains 30,000-34,000 mg/L TDS.

The concentration of dissolved solids is an important indicator of the usefulness of water for various applications. Drinking water, for example, has a recommended maximum contaminant level for TDS of 500mg/L. Livestock can tolerate higher concentrations. As the concentration of salts in irrigation water increases above 500mg/L, the need for careful water management to maintain crop yields becomes increasingly important.

With sufficient drainage to keep salts from accumulating in the soil, up to 1500mg/L TDS can be tolerated by most crops with little loss of yield, but at concentrations above 2100mg/L, water is generally unsuitable for irrigation except the most salt tolerant of crops. One way to approach the salt problem is with desalination. Desalination technologies are available, but the energy required makes the economics of desalting unattractive in almost all circumstances.

v. Thermal Pollution

A large steam-electric power plant requires an enormous amount of cooling water. A typical nuclear plant, for example, warms about 40 m^3 /s of cooling water by 10 ^{0}c as it passes through the plant's condenser. If that heat is released in to a local river or lake, the resulting rise in temperature can dramatically affect life in the vicinity of the thermal plume.

There are some circumstances when warmed water might be considered beneficial with in certain limits, thermal additions can promote fish growth, and fishing might actually be improved in the vicinity of power plant. On the other hand, sudden changes in temperature caused by periodic plant outrages, both planned and unanticipated, can make it difficult for the local ecology to ever acclimate. For some species, such as trout and salmon, any increase in temperature is undesirable.

vi. Heavy Metals

The term heavy metal is less precisely defined. In chemical terms it can refer to metals with specific gravity greater than about 4 or 5, but more often, the term is simply used to denote metals that are toxic. The list of toxic metals includes aluminum, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, strontium, thallium, tin, titanium, & zinc. Some of these metals, such as chromium & iron, are essential nutrients in our diets, but in higher doses are extremely toxic.

Metals may be inhaled, as it is often the case with lead, for example, and they may be ingested. How well they are absorbed in the body depends somewhat on the particular metal in question. Some metal salts, such as those formed with lead, tin, & cadmium, are poorly absorbed, while the salts of others such as arsenic & thallium are almost completely absorbed. The most important route for the elimination of metals is via the kidneys. In fact, kidneys can be considered to be complex filters whose primary purpose is to eliminate toxic substances from the body.

vii. Pesticides

The term pesticide is used to cover a range of chemicals that kill organisms that humans consider undesirable & includes the more specific categories of insecticides, herbicides, rodenticides, &

fungicides. There are three main groups of synthetic organic insecticides = Organochlorine (also known as chlorinated hydrocarbons), Organophosphates & Carbamates. In addition a number of herbicides, including the chlorphenoxy compounds 2, 4, 5, T (which contains the impurity dioxin, which is one of the most potent toxins known) & 2, 4-D are common water pollutants.

The most well-known organochlorine pesticide is DDT which has been widely used to control insects that carry such diseases as malaria, typhus, & plague. DDT is credited with saving literally millions of lives worldwide. In spite of its more recent reputation as a dangerous pesticide, in terms of human toxicity DDT is considered to be relatively safe. It was its impact on food chains, rather than human toxicity that led to its ban. Organochlorine pesticides, such as DDT, have two properties that cause them to be particularly disruptive to food chains. They are very **persistent,** which means they last a long time in the environment before being broken down in to other substances, and they are quite **soluble in lipids**, which means they easily accumulate in fatty tissues.

viii. Volatile Organic Compounds

Volatile organic compounds (**VOCs**) are the most commonly found contaminants in groundwater. They are often used as solvents industrial processes and a number of them are either known or suspected carcinogens or mutagens. Their volatility means they are not often found in concentrations can be hundreds or thousands of times higher. Their volatility also suggests the most common method of treatment, which is to aerate the water to encourage them to vaporize. Five VOCs are especially toxic and their presence in drinking water is cause for special concern. These are: Rinychloride, Tetrachloroethylene, Trichloroethylene (TCE), 1, 2-Dichloroethane and Carbon tetrachloride.

ix. Oxygen, oxidants and reductants

Oxygen is a vitally important species in water. In water, oxygen is consumed rapidly by the oxidation of organic matter, $\{CH_2O\}$: $\{CH_2O\} + O_2$ Microorganisms→ CO2 + H_2O
Unless the water is reaerated efficiently, as by turbulent flow in a shallow stream, it rapidly loses oxygen and will not support higher forms of aquatic life. In addition to the microorganism-mediated oxidation of organic matter, oxygen in water may be consumed by the biooxidation of nitrogenous material, and by the chemical or biochemical oxidation of chemical reducing agents:

$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3^- + H_2O$

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

$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$

All these processes contribute to the deoxygenation of water. The degree of oxygen consumption by microbially-mediated oxidation of contaminants in water is called the biochemical oxygen demand (or biological oxygen demand), BOD. This parameter is commonly measured by determining the quantity of oxygen utilized by suitable aquatic microorganisms during a five-day period. Despite the somewhat arbitrary five-day period, this test remains a respectable measure of the short-term oxygen demand exerted by a pollutant. The addition of oxidizable pollutants to streams produces a typical oxygen sag curve as shown in Figure 2.6.2 below.

Initially, a well-aerated, unpolluted stream is relatively free of oxidizable material; the oxygen level is high; and the bacterial population is relatively low. With the addition of oxidizable pollutant, the oxygen level drops because reaeration cannot keep up with oxygen consumption. In the decomposition zone, the bacterial population rises. The septic zone is characterized by a high bacterial population and very low oxygen levels. The septic zone terminates when the oxidizable pollutant is exhausted, and then the recovery zone begins. In the recovery zone, the bacterial population decreases and the dissolved oxygen level increases until the water regains its original condition.

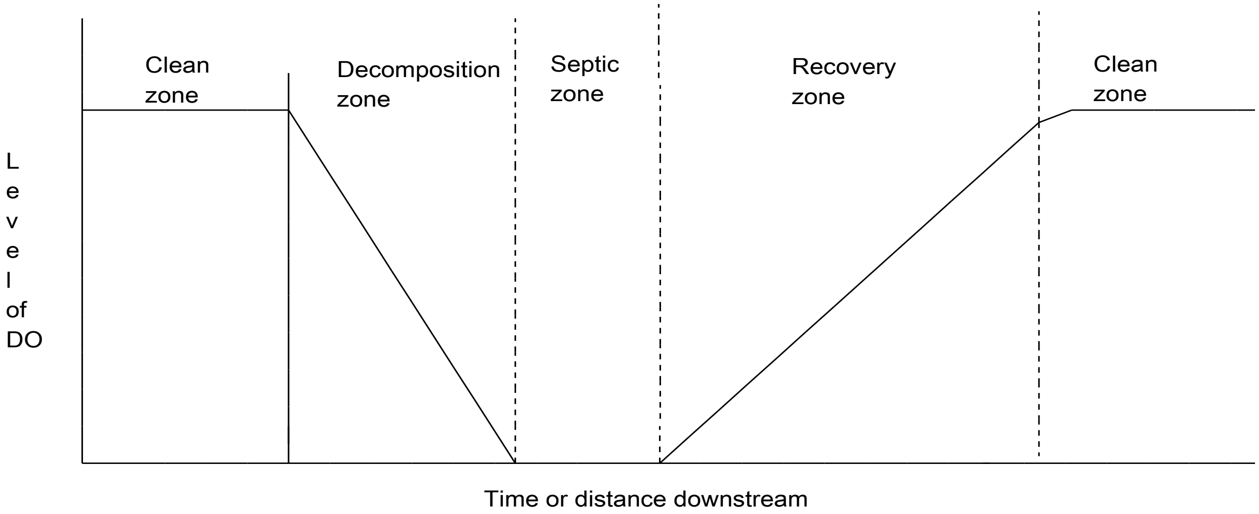


Figure 2.6.2 Oxygen sag curve resulting from the addition of oxidizable pollutant material to a stream.

x. Organic pollutants

Sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants, including organic pollutants. Some of these pollutants, particularly oxygen-demanding substances such as oil, grease, and solids are removed by primary and secondary sewage-treatment processes. Others, such as salts, heavy metals, and refractory (degradation-resistant) organics, are not efficiently removed. Disposal of inadequately treated sewage can cause severe problems. For example, offshore disposal of sewage, once commonly practiced by coastal cities, results in the formation of beds of sewage residues.

xi. Soaps, Detergents, and Detergent Builders

Soaps, detergents and detergent builders are used as cleaning materials. However, these materials are the cause for water pollution in particular and cause environmental problems in general.

xii. Poly Chlorinated Biphenyls (PCB)

First discovered as environmental pollutants in 1966, **polychlorinated biphenyls** (**PCB** compounds) have been found throughout the world in water, sediments, bird tissue, and fish tissue. These compounds constitute an important class of special wastes. The massive production of **radionuclides** (radioactive isotopes) by weapons and nuclear reactors since World War II has been accompanied by increasing concern about the effects of radioactivity upon health and the environment. Radionuclides are produced as fission products of heavy nuclei of such elements as uranium or plutonium. Radionuclides differ from other nuclei in that they emit **ionizing radiation** such as alpha particles, beta particles, and gamma rays.

Chapter Summary

- Aquatic chemistry consider water in rivers, lakes, estuaries, oceans, and underground, as well as the phenomena that determine the distribution and circulation of chemical species in natural waters
- Water has a number of unique properties that are essential to life. Some of the special characteristics of water include its polar character, tendency to form hydrogen bonds, and ability to hydrate metal ions.
- The physical condition of a body of water strongly influences the chemical and biological processes that occur in water.
- Surface water occurs primarily in streams, lakes, and reservoirs
- Wetlands are flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants
- Estuaries are arms of the ocean into which streams flow. The mixing of fresh and salt water gives estuaries unique chemical and biological properties.
- As a result of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic.
- In the hypolimnion, bacterial action on biodegradable organic material may cause the water to become anaerobic (lacking dissolved oxygen).
- As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion.
- The living organisms (**biota**) in an aquatic ecosystem may be classified as either autotrophic or heterotrophic. **Autotrophic** organisms utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms.

- Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of water to support algal growth and other aquatic life, so it can be used as a measure of water fertility.
- Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:
- Calcium is a key element in many geochemical processes, and minerals constitute the primary sources of calcium ion in waters.
- Calcium ion, along with magnesium and sometimes iron (II) ion, accounts for water hardness.
- The most common manifestation of water hardness is the curdy precipitate formed by soap in hard water.
- The properties of metals dissolved in water depend largely upon the nature of metal species dissolved in the water.
- A special case of complexation in which a ligand bonds in two or more places to a metal ion is called **chelation**
- Complexation may have a strong effect upon oxidation-reduction equilibria by shifting reactions,
- **Oxidation-reduction** (**redox**) reactions are those involving changes of oxidation states of reactants.
- One of the most damaging redox phenomena is **corrosion**, defined as the destructive alteration of metal through interactions with its surroundings.
- ***Water Quality Assessment i***s an evaluation of the beneficial use impairment that is occurring, or could potentially occur, due to the presence of a particular chemical(s) or other constituent. It is not an assessment of the frequency of exceedance of a water quality standard.
- Water quality criteria are based on variables that characterize the quality of water and/or the quality of the suspended particulate matter, the bottom sediment and the biota.

- The most common positively charged chemicals found in natural waters are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}). Several other chemicals are present and essential to sustaining life in aquatic systems
- The most important negatively charged ions, called anions, found in natural waters are chloride ($Cl^{–}$), fluoride(F^{-}), sulphate ($SO_4^{2–}$), bicarbonate ($HCO_3^{–}$) and carbonate ($CO_3^{2–}$), which also originate from dissolution of rock and soil minerals.

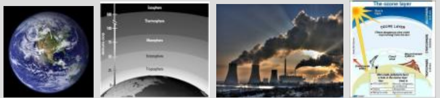
Self test exercises

1. Discuss how thermal stratification of a body of water may affect its chemistry.
2. Relate aquatic life to aquatic chemistry. In so doing, consider the following: autotrophic, producers, heterotrophes, decomposers, eutrophication, dissolved oxygen, biochemical oxygen demand.
3. Discuss the factors that affect the chemistry of water body
4. Discuss the most important unique properties of water. Describe each of the following unique properties of water related to thermal characteristics, transmission of light, surface tension, solvent properties.
5. What are the most important chemical phenomena in water bodies that determine the fate of a toxin in water bodies?
6. Indicate how the concentration of dissolved gas in water is determined.
7. What are the processes that supply and deplete oxygen in aquatic systems? Discuss the importance of oxygen and carbon dioxide in aquatic systems? Can you site any disadvantage of the mentioned gases in aquatic systems?
8. Derive formula used to calculate fraction of CO_2, CO_3^{2-} and HCO_3^- in water.
9. Which species is predominant in water bodies CO_2, CO_3^{2-} or HCO_3^- ? Justify your reason.
10. What is alkalinity? How it can be measured? Differenciate b/n alkalinity and basicity?
11. What are the fates of a metal species thrown into water body?
12. Describe the importance of complexation and redox reactions in aquatic systems.
13. How do we detect the tendency of dissolution of a metal atom introduced into a solution that contains another metal ion? Use your own example.
14. How do you describe equilibrium constant for redox reactions?
15. What is pE? How do you measure pE in natural water?
16. What is corrosion? How does that affect the economy?

17. Describe the types and nature of water pollutants
18. Explain the effects of water pollutants; for your explanation support with examples
19. Relate the oxygen sag curve and bacterial growth pattern on the same curve.
20. Discuss all the water quality parameters and explain the significance and effect of each water quality parameters.

Chapter 3

THE ATMOSPHERE AND ATMOSPHERIC CHEMISTRY



Unit Introduction

Dear student, this chapter deals with the atmosphere and atmospheric chemistry. It deals with Definition of some basic terms, Introduction to Atmospheric Chemistry, Importance and physical characteristics of the atmosphere, Atmospheric chemical reactions such as: (Photochemical reactions, Reactions in Troposphere, Reactions in Stratosphere, Ozone formation and depletion, Reaction mechanism, Reactions in Thermosphere), Atmospheric Pollution, Nature and classification of air pollutants, Particles in the atmosphere, Gaseous inorganic air pollutant, Gaseous organic air pollutants, The endangered global atmosphere(Photochemical smog, Green house and Global warming, The Nuclear winter, Acid rain, Ozone layer destruction)

Learning objective of the unit

Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:-

- Define important terms like atmosphere and atmospheric chemistry
- Explain importance and physical characteristics of the atmosphere
- Describe the stratification of the Atmosphere
- Explain the major chemical reactions in the atmosphere
- Explain sources & reactions of HO_x, ClO_x & NO_x In the stratosphere
- Explain how Antarctic O_3 hole is formed
- Define Atmospheric Pollution

- Mention the Nature and classification of atmospheric pollutants
- Explain how particles in the atmosphere are formed
- Describe the physical and chemical processes for particle formation
- Explain the effects of particles in the atmosphere
- Describe Gaseous organic and inorganic air pollutants
- Explain the endangered global atmosphere
- Explain the source and effects of photochemical smog
- Explain the source and effects of greenhouse gases and global warming
- Explain the source and effects of nuclear winter
- Explain the source and effects of acid rain
- Explain how particles in the atmosphere are formed

3.1. Introduction to Atmospheric Chemistry

Dear student, under this main content you learn about the Atmospheric Chemistry. Do you know some of fundamentals of Atmospheric Chemistry, Let warm up yourself with the following activities.

Learning task 3.1

a) Define Atmospheric Chemistry
b) Mention the major composition of Atmosphere
c) Explain the stratification of the Atmosphere

A**tmosphere** is a thin layer of mixed gases covering the earth's surface. Exclusive of water vapour, atmospheric air is 78.1% (by volume) Nitrogen, 21.0% Oxygen, 0.9% Argon, and 0.03% carbon dioxide. Normally, air contains 1-3% water vapor by volume. In addition, air contains a large variety of trace level gases at levels below 0.002%, including neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, sulfur dioxide, ozone, nitrogen dioxide, ammonia, and carbon monoxide. The atmosphere is divided into several layers on the basis of temperature. Of these, the most significant are the **troposphere** extending in altitude from the earth's surface to approximately 11 km, and the stratosphere from about 11 km to approximately 50 km.

The temperature of the **troposphere** ranges from an average of 15°C at sea level to an average of -56°C at its upper boundary. The average temperature of the stratosphere increases from -56°C at its boundary with the troposphere to –2°C at its upper boundary. The reason for this increase is absorption of solar ultraviolet energy by ozone (O_3) in the stratosphere. Various aspects of the environmental chemistry of the atmosphere are discussed in this chapter.

The most significant feature of atmospheric chemistry is the occurrence of **photochemical reactions** resulting from the absorption by molecules of light photons, designated $h\nu$. (The energy, E, of a photon of visible or ultraviolet light is given by the equation, $E = h\nu$, where h is Planck's constant and ν is the frequency of light, which is inversely proportional to its wavelength. Ultraviolet radiation has a higher frequency than visible light and is, therefore, more energetic and more likely to break chemical bonds in molecules that absorb it.) One of the most significant photochemical reactions is the one responsible for the presence of ozone in the stratosphere, which is initiated when O_2 absorbs highly energetic ultraviolet radiation in the wavelength ranges of 135-176 nanometers (nm) and 240-260 nm in the stratosphere:

$$O_2 + h\nu \rightarrow O + O$$

The oxygen atoms produced by the photochemical dissociation of O_2 react with oxygen molecules to produce ozone, O_3 ; $O + O_2 + M \rightarrow O_3 + M$; where M is a third body, such as a molecule of N_2 , which absorbs excess energy from the reaction. The ozone that is formed is very effective in absorbing ultraviolet radiation in the 220-330 nm wavelength range, which causes the temperature increase observed in the stratosphere. The ozone serves as a very valuable filter to remove ultraviolet radiation from the sun’s rays. If this radiation reached the earth’s surface, it would cause skin cancer and other damage to living organisms.

3.2 Composition of the atmosphere

3.2.1 Gaseous Oxides in the Atmosphere

Oxides of carbon, sulfur, and nitrogen are important constituents of the atmosphere and are pollutants at higher levels. Of these, carbon dioxide, CO_2, is the most abundant. It is a natural atmospheric constituent, and it is required for plant growth. However, the level of carbon dioxide in the atmosphere, now at about 360 ppm by volume, is increasing by about 1 ppm per year. This increase in atmospheric CO_2 may well cause general atmospheric warming; the “greenhouse effect,” with potentially very serious consequences for the global atmosphere and for life on earth. Though not a global threat, carbon monoxide (CO) can be a serious health threat because it prevents blood from transporting oxygen to body tissues.

The two most serious nitrogen oxide air pollutants are nitric oxide (NO) and nitrogen dioxide (NO_2) collectively denoted as “NOx.” These tend to enter the atmosphere as NO, and photochemical processes in the atmosphere can convert NO to NO_2. Further reactions can result in the formation of corrosive nitrate salts or nitric acid, HNO_3. Nitrogen dioxide is particularly significant in atmospheric chemistry because of its photochemical dissociation by light with a wavelength less than 430 nm to produce highly reactive O atoms. This is the first step in the formation of photochemical smog . Sulfur dioxide, SO_2, is a reaction product of the combustion of sulfur-containing fuels such as high-sulfur coal. Part of this sulfur dioxide is converted in the atmosphere to sulfuric acid, H_2SO_4, normally the predominant contributor to acid precipitation.

3.2.2 Hydrocarbons and Photochemical Smog

The most abundant hydrocarbon in the atmosphere is methane, CH_4, released from underground sources as natural gas and produced by the fermentation of organic matter. Methane is one of the least reactive atmospheric hydrocarbons and is produced by diffuse sources, so that its participation in the formation of pollutant photochemical reaction products is minimal. The most significant atmospheric pollutant hydrocarbons are the reactive ones produced as automobile exhaust emissions. In the presence of NO, under conditions of temperature inversion

3.2.3 Particulate Matter

Particles ranging from aggregates of a few molecules to pieces of dust readily visible to the naked eye are commonly found in the atmosphere. Some atmospheric particles, such as sea salt formed by the evaporation of water from droplets of sea spray, are natural and even beneficial atmospheric constituents. Very small particles called **condensation nuclei** serve as bodies for atmospheric water vapor to condense upon and are essential for the formation of rain drops. Colloidal-sized particles in the atmosphere are called **aerosols**. Those formed by grinding up bulk matter are known as **dispersion aerosols**, whereas particles formed from chemical reactions of gases are **condensation aerosols**; the latter tend to be smaller.

Smaller particles are in general the most harmful because they have a greater tendency to scatter light and are the most respirable (tendency to be inhaled into the lungs). Much of the mineral particulate matter in a polluted atmosphere is in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel. Smaller particles of **fly ash** enter furnace flues and are efficiently collected in a properly equipped stack system. However, some fly ash escapes through the stack and enters the atmosphere. Unfortunately, the fly ash thus released tends to consist of smaller particles that do the most damage to human health, plants, and visibility.

3.3 Importance and physical characteristics of the atmosphere

Dear student, under this main content you learn about the importance and physical characteristics of the atmosphere. Do you know some of the importance and physical characteristics of the atmosphere, Let warm up yourself with the following activities.

Learning task 3.2

a) Describe the importance of the atmosphere
b) Explain the physical characteristics of the atmosphere

c) Explain the variation of pressure and density with altitude
d) Describe the atmospheric composition
e) Explain the stratification of the atmosphere

3.3.1 Importance of the atmosphere

The atmosphere is a protective blanket which nurtures life on the Earth and protects it from the hostile environment of outer space. The atmosphere is the source of carbon dioxide for plant photosynthesis and of oxygen for respiration. It provides the nitrogen that nitrogen-fixing bacteria and ammonia-manufacturing plants use to produce chemically-bound nitrogen, an essential component of life molecules. As a basic part of the hydrologic cycle, the atmosphere transports water from the oceans to land, thus acting as the condenser in a vast solar-powered still.

Unfortunately, the atmosphere also has been used as a dumping ground for many pollutant materials ranging from sulfur dioxide to refrigerant Freon a practice which causes damage to vegetation and materials, shortens human life, and alters the characteristics of the atmosphere itself. In its essential role as a protective shield, the atmosphere absorbs most of the cosmic rays from outer space and protects organisms from their effects.

By absorbing electromagnetic radiation below 300 nm, the atmosphere filters out damaging ultraviolet radiation that would otherwise be very harmful to living organisms. Furthermore, because it reabsorbs much of the infrared radiation by which absorbed solar energy is re-emitted to space, the atmosphere stabilizes the earth’s temperature, preventing the tremendous temperature extremes that occur on planets and moons lacking substantial atmospheres.

3.3.2. Physical characteristics of the atmosphere

Atmospheric science deals with the movement of air masses in the atmosphere, atmospheric heat balance, and atmospheric chemical composition and reactions. In order to understand atmospheric chemistry and air pollution, it is important to have an overall appreciation of the atmosphere, its composition, and physical characteristics.

3.3.2.1 Atmospheric Composition

Dry air within several kilometers of ground level consists of two **major components :** Nitrogen, 78.08 % (by volume) and Oxygen, 20.95 % . Two **minor components:** Argon, 0.934 % ; Carbon dioxide, 0.036 % in addition to argon, four more **noble gases**: Neon, 1.818×10^{-3} % ; Helium,

5.24×10^{-4} % ; Krypton, 1.14×10^{-4} % ; Xenon, 8.7×10^{-6} % and **trace gases**. Atmospheric air may contain 0.1–5% water by volume, with a normal range of 1–3%.

3.3.2.2 Variation of Pressure and Density with Altitude

As anyone who has exercised at high altitudes well knows, the density of the atmosphere decreases sharply with increasing altitude as a consequence of the gas laws and gravity. More than 99% of the total mass of the atmosphere is found within approximately 30 km of the Earth's surface. Such an altitude is miniscule compared to the Earth's diameter, so it is not an exaggeration to characterize the atmosphere as a "tissue-thin" protective layer.

Although the total mass of the global atmosphere is huge, approximately 5.14×10^{15} metric tons, it is still only about one millionth of the Earth's total mass. The fact that atmospheric pressure decreases as an approximately exponential function of altitude largely determines the characteristics of the atmosphere. Ideally, in the absence of mixing and at a constant absolute temperature, T, the pressure at any given height, Ph, is given in the exponential form,

$$Ph = P_o e^{-Mgh/RT}$$

$$P_h = P_o e^{-Mgh/RT}$$

Where P_o pressure at zero altitude (sea level); M average molar mass of air (28.97 g/ mol in the troposphere); g is acceleration due to gravity and h is the altitude

$$P_h = P_o e^{-Mgh/RT}$$

At an average sea-level temperature of 288K, the factor RT/Mg(scale height) is 8×10^5 cm or 8km; at an altitude of 8km, the pressure is only about 39% of that at sea-level. Conversion of the above equation to the logarithmic (base 10) form and expression of h in km yields;

$$\log P_h = \log P_o - \frac{Mgh \times 10^5}{2.303RT}$$

If we take the pressure at sea level to be exactly 1 atm gives the following expression:

$$\log P_h = -\frac{Mgh \times 10^5}{2.303RT}$$

Plot of P_h and temperature Vs altitude is nonlinear because of variations arising from nonlinear variation in temperature with altitude.

The characteristics of the atmosphere vary widely with altitude, time (season), location (latitude), and even solar activity. At very high altitudes, normally reactive species such as atomic oxygen, O, persist for long periods of time. That occurs because the pressure is very low at these altitudes such that the distance traveled by a reactive species

3.3.2.3 Stratification of the Atmosphere

As shown in Figure 3.2.2.3, the atmosphere is stratified on the basis of the temperature/density relationships resulting from interactions between physical and photochemical (light-induced chemical phenomena) processes in air. The lowest layer of the atmosphere extending from sea level to an altitude of 10-16 km is the **troposphere**, characterized by a generally homogeneous composition of major gases other than water and decreasing temperature with increasing altitude from the heat-radiating surface of the earth.

The upper limit of the troposphere, which has a temperature minimum of about -56°C, varies in altitude by a kilometer or more with atmospheric temperature, underlying terrestrial surface, and time. The homogeneous composition of the troposphere results from constant mixing by circulating air masses. However, the water vapor content of the troposphere is extremely variable because of cloud formation, precipitation, and evaporation of water from terrestrial water bodies.

The very cold temperature of the **tropopause** layer at the top of the troposphere serves as a barrier that causes water vapor to condense to ice so that it cannot reach altitudes at which it would photo dissociate through the action of intense high-energy ultraviolet radiation. If this happened, the hydrogen produced would escape the earth's atmosphere and be lost.

The atmospheric layer directly above the troposphere is the **stratosphere**, in which the temperature rises to a maximum of about -2°C with increasing altitude. This phenomenon is due to the presence of ozone, O_3, which may reach a level of around 10 ppm by volume in the mid-range of the stratosphere. The heating effect is caused by the absorption of ultraviolet radiation energy by ozone, a phenomenon discussed later in this chapter. The absence of high levels of radiation-absorbing species in the **mesosphere** immediately above the stratosphere results in a further temperature decrease to about –92°C at an altitude around 85 km.

The upper regions of the mesosphere and higher define a region called the exosphere from which molecules and ions can completely escape the atmosphere. Extending to the far outer reaches of the atmosphere is the **thermosphere**, in which the highly rarified gas reaches temperatures as high as 1200°C by the absorption of very energetic radiation of wavelengths less than approximately 200 nm by gas species in this region.

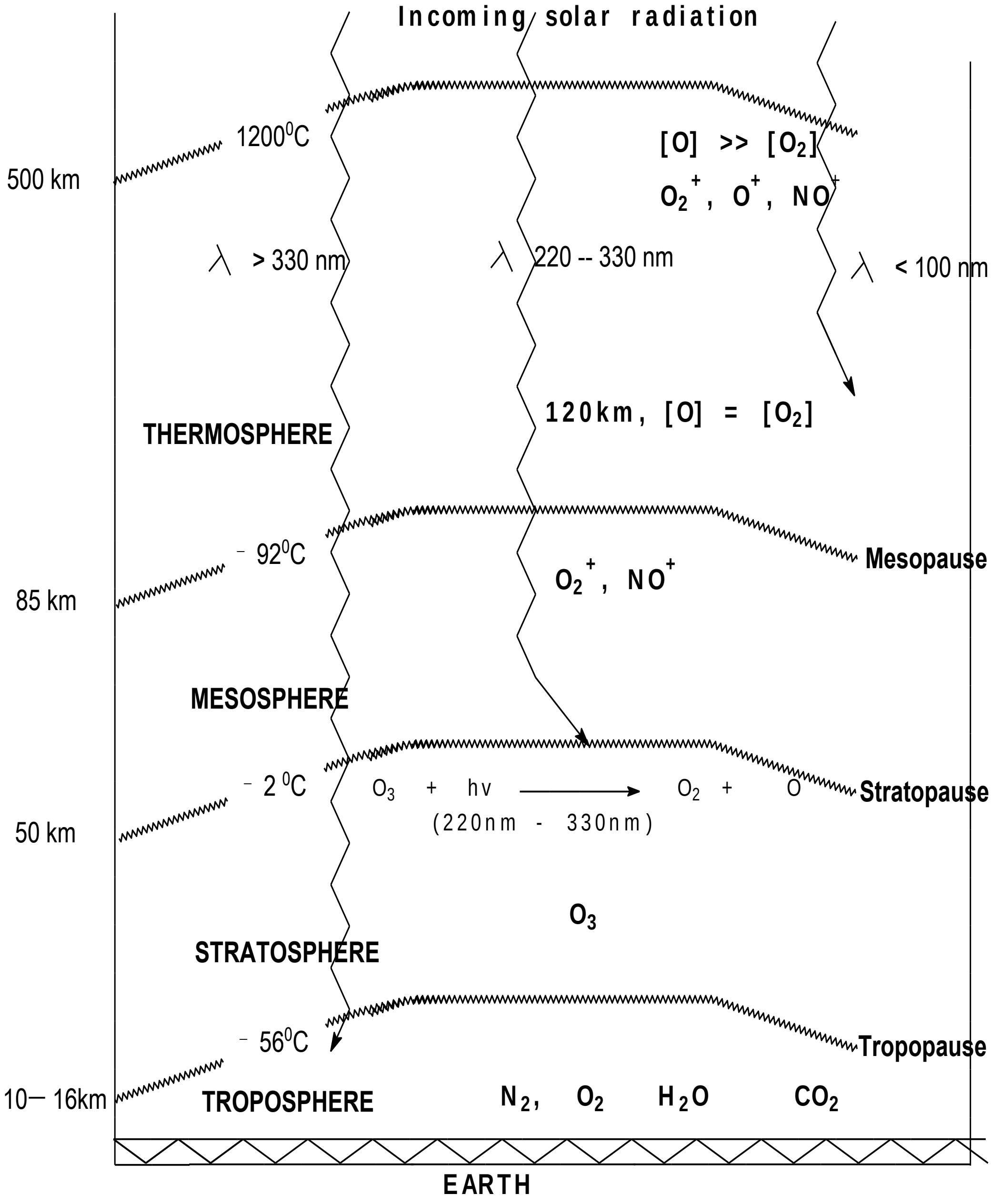


Figure 3.2.2.3 Stratification of the atmosphere

3.4. Atmospheric chemical reactions

Dear student, under this main content you learn about the atmospheric chemical reactions, chemical and photochemical reactions in the atmosphere. Do you know some of the chemical and photochemical reactions in the atmosphere? Let warm up yourself with the following activities.

Learning task 3.4

a) Mention major atmospheric chemical processes

b) Describe representation of major atmospheric chemical processes

c) Mention gaseous atmospheric chemical species that can cause atmospheric pollution

d) Explain the difference between unstable reactive species and photochemically active species

Dear student, the study of atmospheric chemical reactions is difficult. One of the primary obstacles encountered in studying atmospheric chemistry is that the chemist generally must deal with incredibly low concentrations, so that the detection and analysis of reaction products is quite difficult. Simulating high-altitude conditions in the laboratory can be extremely hard because of interferences, such as those from species given off from container walls under conditions of very low pressure. The major atmospheric chemical processes are represented in figure 3.4. below.

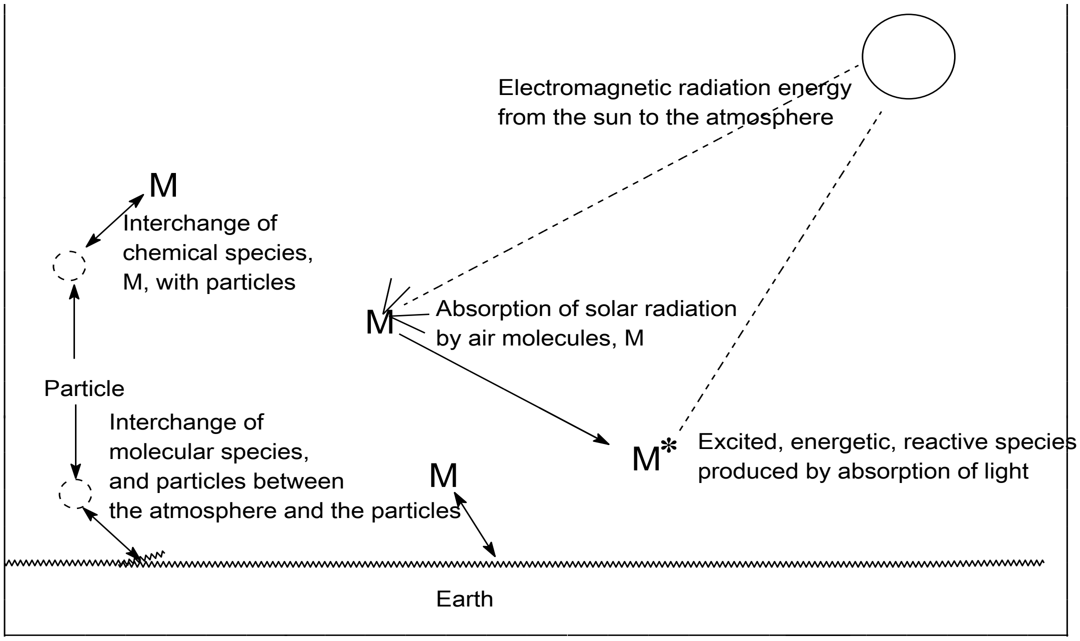


Figure 3.4 Representation of major atmospheric chemical processes.

Many chemical reactions that require a third body to absorb excess energy occur very slowly in the upper atmosphere where there is a sparse concentration of third bodies, but occur readily in a container whose walls effectively absorb energy. Container walls may serve as catalysts for some important reactions, or they may absorb important species and react chemically with the more reactive ones. ***Atmospheric chemistry involves the unpolluted atmosphere, highly polluted atmospheres, and a wide range of gradations in between.***

The same general phenomena govern all and produce one huge atmospheric cycle in which there are numerous sub cycles. Gaseous atmospheric chemical species fall into the following somewhat arbitrary and overlapping classifications: Inorganic oxides (CO, CO_2, NO_2, SO_2), oxidants (O_3, H_2O_2, HO• radical, HO_2• radical, ROO• radicals, NO_3), reductants (CO, SO_2, H_2S), organics (also reductants; in the unpolluted atmosphere, CH_4 is the predominant organic species, whereas alkanes, alkenes, and aryl compounds are common around sources of organic pollution), oxidized organic species (carbonyls, nitrates), photochemically active species (NO_2, formaldehyde), acids (H_2SO_4), bases (NH_3), salts (NH_4HSO_4,), and unstable reactive species (electronically excited NO_2, HO• radical).

In addition, both solid and liquid particles in atmospheric aerosols and clouds play a strong role in atmospheric chemistry as sources and sinks for gas-phase species, as sites for surface reactions (solid particles), and as bodies for aqueous-phase reactions (liquid droplets). Two constituents of utmost importance in atmospheric chemistry are radiant energy from the sun, predominantly in the ultraviolet region of the spectrum, and the hydroxyl radical, HO•. The former provides a way to pump a high level of energy into a single gas molecule to start a series of atmospheric chemical reactions, and the latter is the most important reactive intermediate and “currency” of daytime atmospheric chemical phenomena; NO_3 radicals are important intermediates in nighttime atmospheric chemistry.

3.4.1 Photochemical Reactions /Processes/

Dear student, under this main content you learn about the photochemical Processes and photochemical reactions in the atmosphere. Do you know some of the photochemical reactions in the atmosphere, Let warm up yourself with the following activities.

Learning task 3.4.1

a) Explain how photochemical processes and photochemical reactions occur
b) Define the following terms: Luminescence, fluorescence, phosphorescence Chemiluminescence
c) Explain how electronically excited molecules can be formed
d) Explain the difference between Intramolecular transfer and Intermolecular energy transfer

The absorption by chemical species of light, broadly defined here to include ultraviolet radiation from the sun, can bring about reactions, called **photochemical reactions**, which do not otherwise occur under the conditions (particularly the temperature) of the medium in the absence of light. Thus, photochemical reactions, even in the absence of a chemical catalyst, occur at temperatures much lower than those which otherwise would be required. Photochemical reactions, which are induced by intense solar radiation, play a very important role in determining the nature and ultimate fate of a chemical species in the atmosphere. Nitrogen dioxide, NO_2, is one of the most photochemically active species found in a polluted atmosphere and is an essential participant in the smog-formation process. A species such as NO_2 may absorb light of energy hv, producing an **electronically excited molecule**, designated in the reaction below by an asterisk, *.

$$NO_2 + h\nu \rightarrow NO_2^*$$

Electronically excited molecules are one of the three relatively reactive and unstable species that are encountered in the atmosphere and are strongly involved with atmospheric chemical processes. The other two species are atoms or molecular fragments with unshared electrons, called **free radicals**, and **ions** consisting of electrically-charged atoms or molecular fragments.

Electronically excited molecules are produced when stable molecules absorb energetic electromagnetic radiation in the ultraviolet or visible regions of the spectrum. A molecule may possess several possible excited states, but generally ultraviolet or visible radiation is energetic enough to excite molecules only to several of the lowest energy levels. The nature of the excited state may be understood by considering the disposition of electrons in a molecule. Most molecules have an even number of electrons.

These excited states are relatively energized compared to the ground state and are chemically reactive species. Their participation in atmospheric chemical reactions, such as those involved in smog formation, will be discussed later in detail. In order for a photochemical reaction to occur, light must be absorbed by the reacting species. If the absorbed light is in the visible region of the sun's spectrum, the absorbing species is colored. Colored NO_2 is a common example of such a species in the atmosphere.

The reactions that occur following absorption of a photon of light to produce an electronically excited species are largely determined by the way in which the excited species loses its excess energy. This may occur by one of the following processes:

- **Physical quenching** - loss of energy to another molecule or atom (M) followed by dissipation of the energy as heat: $O_2^* + M \rightarrow O_2 + M$(higher translational energy)
- **Dissociation** of the excited molecule (the process responsible for the predominance of atomic oxygen in the upper atmosphere): $O_2^* \rightarrow O + O$
- **Direct reaction** with another species: $O_2^* + O_3 \rightarrow 2O_2 + O$
- **Luminescence** consisting of loss of energy by the emission of electromagnetic radiation

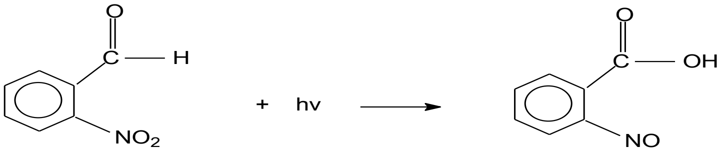
  $NO_2^* \rightarrow NO_2 + h\nu$

  If the re-emission of light is almost instantaneous, luminescence is called **fluorescence**, and if it is significantly delayed, the phenomenon is **phosphorescence**.
- **Chemiluminescence** is said to occur when the excited species (such as NO_2^* below) is formed by a chemical process: $O_3 + NO \rightarrow NO_2^* + O_2$(higher energy)
- **Intermolecular energy transfer** in which an excited species transfers energy to another species which then becomes excited: $O_2^* + Na \rightarrow O_2 + Na^*$

  A subsequent reaction by the second species is called a **photosensitized** reaction.

- **Intramolecular transfer** in which energy is transferred within a molecule

  XY* → XY†(where † denotes another excited state of the same molecule)
- **Spontaneous isomerization** as in the conversion of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid, a reaction used in chemical actinometers to measure exposure to electromagnetic radiation:



Photoionization through loss of an electron: $N_2^* \rightarrow N_2^+ + e^-$

Electromagnetic radiation absorbed in the infrared region lacks the energy to break chemical bonds, but does cause the receptor molecules to gain vibrational and rotational energy. The energy absorbed as infrared radiation ultimately is dissipated as heat and raises the temperature of the whole atmosphere.

3.4.2 Reactions in Troposphere

Dear student, under this main content you learn about reactions in troposphere. Do you know some of the reactions in troposphere, Let warm up yourself with the following activities

Learning task 3.4.2

a) What is troposphere?
b) Mention some of the dominant species in the troposphere
c) Explain the source and effects of species in the troposphere
d) Explain the common reactions in the troposphere

The main reactions in troposphere takes place are: Acid – base reactions**,** photochemical smog formation, acid rain formation, redox reaction, complexation reaction, precipitation and others. **For example**: - Acid-base reactions occur between acidic and basic species in the atmosphere.

The atmosphere is normally at least slightly acidic because of the presence of a low level of carbon dioxide, which dissolves in atmospheric water droplets and dissociates slightly:

$CO_2(g) \rightarrow CO_2(aq)$

$CO_2(aq) + H_2O \rightarrow H^+ + HCO_3^-$

Atmospheric sulfur dioxide forms a somewhat stronger acid when it dissolves in water:

$SO_2(g) + H_2O \rightarrow H^+ + HSO_3^-$

In terms of pollution, however, strongly acidic HNO_3 and H_2SO_4 formed by the atmospheric oxidation of N oxides, SO_2, and H_2S are much more important because they lead to the formation of damaging acid rain. As reflected by the generally acidic pH of rainwater, basic species are relatively less common in the atmosphere. Particulate calcium oxide, hydroxide, and carbonate can get into the atmosphere from ash and ground rock, and can react with acids such as in the following reaction: $Ca(OH)_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + 2H_2O$

The most important basic species in the atmosphere is gas-phase ammonia, NH_3. The major source of atmospheric ammonia is from biodegradation of nitrogen containing biological matter and from bacterial reduction of nitrate:

$NO_3^-(aq) + 2\{CH_2O\}(biomass) + H^+ \rightarrow NH_3(g) + 2CO_2 + H_2O$

Ammonia is particularly important as a base in the air because it is the only water-soluble base present at significant levels in the atmosphere. Dissolved in atmospheric water droplets, it plays a strong role in neutralizing atmospheric acids:

$NH_3\ (aq) + HNO_3\ (aq) \rightarrow NH_4NO_3\ (aq)$

$NH_3\ (aq) + H_2SO_4\ (aq) \rightarrow NH_4HSO_4\ (aq)$

These reactions have three effects; these are:

- They result in the presence of NH_4^+ ion in the atmosphere as dissolved or solid salts,
- They serve in part to neutralize acidic constituents of the atmosphere, and
- They produce relatively corrosive ammonium salts.

3.4.3 Reactions in Stratosphere

Dear student, under this main content you learn about reactions in Stratosphere. Do you know some of the reactions in Stratosphere, Let warm up yourself with the following activities

Learning task 3.4.3

a) What is Stratosphere?
b) Mention some of the dominant species in the Stratosphere
c) Explain the source and effects of species in the Stratosphere
d) Explain how ozone formation and depletion takes place in Stratosphere
e) Describe the common reactions in the Stratosphere
f) Explain how Antartica Ozone hole is formed
g) Explain sources, reactions and effects of HO_x, ClO_x & NO_x In the stratosphere

3.4.3.1 Ozone layer formation and depletion

Dear student, do you know how ozone is formed and depleted?

i) Ozone formation and depletion in Stratosphere

Stratospheric ozone, O_3, serves as a shield to absorb harmful ultraviolet radiation in the stratosphere, protecting living beings on the earth from the effects of excessive amounts of such radiation. The two reactions by which stratospheric ozone is ***produced (formed)*** are,

$O_2 + h\nu \rightarrow O + O$ ($\lambda < 242.4$ nm)

$O + O_2 + M \rightarrow O_3 + M$ (energy-absorbing N_2 or O_2)

And it is **depleted (destroyed)** by photodissociation,

$O_3 + h\nu \rightarrow O_2 + O$ ($\lambda < 325$ nm) and a series of reactions from which the net result is the following: $O + O_3 \rightarrow 2O_2$

The concentration of ozone in the stratosphere is a steady-state concentration resulting from the balance of ozone production and destruction by the above processes. The quantities of ozone involved are interesting. A total of about 350,000 metric tons of ozone are formed and destroyed daily. Ozone never makes up more than a small fraction of the gases in the ozone layer. In fact, if all the atmosphere's ozone were in a layer at 273 K and 1 atm, it would be only 3 mm thick! Ozone absorbs ultraviolet radiation very strongly in the region 220-330 nm. Therefore, it is effective in filtering out dangerous UV-B radiation, $290 \text{ nm} < \lambda < 320 \text{ nm}$. (UV-A radiation, 320 nm-400 nm, is relatively less harmful and UV-C radiation, < 290 nm does not penetrate to the troposphere.) If UV-B were not absorbed by ozone, severe damage would result to exposed forms of life on the earth.

Absorption of electromagnetic radiation by ozone converts the radiation's energy to heat and is responsible for the temperature maximum encountered at the boundary between the stratosphere and the mesosphere at an altitude of approximately 50 km. The reason that the temperature maximum occurs at a higher altitude than that of the maximum ozone concentration arises from the fact that ozone is such an effective absorber of ultraviolet light, so that most of this radiation is absorbed in the upper stratosphere where it generates heat and only a small fraction reaches the lower altitudes, which remain relatively cool. Increased intensities of ground-level ultraviolet radiation caused by stratospheric ozone destruction would have some significant adverse consequences.

One major effect would be on plants, including crops used for food. The destruction of microscopic plants that are the basis of the ocean's food chain (phytoplankton) could severely reduce the productivity of the world's seas. Human exposure would result in an increased incidence of cataracts. The effect of most concern to humans is the elevated occurrence of skin cancer in individuals exposed to ultraviolet radiation. This is because UV-B radiation is absorbed by cellular DNA resulting in photochemical reactions that alter the function of DNA so that the genetic code is improperly translated during cell division.

The major cause in ozone depletion consists of chlorofluorocarbon (CFC) compounds, commonly known as "Freons." These volatile compounds have been used and released to a very large extent in recent decades. The major use associated with CFCs is as refrigerant fluids. Other applications have included solvents, aerosol propellants, and blowing agents in the fabrication of foam plastics. The same extreme chemical stability that makes CFCs nontoxic enables them to persist for years in the atmosphere and to enter the stratosphere. In the stratosphere, the photochemical dissociation of CFCs by intense ultraviolet radiation yields chlorine atoms, each of which can go through chain reactions, particularly the following:

$CF_2Cl_2 + h\nu \rightarrow Cl\bullet + CClF_2\bullet$

$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

$ClO\bullet + O \rightarrow Cl\bullet + O_2$

The net effect of these reactions is catalysis of the destruction of several thousand molecules of O_3 for each Cl atom produced. Because of their widespread use and persistency, the two CFCs of most concern in ozone destruction are CFC-11 and CFC-12, $CFCl_3$, and CF_2Cl_2, respectively. Even in the intense ultraviolet radiation of the stratosphere the most persistent chlorofluorcarbons have lifetimes of the order of 100 years.

ii) Antarctic O_3 hole

Dear student, have you heard about Antarctic O_3 hole?

The most prominent instance of ozone layer destruction is the so-called ***"Antarctic ozone hole"*** that has shown up in recent years. This phenomenon is manifested by the appearance during the Antarctic's late winter and early spring of severely depleted stratospheric ozone (up to 50%) over the polar region. The reasons why this occurs are related to the normal effect of NO_2 in limiting Cl-atom-catalyzed destruction of ozone by combining with ClO, $ClO + \mathbf{NO_2 \rightarrow ClONO_2}$

In the polar regions, particularly Antarctica, NOx gases are removed along with water by freezing in polar stratospheric clouds(PSC) at temperatures below -70°C as compounds such as $ClONO_2$ and $HNO_3\bullet 3H_2O$. During the Antarctic winter, HOCl and Cl_2 are generated and accumulate at the surfaces of the solid cloud particles by the reactions,

$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$

where the HCl comes primarily from the reaction of stratospheric methane, CH_4, with Cl• atoms produced from chlorofluorocarbons. The preceding reactions are aided by the tendency of the HNO_3 product to become hydrogen-bonded with water in the cloud particles. The result of these processes is that over the winter months photoreactive Cl_2 and HOCl accumulate in the Antarctic stratospheric region in the absence of sunlight then undergo a burst of photochemical activity when spring arrives as shown by the following reactions:

$HOCl + h\nu \rightarrow HO\bullet + Cl\bullet$

$Cl_2 + h\nu \rightarrow Cl\bullet + Cl\bullet$

The Cl atoms react to destroy ozone according to the above reactions. Under conditions of Antarctic spring, not enough O• atoms are available to regenerate Cl atoms from ClO•. It is now known that ClO• forms the ClO-OCl dimer, which regenerates Cl• by the following reactions:

$ClOOCl + h\nu \rightarrow ClOO\bullet + Cl\bullet$

$ClOO\bullet + h\nu \rightarrow O_2 + Cl\bullet$

Role of PSCs in the formation of the Antarctic O_3 hole

1. PSCs promote the conversion of inorganic chlorine & chlorine reservoir species to active chlorine

Pathways

A) I. Absorption of $HCl_{(g)}$ by PSCs

$HCl_{(g)} \rightarrow HCl_{(s)}$

II. Heterogeneous reaction of gaseous $ClNO_3$ with HCl on PSCs

$HCl + ClNO_3 \rightarrow HNO_{3(s)} + Cl_{2\,(g)}$

B) Conversion of HCl to $ClNO_{2(g)}$ in the presence of $N_2O_{5(g)}$

$HCl_{(g)} \rightarrow HCl_{(s)}$

$HCl_{(s)} + N_2O_5 \rightarrow ClNO_2 + HNO_{3(s)}$

C) Conversion of $ClNO_{3(g)}$ to HOCl

$ClNO_3 + H_2O_{(s)} \rightarrow HOCl + HNO_{3(s)}$

The products, Cl_2, HOCl & $ClNO_2$, absorb light when spring comes to deplete O_3 as shown below:

$Cl_2 + hv \rightarrow 2Cl$

$HOCl + h\nu \rightarrow HO + Cl$

$ClNO_2 + h\nu \rightarrow Cl + NO_2$

$O_3 + Cl \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Net: $\mathbf{O_3 + O \rightarrow 2O_2}$

Role 2 Enhance polar ClO_x cycle

PSCs retain gaseous nitrogen species through: formation of $HNO_3{\cdot}3H_2O$ and formation of HNO_3 from gaseous nitrogen species such as $ClNO_3$ and N_2O_5. Chlorofluorocarbons (CFCs) are inert in the troposphere. CFCs undergo photochemical reactions in the stratosphere to release Cl radical through homolytic bond cleavage that degrade ozone

$CF_2Cl_2 + hv \rightarrow CF_2Cl\bullet + Cl\bullet$

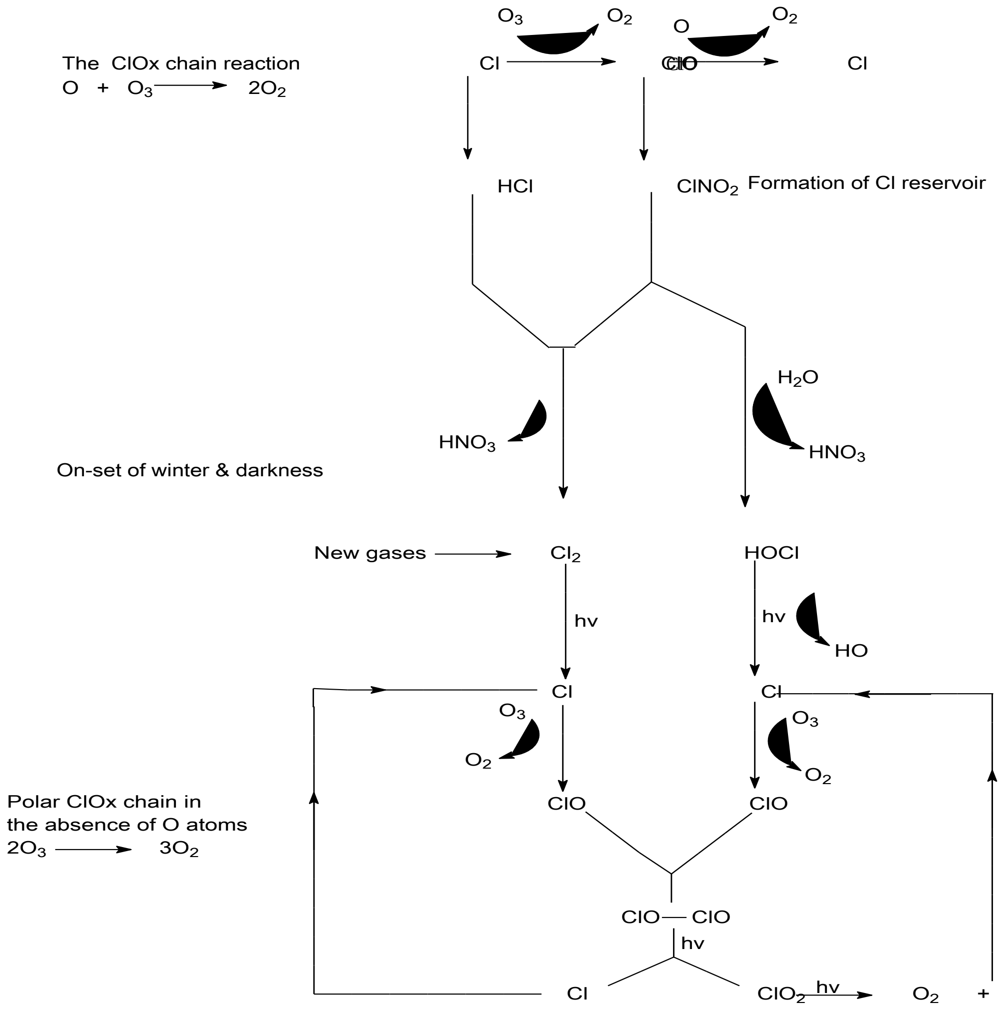


Fig 3.4.3.1 Reaction sequence responsible for Antarctic Ozone hole

Summary

Cold T^0 is responsible for the formation of PSC and Polar winter is responsible for Polar Vortex. Isolation of polar vortex results for growth of PSC sinks to lower altitudes and gave rise for spring sunlight. If O_3 depletion is resulted from ClOx cycle, the depletion would have occurred b/n 35 – 45 km.

The ClOx cycle requires atomic oxygen O

i.e. $ClO + O \rightarrow Cl + O_2$

But in the polar stratosphere, the low sun elevation results in essentially no photo–dissociation of O_2. O_3 destruction in the Antarctica couldn't be explained by ClOx destruction mechanism alone

Stratospheric O_3 destruction reactions

Polar ClOx cycle

$ClO + ClO + M \rightarrow ClO-ClO + M$

$ClO-ClO + hv \rightarrow ClOO + Cl$

$ClOO + hv \rightarrow Cl + O2$

O_3 destruction

$Cl + O_3 \rightarrow ClO + O_2$

How does the polar ClOx stop?

The chain reaction is stopped when the ice particles melt, releasing adsorbed HNO_3

$HNO_3 + hv \rightarrow \bullet OH + NO_2$

NO_2 sequestrates ClO, which shutdown the polar ClOx chain reaction.

$NO_2 + ClO \rightarrow ClONO_2$

iii) Volcanoes can deplete O_3. How?

Dear student, Volcanoes can deplete O_3. The principal mechanism for this is not injection of chlorine into the stratosphere, but rather the injection of sulfate aerosols which change the radiation balance in the stratosphere by scattering light, and which convert inactive chlorine compounds to active, O_3 depleting form.

3.4.3.3 Sources & reactions of HO_x, ClO_x & NO_x In the stratosphere

i) Sources & reactions of HO_x in the stratosphere

Dear student, CH_4 is stable in the troposphere, however, if it crosses the tropopause it under goes oxidation to give CO_2 and H_2O that subsequently undergoes photo-ionization to generate OH and H that degrades O_3 as shown below:

$$CH_4 + O_2 + hv \rightarrow CO_2 + H_2O$$
$$H_2O + hv \rightarrow HO\bullet + H\bullet$$
$$O^* + H_2O \rightarrow 2HO\bullet$$
$$CH_4 + O \rightarrow CH_3\bullet + HO\bullet$$
$$H_2O_2 + hv \rightarrow 2\ HO\bullet$$
$$HNO_2 + hv \rightarrow NO + HO\bullet$$

Reactions of •OH in the stratosphere

$$HO\bullet + O_3 \rightarrow HO_2\bullet + O_2$$
$$HO_2\bullet + O_3 \rightarrow OH\bullet + 2O_2$$

Net reaction $\mathbf{2O_3 \rightarrow 3O_2}$

ii) Hydroxyl and Hydroperoxyl Radicals in the Atmosphere

The hydroxyl radical, HO•, is the single most important reactive intermediate species in atmospheric chemical processes. It is formed by several mechanisms. At higher altitudes it is produced by photolysis of water:

$$H_2O + hv \rightarrow HO\bullet + H$$
$$HONO + hv \rightarrow HO\bullet + NO$$

In the relatively unpolluted troposphere, hydroxyl radical is produced as the result of the photolysis of ozone, $O_3 + hv\ (\lambda < 315\text{ nm}) \rightarrow O^* + O_2$ followed by the reaction of a fraction of the excited oxygen atoms with water molecules: $O^* + H_2O \rightarrow 2HO\bullet$

Among the important atmospheric trace species that react with hydroxyl radical are carbon monoxide, sulfur dioxide, hydrogen sulfide, methane, and nitric oxide. Hydroxyl radical is most frequently removed from the troposphere by reaction with methane or carbon monoxide:

$$CH_4 + HO\bullet \rightarrow H_3C\bullet + H_2O$$

$CO + HO\bullet \rightarrow CO_2 + H$

The highly reactive methyl radical, $H_3C\bullet$, reacts with O_2, $H_3C\bullet + O_2 \rightarrow H_3COO\bullet$ to form **methylperoxyl radical**, $H_3COO\bullet$. The hydrogen atom produced in the above reaction reacts with O_2 to produce **hydroperoxyl radical**: $H + O_2 \rightarrow HOO\bullet$

The hydroperoxyl radical can undergo chain termination reactions, such as

$HOO\bullet + HO\bullet \rightarrow H_2O + O_2$

$HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$

or reactions that regenerate hydroxyl radical:

$HOO\bullet + NO \rightarrow NO_2 + HO\bullet$

$HOO\bullet + O_3 \rightarrow 2O_2 + HO\bullet$

The global concentration of hydroxyl radical averaged diurnally and seasonally, is estimated to range from 2×10^5 to 1×10^6 radicals per cm^3 in the troposphere. Because of the higher humidity and higher incident sunlight which result in elevated O* levels, the concentration of HO• is higher in tropical regions. The southern hemisphere probably has about a 20% higher level of HO• than does the northern hemisphere because of greater production of anthropogenic, HO•-consuming CO in the northern hemisphere. The hydroperoxyl radical, HOO•, is an intermediate in some important chemical reactions.

In addition to its production by the reactions discussed above, in polluted atmospheres, hydroperoxyl radical is made by the following two reactions, starting with photolytic dissociation of formaldehyde to produce a reactive formyl radical:

$\bullet HCHO + h\nu \rightarrow H + HCO$

$\bullet HCO + O_2 \rightarrow HOO\bullet + CO$

The hydroperoxyl radical reacts more slowly with other species than does the hydroxyl radical. The kinetics and mechanisms of hydroperoxyl radical reactions are difficult to study because it is hard to retain these radicals free of hydroxyl radicals.

iii) Sources & reactions of ClOx in the stratosphere

Chlorofluorocarbons (CFCs) are inert in the troposphere. CFCs undergo photochemical reactions in the stratosphere to release Cl radical through homolytic bond cleavage that degrade ozone

$CF_2Cl_2 \quad + \quad h\nu \qquad CF_2Cl\bullet \quad + \quad Cl\bullet$

$Cl\bullet + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Net reaction: $\mathbf{O_3 + O \rightarrow 2O_2}$

Termination reactions:

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + NO_2 + M \rightarrow ClNO_3 + M$

HCl & $ClNO_3$ are reservoirs of Cl. Therefore, how does Cl released from its reservoirs?

$ClNO_3 + hv \rightarrow Cl + NO_3$

$HCl + OH \rightarrow Cl + H_2O$

iv) Sources & reactions of NOx in the stratosphere

Biospheric N_2O from nitrification and denitrification and N_2O is stable in the troposphere and cross the tropopause without change: $O + N_2O \rightarrow 2NO$ (5 %) & $N_2O + hv \rightarrow N_2 + O$ (95 %)

NOx cycle

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + h\upsilon \rightarrow NO + O$

Net rxn : $\mathbf{O_3 + h\upsilon \rightarrow O_2 + O}$

$O + NO_2 \rightarrow NO + O_2$

$NO + O_3 \rightarrow NO_2 + O_2$

Net rxn: $\mathbf{O + O_3 \rightarrow^{M} 2O_2 + M}$

Termination reactions

Daytime : $NO_2 + OH\bullet + M \rightarrow HNO_3 + M$

Night time : $NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_3 + NO_2 \rightarrow N_2O_5 + M$

HNO_3 and N_2O_5 have a longer lifetime than NOx. Thus they are reservoirs of NOx

Conversion from the reservoirs

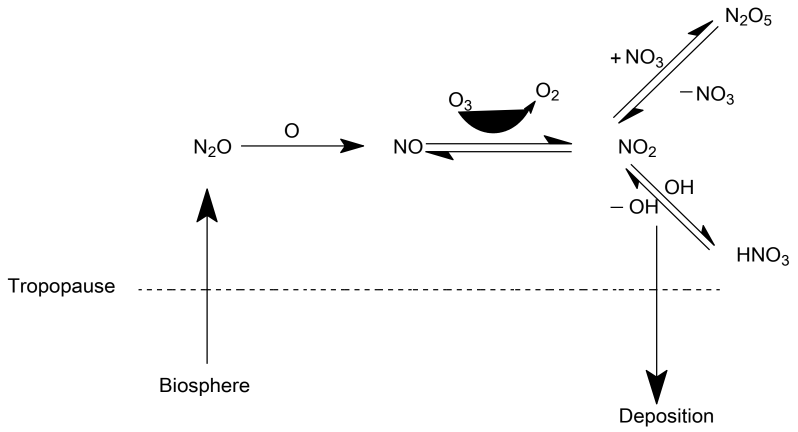
$HNO_3 + hv \rightarrow NO_2 + OH\bullet$

$HNO_3 + OH\bullet \rightarrow NO_3 + H_2O$

$NO_3 + hv \rightarrow NO_2 + O$

$$N_2O_5 + hv \rightarrow NO_3 + NO_2$$

Reactions of NOx



v) Reactions of atmospheric oxygen

Dear student, the oxygen cycle is critically important in atmospheric chemistry, geochemical transformations, and life processes.

Oxygen in the troposphere plays a strong role in processes that occur on the earth's surface. Atmospheric oxygen takes part in energy-producing reactions, such as the burning of fossil fuels:

$$\mathbf{CH_4 \text{ (in natural gas)} + 2O_2 \rightarrow CO_2 + 2H_2O}$$

Atmospheric oxygen is utilized by aerobic organisms in the degradation of organic material. Some oxidative weathering processes consume oxygen, such as: $\mathbf{4FeO + O_2 \rightarrow 2Fe_2O_3}$. Oxygen exchanges among the atmosphere, geosphere, hydrosphere, and biosphere. Oxygen is returned to the atmosphere through plant photosynthesis: $\mathbf{CO_2 + H_2O + \mathit{h}v \rightarrow \{CH_2O\} + O_2}$

All molecular oxygen now in the atmosphere is thought to have originated through the action of photosynthetic organisms, which shows the importance of photosynthesis in the oxygen balance of the atmosphere. Molecular oxygen is somewhat unusual in that its ground state is a triplet state with two unpaired electrons, designated here as $3O_2$, which can be excited to singlet molecular oxygen, designated here as $1O_2$. The latter can be produced by several processes, including direct photochemical excitation, transfer of energy from other electronically excited molecules, ozone photolysis, and high-energy oxygen-producing reactions.

Because of the extremely rarefied atmosphere and the effects of ionizing radiation, elemental oxygen in the upper atmosphere exists to a large extent in forms other than diatomic O_2. In addition to O_2, the upper atmosphere contains oxygen atoms, O; excited oxygen molecules, O_2^*; and ozone, O_3. Atomic oxygen, O, is stable primarily in the thermosphere, where the atmosphere is so rarefied that the three-body collisions necessary for the chemical reaction of atomic oxygen seldom occur (the third body in this kind of three-body reaction absorbs energy to stabilize the products). Atomic oxygen is produced by a photochemical reaction: $\mathbf{O_2 + h\nu \rightarrow O + O}$

Oxygen atoms in the atmosphere can exist in the ground state (O) and in excited states (O*). These are produced by the photolysis of ozone, which has relatively weak bond energy of
26 kcal/mole at wavelengths below 308 nm,

$O_3 + h\nu(\lambda < 308\ \text{nm}) \rightarrow O^* + O_2$ or by highly energetic chemical reactions such as

$O + O + O \rightarrow O_2 + O^*$

Excited atomic oxygen emits visible light at wavelengths of 636 nm, 630 nm, and 558 nm. This emitted light is partially responsible for **airglow**, a very faint electromagnetic radiation continuously emitted by the earth's atmosphere.

The region of maximum ozone concentration is found within the range of 25-30 km high in the stratosphere where it may reach 10 ppm. Ozone absorbs ultraviolet light very strongly in the region 220-330 nm. If this light were not absorbed by ozone, severe damage would result to exposed forms of life on the earth. Absorption of electromagnetic radiation by ozone converts the radiation's energy to heat and is responsible for the temperature maximum encountered at the boundary between the stratosphere and the mesosphere at an altitude of approximately 50 km.

The reason that the temperature maximum occurs at a higher altitude than that of the maximum ozone concentration arises from the fact that ozone is such an effective absorber of ultraviolet light, that most of this radiation is absorbed in the upper stratosphere where it generates heat, and only a small fraction reaches the lower altitudes, which remain relatively cool.

The overall reaction: $2O_3 \rightarrow 3O_2$, is favored thermodynamically so that ozone is inherently unstable. Its decomposition in the stratosphere is catalyzed by a number of natural and pollutant trace constituents, including NO, NO_2, H, HO•, HOO•, ClO, Cl, Br, and BrO. Ozone decomposition also occurs on solid surfaces, such as metal oxides and salts produced by rocket exhausts.

Although the mechanisms and rates for the photochemical production of ozone in the stratosphere are reasonably well known, the natural pathways for ozone removal are less well understood. In addition to undergoing decomposition by the action of ultraviolet radiation, stratospheric ozone reacts with atomic oxygen, hydroxyl radical, and NO:

$O_3 + h\nu \rightarrow O_2 + O$

$O_3 + O \rightarrow O_2 + O_2$

$O_3 + HO\bullet \rightarrow O_2 + HOO\bullet$

The HO• radical is regenerated from HOO• by the reaction, $HOO\bullet + O \rightarrow HO\bullet + O_2$

The NO consumed in this reaction is regenerated from NO_2, and some NO is produced from N_2O:

$O_3 + NO \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

Recall that N_2O is a natural component of the atmosphere and is a major product of the denitrification process by which fixed nitrogen is returned to the atmosphere in gaseous form.

vi) Reactions of atmospheric Nitrogen

The 78% by volume of nitrogen contained in the atmosphere constitutes an inexhaustible reservoir of that essential element. A small amount of nitrogen is fixed in the atmosphere by lightning, and some is also fixed by combustion processes, particularly in internal combustion and turbine engines. Before the use of synthetic fertilizers reached its current high levels, chemists were concerned that denitrification processes in the soil would lead to nitrogen depletion on the Earth. Now, with millions of tons of synthetically fixed nitrogen being added to the soil each year, major concern has shifted to possible excess accumulation of nitrogen in soil, fresh water, and the oceans.

Unlike oxygen, which is almost completely dissociated to the monatomic form in higher regions of the thermosphere, molecular nitrogen is not readily dissociated by ultraviolet radiation. However, at altitudes exceeding approximately 100 km, atomic nitrogen is produced by photochemical reactions: $N_2 + h\nu \rightarrow N + N$

Other reactions which may produce monatomic nitrogen are:

$$N_2^+ + O \rightarrow NO^+ + N$$

$$NO^+ + e^- \rightarrow N + O$$

$$O^+ + N_2 \rightarrow NO^+ + N$$

As shown in reactions, NO is involved in the removal of stratospheric ozone and is regenerated by the reaction of NO_2 with atomic O, itself a precursor to the formation of ozone. An ion formed from NO, the NO^+ ion, is one of the predominant ionic species in the so-called E region of the ionosphere. A plausible sequence of reactions by which NO^+ is formed is the following:

$$N_2 + h\nu \rightarrow N_2^+ + e^-$$

$$N_2^+ + O \rightarrow NO^+ + N$$

Pollutant oxides of nitrogen, particularly NO_2, are key species involved in air pollution and the formation of photochemical smog. For example, NO_2 is readily dissociated photochemically to NO and reactive atomic oxygen: $NO_2 + h\nu \rightarrow NO + O$. This reaction is the most important primary photochemical process involved in smog formation.

vii) Effect of Atmospheric carbon dioxide

Although only about 0.035% (350 ppm) of air consists of carbon dioxide, it is the atmospheric “nonpollutant” species of most concern. Carbon dioxide, along with water vapor, is primarily responsible for the absorption of infrared energy re-emitted by the earth such that some of this energy is reradiated back to the earth’s surface. Current evidence suggests that changes in the atmospheric carbon dioxide level will substantially alter the earth’s climate through the greenhouse effect.

The most obvious factor contributing to increased atmospheric carbon dioxide is consumption of carbon-containing fossil fuels. In addition, release of CO_2 from the biodegradation of biomass and uptake by photosynthesis are important factors determining overall CO_2 levels in the atmosphere.

Therefore, the current worldwide destruction of forests and conversion of forest lands to agricultural uses contributes substantially to a greater overall increase in atmospheric CO_2 levels.

viii) Effect of Atmospheric water

The water vapor content of the troposphere is normally within a range of 1–3% by volume with a global average of about 1%. However, air can contain as little as 0.1% or as much as 5% water. The percentage of water in the atmosphere decreases rapidly with increasing altitude. Water vapor absorbs infrared radiation even more strongly than does carbon dioxide, thus greatly influencing the earth’s heat balance. Clouds formed from water vapor reflect light from the sun and have a temperature-lowering effect.

On the other hand, water vapor in the atmosphere acts as a kind of “blanket” at night, retaining heat from the earth’s surface by absorption of infrared radiation. Thus, little water is transferred from the troposphere to the stratosphere, and the main source of water in the stratosphere is the photochemical oxidation of methane: **$CH_4 + 2O_2 + hv$ (several steps) $\rightarrow CO_2 + 2H_2O$** .The water thus produced serves as a source of stratospheric hydroxyl radical as shown by the following reaction: **$H_2O + hv \rightarrow HO\bullet + H$**

3.4.4 Reactions in Thermosphere

Dear student, under this main content you learn about reactions in Thermosphere. Do you know some of the reactions in Thermosphere, Let warm up yourself with the following activities

Learning task 3.4.4

a) What is Thermosphere?
b) Mention some of the dominant species in the Thermosphere
c) Explain the source and effects of species in the Thermosphere
d) Describe the common reactions in the Thermosphere

Thermosphere is one of the stratification of atmosphere. It is rich in Oxygen atom; hence two types of reactions are common in Thermosphere; these are:

i) photo-dissociation
ii) photo-ionization

i) Photo-dissociation

This reaction involves the rapture of chemical bonds from the absorption of photons to form atoms or molecules: **$O_2 + hv \rightarrow 2O + 120$ kcal/mol**

This reaction absorbs most of the high energy radiation. It releases considerable amount of heat that is responsible for the increase in temperature in the thermosphere. In this region 99% of the available oxygen is in the form of atomic oxygen and the dissociation of nitrogen is limited because of stable triple bonds in molecular nitrogen

ii) Photo-ionization

This reaction generates ions by absorption of photons and ejection of single electrons from molecules. N_2, O_2, & O absorb radiations of $\lambda < 240$ nm.

$$O_2 + hv \rightarrow O_2^+ + e^-$$

$$O + hv \rightarrow O^+ + e^-$$

3.5 Atmospheric Pollution

Dear student, under this main content you learn about Atmospheric Pollution. Do you know some of the causes for Atmospheric Pollution, Let warm up yourself with the following activities.

Learning task 3.5

a) What is Atmospheric Pollution
b) Mention the common atmospheric pollutants
c) Describe the source of atmospheric pollutants
d) Explain the nature and classification of atmospheric pollutants

Atmospheric (air) pollution occurs when the concentration of certain substances become high enough to toxify the atmospheric environment. Common air pollutants such as: oxides of sulfur

(SOx), oxides of nitrogen (NOx), oxides of carbon(CO & CO_2), CH_4, C_6H_6, Ground level O_3, Volatile organic compounds (VOC), Chlorofluorocarbon(CFC) and heavy metals such as (Pb).

3.6. Nature and classification of atmospheric pollutants

The main atmospheric pollutants are particles in the atmosphere, gaseous inorganic pollutants, gaseous organic pollutants, photochemical smog, green house and global warming, nuclear winter and acid rain.

3.6.1 Particles in the atmosphere as means of air pollution

Dear student, under this main content you learn about Particles in the atmosphere. Do you know some of the causes for Particles in the atmosphere, Let warm up yourself with the following activities

Learning task 3.6.1

a) What are particles?
b) Describe important terms describing atmospheric particles
c) Explain the physical behavior of particles in the atmosphere
d) Explain the physical and chemical processes for particle formation
e) Compare and contrast Inorganic particles and organic particles
f) Mention the effects of particles on the atmosphere
g) Explain how Control of particulate emissions can be controlled

Particles in the atmosphere, which range in size from about one-half millimeter down to molecular dimensions, are made up of an amazing variety of materials and discrete objects that may consist of either solids or liquid droplets. Particles abound in the atmosphere. Even the Arctic, remote from sources of industrial pollution, is afflicted with an “Arctic Haze” of airborne particles from October to May each year. **Particulates** are a term that has come to stand for particles in the atmosphere, although *particulate matter* or simply *particles*, is preferred usage.

Table 3.6.1 Important terms describing atmospheric particles

Term	Meaning
Aerosols	Colloidal–sized atmospheric particles
Condensation aerosols	Formed by condensation of vapors or reactions of gases
Dispersion aerosols	Formed by grinding of solids, atomization of liquids, or dispersion of dusts
Fog	Term denoting high level of water droplets
Haze	Denotes decreased visibility due to the presence of particles
Mists	Liquid particles
Smoke	Particles formed by incomplete combustion of fuel

3.6.1.1 Physical behavior of particles in the atmosphere

As shown in Figure 3.5.1, atmospheric particles undergo a number of processes in the atmosphere. Small colloidal particles are subject to *diffusion processes*. Smaller particles *coagulate* together to form larger particles. *Sedimentation* or *dry deposition* of particles, which have often reached sufficient size to settle by coagulation, is one of two major mechanisms for particle removal from the atmosphere. The other is *scavenging* by raindrops and other forms of precipitation. Particles also react with atmospheric gases.

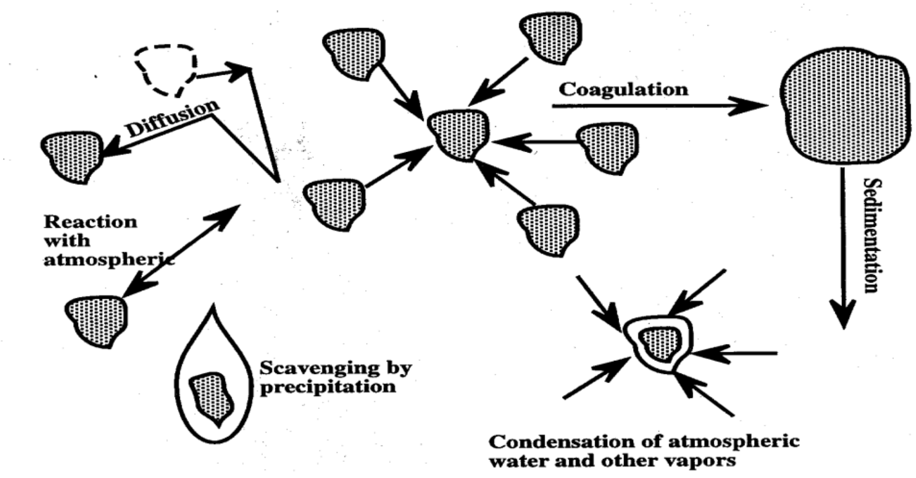


Figure 3.6.1 Processes that particle undergo in the atmosphere.

Particle size usually expresses the diameter of a particle, though sometimes it is used to denote the radius. The rate at which a particle settles is a function of particle diameter and density. The settling rate is important in determining the effect of the particle in the atmosphere. For spherical particles greater than approximately 1 μm in diameter, Stokes' law applies,

$$V = \frac{gd^2(\rho_1 - \rho_2)}{18\eta}$$

where n is the settling velocity in cm/sec, g is the acceleration of gravity in cm/sec^2, ρ_1 is the density of the particle in g/cm^3, ρ_2 is the density of air in g/cm^3, and h is the viscosity of air in poise. Stokes' law can also be used to express the effective diameter of an irregular nonspherical particle. These are called **Stokes diameters** (aerodynamic diameters) and are normally the ones given when particle diameters are expressed. Furthermore, since the density of a particle is often not known, an arbitrary density of 1 g/cm^3 is conventionally assigned to ρ_1; when this is done, the diameter calculated from Equation is called the **reduced sedimentation diameter**.

Size and Settling of Atmospheric Particles

Most kinds of aerosol particles have unknown diameters and densities and occur over a range of sizes. For such particles, the term **mass median diameter (MMD)** may be used to describe aerodynamically equivalent spheres having an assigned density of 1 g/cm^3 at a 50% mass collection efficiency, as determined in sampling devices calibrated with spherical aerosol particles having a known, uniform size. (Polystyrene latex is commonly used as a material for the preparation of such standard aerosols.) The determination of MMD is accomplished by plotting the log of particle size as a function of the percentage of particles smaller than the given size on a probability scale.

3.6.1.2. Physical processes for particle formation

Dispersion aerosols, such as dusts, formed from the disintegration of larger particles are usually above 1 μm in size. Typical processes for forming dispersion aerosols include evolution of dust from coal grinding, formation of spray in cooling towers, and blowing of dirt from dry soil. Many dispersion aerosols originate from natural sources such as sea spray, windblown dust, and volcanic dust. However, vast varieties of human activities break up material and disperse it to the atmosphere.

Quarries and rock crushers spew out plumes of ground rock. Cultivation of land has made it much more susceptible to dust-producing wind erosion. However, since much more energy is required to break material down into small particles than is required for or released by the synthesis of particles through chemical synthesis or the adhesion of smaller particles, most dispersion aerosols are relatively large. Larger particles tend to have fewer harmful effects than smaller ones. As examples, larger particles are less *respirable* in that they do not penetrate so far into the lungs as smaller ones, and larger particles are relatively easier to remove from air pollution effluent sources.

3.6.1.3. Chemical processes for particle formation

Chemical processes in the atmosphere convert large quantities of atmospheric gases to particulate matter. Among the chemical species most responsible for this conversion are the organic pollutants and nitrogen oxides that cause formation of ozone and photochemical smog in the troposphere. To an extent, therefore, control of hydrocarbon and NOx emissions to reduce smog will also curtail atmospheric particulate matter pollution. A major fraction of ambient particulate matter arises from atmospheric gas-to particle conversion. Attempts to reduce particulate matter levels require control of the same organic and nitrogen oxide (NOx) emissions that are precursors to urban and regional ozone formation.

Most chemical processes that produce particles are combustion processes, including fossil-fuel-fired power plants; incinerators; home furnaces, fireplaces, and stoves; cement kilns; internal combustion engines; forest, brush, and grass fires; and active volcanoes.

3.6.1.4 Inorganic Particles

Dear student, How you explain Inorganic particles? Their source and effects?

Metal oxides constitute a major class of inorganic particles in the atmosphere. These are formed whenever fuels containing metals are burned. For example, particulate iron oxide is formed during the combustion of pyrite-containing coal: $\mathbf{3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2}$

Organic vanadium in residual fuel oil is converted to particulate vanadium oxide. Part of the calcium carbonate in the ash fraction of coal is converted to calcium oxide and is emitted into the atmosphere through the stack: $\mathbf{CaCO_3 + heat \rightarrow CaO + CO_2}$

A common process for the formation of aerosol mists involves the oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic substance that accumulates atmospheric water to form small liquid droplets: $\mathbf{2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4}$

In the presence of basic air pollutants, such as ammonia or calcium oxide, the sulfuric acid reacts to form salts:

$$\mathbf{H_2SO_4(droplet) + 2NH_3(\mathit{g}) \rightarrow (NH_4)_2SO_4\ (droplet)}$$

$$\mathbf{H_2SO_4(droplet) + CaO(\mathit{s}) \rightarrow CaSO_4(\ droplet) + H_2O}$$

Under low-humidity conditions water is lost from these droplets and a solid aerosol is formed. The preceding examples show several ways in which solid or liquid inorganic aerosols are formed by chemical reactions. Such reactions constitute an important general process for the formation of aerosols, particularly the smaller particles.

i) The composition of Inorganic particles

In general, the proportions of elements in atmospheric particulate matter reflect relative abundances of elements in the parent material. The source of particulate matter is reflected in its elemental composition, taking into consideration chemical reactions that may change the composition. For example, particulate matter largely from an ocean spray origin in a coastal area receiving sulfur dioxide pollution may show anomalously high sulfate and corresponding low chloride content. The sulfate comes from atmospheric oxidation of sulfur dioxide to form nonvolatile ionic sulfate, whereas some chloride originally from the NaCl in the seawater may be lost from the solid aerosol as volatile HCl:

$$\mathbf{2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4}$$

$$\mathbf{H_2SO_4 + 2NaCl\ (particulate) \rightarrow Na_2SO_4\ (particulate) + 2HCl}$$

For example acids other than sulfuric acid can also be involved in the modification of sea salt particles. An examination with an electron microscope equipped with an X-ray emission analyzer of sea-salt particles taken at Tsukuba, Japan, 50 km from the Pacific Coast, showed a marked deficiency of chloride. This was attributed primarily to reaction with pollutant nitric acid as indicated by high levels of nitrate in the samples. The presence of significant levels of zinc in the particles indicated contamination from pollution sources.

The chemical composition of atmospheric particulate matter is quite diverse. Among the constituents of inorganic particulate matter found in polluted atmospheres are salts, oxides, nitrogen compounds, sulfur compounds, various metals, and radionuclides. In coastal areas sodium and chlorine get into atmospheric particles as sodium chloride from sea spray. The major trace elements that typically occur at levels above 1 $\mu g/m^3$ in particulate matter are aluminum, calcium, carbon, iron, potassium, sodium, and silicon; note that most of these tend to originate from terrestrial sources. Lesser quantities of copper, lead, titanium, and zinc, and even lower levels of antimony, beryllium, bismuth, cadmium, cobalt, chromium, cesium, lithium, manganese, nickel, rubidium, selenium, strontium, and vanadium are commonly observed.

Fly Ash

Much of the mineral particulate matter in a polluted atmosphere is in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel. Much of the mineral matter in fossil fuels such as coal or lignite is converted during combustion to a fused, glassy bottom ash which presents no air pollution problems. Smaller particles of **fly ash** enter furnace flues and are efficiently collected in a properly equipped stack system. However, some fly ash escapes through the stack and enters the atmosphere. Unfortunately, the fly ash thus released tends to consist of smaller particles that do the most damage to human health, plants, and visibility.

Asbestos

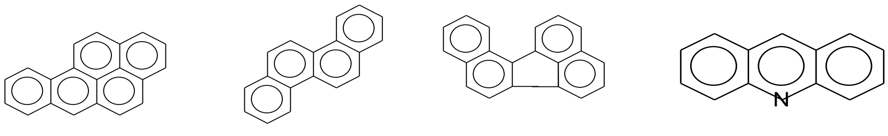
Asbestos is the name given to a group of fibrous silicate minerals, typically those of the serpentine group, approximate formula $Mg_3P(Si_2O_5)(OH)_4$. The tensile strength, flexibility, and nonflammability of asbestos have led to many uses including structural materials, brake linings, insulation, and pipe manufacture. For example, in 1979, 560,000 metric tons of asbestos were used in the U.S. By 1988 annual consumption had dropped to 85,000 metric tons, most of it used for brake linings and pads, roofing products, cement/asbestos pipe, gaskets, heat-resistant packing, and specialty papers. In 1989, the U.S. Environmental Protection Agency announced regulations that phased out most uses of asbestos by 1996. Asbestos is of concern as an air pollutant because when inhaled it may cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs). Therefore, uses of asbestos have been severely curtailed and widespread programs have been undertaken to remove the material from buildings.

3.6.1.5 Organic Particles

A significant portion of organic particulate matter is produced by internal combustion engines in complicated processes that involve pyrosynthesis and nitrogenous compounds. These products may include nitrogen-containing compounds and oxidized hydrocarbon polymers. Lubricating oil and its additives may also contribute to organic particulate matter. A study of particulate matter emitted by gasoline auto engines (with and without catalysts) and diesel truck engines measured more than 100 compounds quantitatively. Among the prominent classes of compounds found were *n*-alkanes, *n*-alkanoic acids, benzaldehydes, benzoic acids, azanaphthalenes, polycyclic aromatic hydrocarbons, oxygenated PAHs, pentacyclic triterpanes, and steranes.

i) Polycyclic aromatic hydrocarbons (PAH) Synthesis

The organic particles of greatest concern are PAH hydrocarbons, which consist of condensed ring aromatic (aryl) molecules. The most often cited example of a PAH compound is benzo(a)pyrene, a compound that the body can metabolize to a carcinogenic form: PAHs may be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Hydrocarbons with very low molecular masses, including even methane, may act as precursors for the polycyclic aromatic compounds. Low-molar-mass hydrocarbons form PAHs by pyrosynthesis. This happens at temperatures exceeding approximately 500°C at which carbon-hydrogen and carbon-carbon bonds are broken to form free radicals. These radicals undergo dehydrogenation and combine chemically to form aryl ring structures which are resistant to thermal degradation.



Benzo(a)pyrene Chrysene Benzo(j)fluoranthene Acridine

Figure 3.6.1.5 Structure of some polycyclic aromatic hydrocarbons

ii) The composition of organic particles

Organic atmospheric particles occur in a wide variety of compounds. For analysis, such particles can be collected onto a filter; extracted with organic solvents; fractionated into neutral, acid, and basic groups; and analyzed for specific constituents by chromatography and mass spectrometry. The neutral group contains predominantly hydrocarbons, including aliphatic, aromatic, and oxygenated fractions. The aliphatic fraction of the neutral group contains a high percentage of long-chain hydrocarbons, predominantly those with 16-28 carbon atoms. These relatively unreactive compounds are not particularly toxic and do not participate strongly in atmospheric chemical reactions. The aromatic fraction, however, contains carcinogenic polycyclic aromatic hydrocarbons, which are discussed below.

Aldehydes, ketones, epoxides, peroxides, esters, quinones, and lactones are found among the oxygenated neutral components, some of which may be mutagenic or carcinogenic. The acidic group contains long-chain fatty acids and nonvolatile phenols. Among the acids recovered from air-pollutant particulate matter are lauric, myristic, palmitic, stearic, behenic, oleic, and linoleic acids. The basic group consists largely of alkaline N-heterocyclic hydrocarbons such as acridine.

Polycyclic aromatic hydrocarbons (PAH) in atmospheric particles have received a great deal of attention because of the known carcinogenic effects of some of these compounds, which are discussed in greater detail in Chapter 23. Prominent among these compounds are benzo(a)pyrene, benz(a)anthracene, chrysene, benzo- (e)pyrene, benz(e)acephenanthrylene, benzo(j)fluoranthene, and indenol.

3.6.1.6 Toxic metals particulates

Some of the metals found predominantly as particulate matter in polluted atmospheres are known to be hazardous to human health. All of these except beryllium are so-called “heavy metals.” Lead is the toxic metal of greatest concern in the urban atmosphere because it comes closest to being present at a toxic level; mercury ranks second. Others include beryllium, cadmium, chromium, vanadium, nickel, and arsenic (a metalloid).

Atmospheric Mercury

Atmospheric mercury is of concern because of its toxicity, volatility, and mobility. Some atmospheric mercury is associated with particulate matter. Much of the mercury entering the atmosphere does so as volatile elemental mercury from coal combustion and volcanoes. Volatile organomercury compounds such as dimethylmercury, $(CH_3)_2Hg$, and monomethylmercury salts, such as CH_3HgBr, are also encountered in the atmosphere.

Atmospheric Lead

With the reduction of leaded fuels, atmospheric lead is of less concern than it used to be. However, during the decades that leaded gasoline containing tetraethyllead was the predominant automotive fuel, particulate lead halides were emitted in large quantities. This occurs through the action of dichloroethane and dibromoethane added as halogenated scavengers to prevent the accumulation of lead oxides inside engines.

3.6.1.7. Radioactive particulates

Some of the radioactivity detected in atmospheric particles is of natural origin. This activity includes that produced when cosmic rays act on nuclei in the atmosphere to produce radionuclides, including 7Be, 10Be, 14C, 39Cl, 3H, 22Na, 32P, and 33P. A significant natural source of radionuclides in the atmosphere is **radon**, a noble gas product of radium decay. Radon may enter the atmosphere as either of two isotopes, 222Rn (half-life 3.8 days) and 220Rn (half-life 54.5 seconds). Both are alpha emitters in decay chains that terminate with stable isotopes of lead. The initial decay products, 218Po and 216Po, are nongaseous and adhere readily to atmospheric particulate matter.

3. 6.1.8. Water as particulate matter

Droplets of water are very widespread in the atmosphere. Although a natural phenomenon, such droplets can have significant and sometimes harmful effects. The most important such consequence is reduction of visibility, with accompanying detrimental effects on driving, flying, and boat navigation. Water droplets in fog act as carriers of pollutants. The most important of these are solutions of corrosive salts, particularly ammonium nitrates and sulfates, and solutions of strong acids.

Another important oxidation that takes place in atmospheric water droplets is the oxidation of aldehydes to organic carboxylic acids. The hydroxyl radical, HO•, is very important in initiating atmospheric oxidation reactions such as those noted above. Hydroxyl radical as HO• can enter water droplets from the gas-phase atmosphere, it can be produced in water droplets photochemically, or it can be generated from H_2O_2 and $•O_2^-$ radical-ion, which dissolves in water from the gas phase and then produces HO• by solution chemical reaction:

$$H_2O_2 + O_2^- \rightarrow HO• + O_2 + OH^-$$

Several solutes can react photochemically in aqueous solution to produce hydroxyl radical. One of these is hydrogen peroxide: $H_2O_2\ (aq) + h\text{v} \rightarrow 2HO•\ (aq)$

Nitrite as NO_2^- or HNO_2, nitrate (NO_3^-), and iron(III) as $Fe(OH)_2^+(aq)$ can also react photochemically in aqueous solution to produce HO• .It has been observed that ultraviolet radiation at 3l3 nm and simulated sunlight can react to produce HO• radical in authentic samples of water collected from cloud and fog sources.

Based on the results of this study and related investigations, it may be concluded that the aqueous-phase formation of hydroxyl radical is an important, and in some cases dominant means by which this key atmospheric oxidant is introduced into atmospheric water droplets. Iron is an inorganic solute of particular importance in atmospheric water. This is because of the participation of iron(III) in the atmospheric oxidation of sulfur(IV) to sulfur(VI)—that is, the conversion of $SO_2(aq)$, HSO_3^-, and SO_3^{2-} to sulfates and H_2SO_4.

3.6.1.9. Effects of particles

Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility. They provide active surfaces upon which heterogeneous atmospheric chemical reactions can occur, and nucleation bodies for the condensation of atmospheric water vapor, thereby exerting a significant influence upon weather and air pollution phenomena. The most visible effects of aerosol particles upon air quality result from their optical effects. Particles smaller than about 0.1μm in diameter scatter light much like molecules, that is, Rayleigh scattering.

Generally, such particles have an insignificant effect upon visibility in the atmosphere. The light-scattering and intercepting properties of particles larger than 1 μm are approximately proportional to the particles' cross-sectional areas. Particles of 0.1 μm – 1 μm cause interference phenomena because they are about the same dimensions as the wavelengths of visible light, so their light-scattering properties are especially significant.

Atmospheric particles inhaled through the respiratory tract may damage health. Relatively large particles are likely to be retained in the nasal cavity and in the pharynx, whereas very small particles are likely to reach the lungs and be retained by them. The respiratory system possesses mechanisms for the expulsion of inhaled particles. A strong correlation has been found between increases in the daily mortality rate and acute episodes of air pollution. In such cases, high levels of particulate matter are accompanied by elevated concentrations of SO_2 and other pollutants, so that any conclusions must be drawn with caution.

3.6.1.10. Control of particulate emissions

The removal of particulate matter from gas streams is the most widely practiced means of air pollution control. A number of devices have been developed for this purpose which differs widely in effectiveness, complexity, and cost. The selection of a particle removal system for a gaseous waste stream depends upon the particle loading, nature of particles (size distribution), and type of gas-scrubbing system used.

i) Particle Removal by Sedimentation and Inertia

The simplest means of particulate matter removal is **sedimentation**, a phenomenon that occurs continuously in nature. Gravitational settling chambers may be employed for the removal of particles from gas streams by simply settling under the influence of gravity. These chambers take up large amounts of space and have low collection efficiencies, particularly for small particles. Gravitational settling of particles is enhanced by increased particle size, which occurs spontaneously by coagulation. Thus, over time, the sizes of particles increase and the number of particles decreases in a mass of air that contains particles.

Brownian motion of particles less than about 0.1 μm in size is primarily responsible for their contact, enabling coagulation to occur. Particles greater than about 0.3 μm in radius do not diffuse appreciably and serve primarily as receptors of smaller particles.

Inertial mechanisms are effective for particle removal. These depend upon the fact that the radius of the path of a particle in a rapidly moving, curving air stream is larger than the path of the stream as a whole. Therefore, when a gas stream is spun by vanes, a fan, or a tangential gas inlet, the particulate matter may be collected on a separator wall because the particles are forced outward by centrifugal force. Devices utilizing this mode of operation are called **dry centrifugal collectors (cyclones).**

ii) Particle filtration

Fabric filters, as their name implies, consist of fabrics that allow the passage of gas but retain particulate matter. These are used to collect dust in bags contained in structures called *baghouses*. Periodically, the fabric composing the filter is shaken to remove the particles and to reduce back-pressure to acceptable levels. Collected particulate matter is removed from bags by mechanical agitation, blowing air on the fabric, or rapid expansion and contraction of the bags.

Scrubbers

A venturi scrubber passes gas through a device which leads the gas stream through a converging section, throat, and diverging section. Injection of the scrubbing liquid at right angles to incoming gas breaks the liquid into very small droplets, which are ideal for scavenging particles from the gas stream. In the reduced-pressure (expanding and, therefore, cooling) region of the venturi, some condensation can occur of vapor from liquid initially evaporated in the generally hot waste gas, adding to the scrubbing efficiency. In addition to removing particles, venturis may serve as quenchers to cool exhaust gas, and as scrubbers for pollutant gases.

Ionizing wet scrubbers place an electrical charge on particles upstream from a wet scrubber. Larger particles and some gaseous contaminants are removed by scrubbing action. Smaller particles tend to induce opposite charges in water droplets in the scrubber and in its packing material and are removed by attraction of the opposite charges.

iii) Electrostatic Removal

Aerosol particles may acquire electrical charges. In an electric field, such particles are subjected to a force, F (dynes), given by $F = Eq$; where E is the voltage gradient (statvolt/cm) and q is the electrostatic charge on the particle (in esu). This phenomenon has been widely used in highly efficient **electrostatic precipitators**, when the gas stream is passed through a high-voltage, direct current corona. Because of the charge, the particles are attracted to a grounded surface from which they may be later removed. Ozone may be produced by the corona discharge. Similar devices used as household dust collectors may produce toxic ozone if not operated properly.

3.6.2 Gaseous inorganic air pollutants

Dear student, under this main content you learn about Gaseous inorganic air pollutants. Do you know some of the causes for Gaseous inorganic air pollutants, Let warm up yourself with the following activities.

Learning task 3.6.2

a) What are Gaseous inorganic air pollutants?
b) Mention some of Inorganic pollutant gases
c) Describe the effects of Carbon Monoxide Emissions
d) Explain how carbon monoxide is produced and controlled in the atmosphere

3.6.2.1 Inorganic pollutant gases

A number of gaseous inorganic pollutants enter the atmosphere as the result of human activities. Those added in the greatest quantities are CO, SO_2, NO, and NO_2 (these quantities are relatively small compared to the amount of CO_2 in the atmosphere). Other inorganic pollutant gases include NH_3, N_2O, N_2O_5, H_2S, Cl_2, HCl, and HF. substantial quantities of some of these gases are added to the atmosphere each year by human activities. Globally, atmospheric emissions of carbon monoxide, sulfur oxides, and nitrogen oxides are of the order of one to several hundred million tons per year.

3.6.2.2 Production and control of carbon monoxide

Carbon monoxide, CO, causes problems in cases of locally high concentrations because of its toxicity. The overall atmospheric concentration of carbon monoxide is about 0.1 ppm corresponding to a burden in the earth’s atmosphere of approximately 500 million metric tons of

CO with an average residence time ranging from 36 to 110 days. Much of this CO is present as an intermediate in the oxidation of methane by hydroxyl radical.

Therefore, any oxidation process for methane that produces carbon monoxide as an intermediate is certain to contribute substantially to the overall carbon monoxide burden, probably around two-thirds of the total CO. Degradation of chlorophyll during the autumn months releases CO, amounting to perhaps as much as 20% of the total annual release. Anthropogenic sources account for about 6% of CO emissions. The remainder of atmospheric CO comes from largely unknown sources. These include some plants and marine organisms known as siphonophores, an order of Hydrozoa. Carbon monoxide is also produced by decay of plant matter other than chlorophyll.

Because of carbon monoxide emissions from internal combustion engines, the highest levels of this toxic gas tend to occur in congested urban areas at times when the maximum number of people are exposed, such as during rush hours. At such times, carbon monoxide levels in the atmosphere have become as high as 50-100 ppm. Atmospheric levels of carbon monoxide in urban areas show a positive correlation with the density of vehicular traffic, and a negative correlation with wind speed. Urban atmospheres may show average carbon monoxide levels of the order of several ppm, much higher than those in remote areas.

i) Control of Carbon Monoxide Emissions

Since the internal combustion engine is the primary source of localized pollutant carbon monoxide emissions, control measures have been concentrated on the automobile. Carbon monoxide emissions may be lowered by employing a leaner air-fuel mixture, that is, one in which the weight ratio of air to fuel is relatively high. At air fuel (weight: weight) ratios exceeding approximately 16:1, an internal combustion engine emits very little carbon monoxide. Modern automobiles use catalytic exhaust reactors to cut down on carbon monoxide emissions. Excess air is pumped into the exhaust gas, and the mixture is passed through a catalytic converter in the exhaust system, resulting in oxidation of CO to CO_2.

ii) Fate of atmospheric Carbon monoxide (CO)

It is generally agreed that carbon monoxide is removed from the atmosphere by reaction with hydroxyl radical, HO•: $\mathbf{CO + HO\bullet \rightarrow CO_2 + H}$

The reaction produces hydroperoxyl radical as a product: **$O_2 + H + M \rightarrow HOO\bullet + M$**

$HO\bullet$ is regenerated from $HOO\bullet$ by the following reactions:

$$HOO\bullet + NO \rightarrow HO\bullet + NO_2$$

$$HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$$

The latter reaction is followed by photochemical dissociation of H_2O_2 to regenerate

$HO\bullet$: $H_2O_2 + h\nu \rightarrow 2HO\bullet$

Methane is also involved through the atmospheric **$CO/HO\bullet/\ CH_4$ cycle**. Soil microorganisms act to remove CO from the atmosphere. Therefore, soil is a sink for carbon monoxide.

3.6.2.3 Sulfur dioxide sources and the sulfur cycle

Dear student, under this main content you learn about sulfur dioxide sources and the sulfur cycle. Do you know some of the Sulfur dioxide sources and the sulfur cycle, Let warm up yourself with the following activities

Learning task 3.6.2.3

a) Explain the sources of sulfur dioxide in the atmosphere
b) Describe the major sulfur dioxide reactions in the atmosphere
c) Explain the major factors that influence the atmospheric chemical reactions of sulfur dioxide
d) Describe the global atmospheric sulfur cycle
e) Mention the major effects of atmospheric sulfur dioxide
f) Explain how sulfur dioxide is removed from the atmosphere

Dear student, there are many uncertainties regarding the sources, reactions, and fates of these atmospheric sulfur species. On a global basis, sulfur compounds enter the atmosphere to a very large extent through human activities. Approximately 100 million metric tons of sulfur per year enters the global atmosphere through anthropogenic activities, primarily as SO_2 from the combustion of coal and residual fuel.

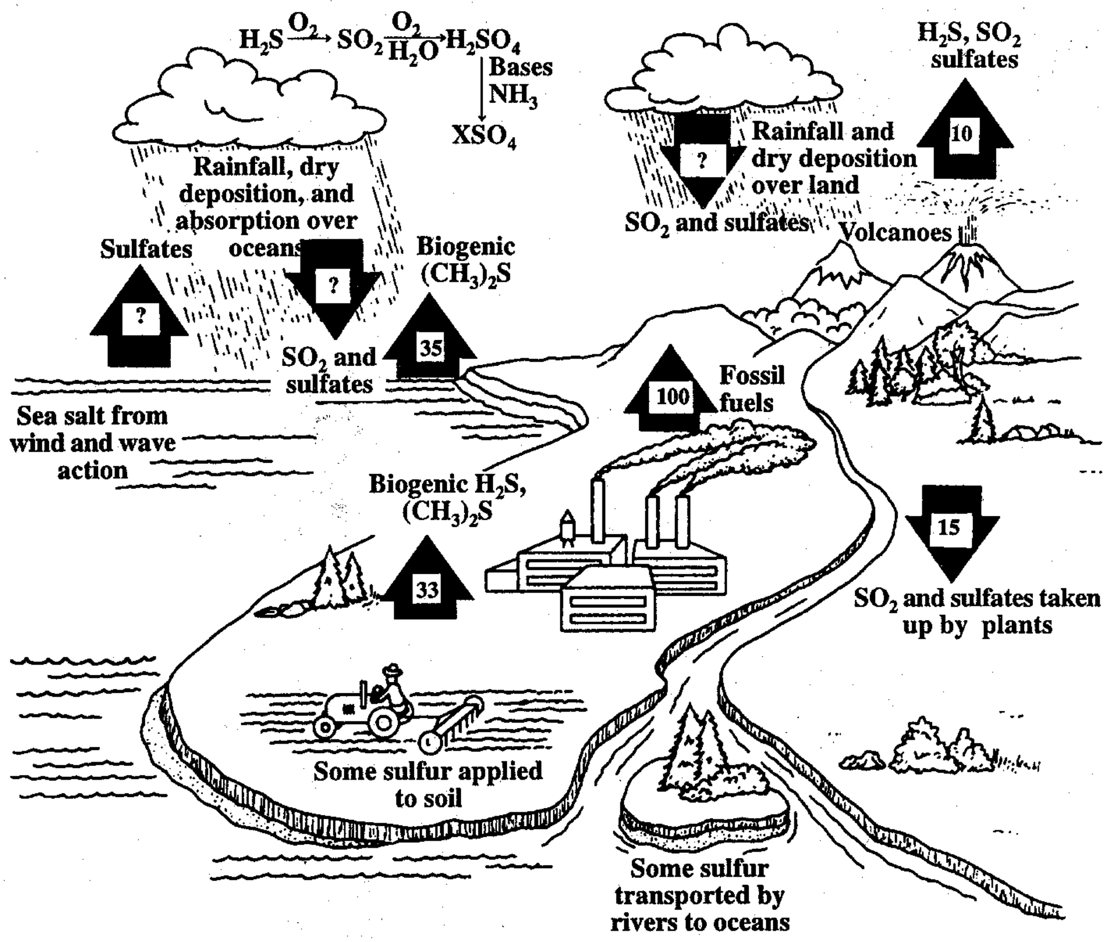


Figure 3.6.2.3 the global atmospheric sulfur cycle.

As it is indicated in figure 3.5.2.3 above, fluxes of sulfur represented by the arrows are in millions of metric tons per year. Those marked with a question mark are uncertain, but large, probably of the order of 100 million metric tons per year. The greatest uncertainties in the cycle have to do with nonanthropogenic sulfur, which enters the atmosphere largely as SO_2 and H_2S from volcanoes, and as $(CH_3)_2S$ and H_2S from the biological decay of organic matter and reduction of sulfate.

The single largest source of natural sulfur discharged to the atmosphere is now believed to be biogenic dimethyl sulfide, $(CH_3)_2S$, from marine sources. Any H_2S that does get into the atmosphere is converted rapidly to SO_2 by the following overall process:

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O$$

The initial reaction is hydrogen ion abstraction by hydroxyl radical,

$$H_2S + HO\bullet \rightarrow HS\bullet + H_2O$$

followed by the following two reactions to give SO_2:

$$HS\bullet + O_2 \rightarrow HO\bullet + SO$$

$$SO + O_2 \rightarrow SO_2 + O$$

The primary source of anthropogenic sulfur dioxide is coal, from which sulfur must be removed at great expense to keep sulfur dioxide emissions at acceptable levels. Approximately half of the sulfur in coal is in some form of pyrite, FeS_2, and the other half is organic sulfur. The production of sulfur dioxide by the combustion of pyrite is given by the following reaction:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Essentially all of the sulfur is converted to SO_2 and only 1 or 2% to SO_3.

i) Sulfur dioxide reactions in the atmosphere

Many factors, including temperature, humidity, light intensity, atmospheric transport, and surface characteristics of particulate matter, may influence the atmospheric chemical reactions of sulfur dioxide. Like many other gaseous pollutants, sulfur dioxide reacts to form particulate matter, which then settles or is scavenged from the atmosphere by rainfall or other processes. It is known that high levels of air pollution normally are accompanied by a marked increase in aerosol particles and a consequent reduction in visibility.

Reaction products of sulfur dioxide are thought to be responsible for some aerosol formation. Whatever the processes involved, much of the sulfur dioxide in the atmosphere is ultimately oxidized to sulfuric acid and sulfate salts, particularly ammonium sulfate and ammonium hydrogen sulfate.

Some of the possible ways in which sulfur dioxide may react in the atmosphere are:

1) photochemical reactions;
2) photochemical and chemical reactions in the presence of nitrogen oxides and/or hydrocarbons, particularly alkenes;
3) chemical processes in water droplets, particularly those containing metal salts and ammonia; and
4) Reactions on solid particles in the atmosphere.

It should be kept in mind that the atmosphere is a highly dynamic system with great variations in temperature, composition, humidity, and intensity of sunlight; therefore, 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 nm is not sufficiently energetic to bring about the photo dissociation of SO_2, so direct photochemical reactions in the troposphere are of no significance. The oxidation of sulfur dioxide at the parts-per-million level in an otherwise unpolluted atmosphere is a slow process. Therefore, other pollutant species must be involved in the process in atmospheres polluted with SO_2.The presence of hydrocarbons and nitrogen oxides greatly increases the oxidation rate of atmospheric SO_2.

Among the oxidizing species present which could bring about this fast reaction are HO•, HOO•, O, O_3, NO_3, N_2O_5, ROO•, and RO•. As discussed before, the latter two species are reactive organic free radicals containing oxygen. Although ozone, O_3, is an important product of photochemical smog, it is believed that the oxidation of SO_2 by ozone in the gas phase is too slow to be appreciable, but it is probably significant in water droplets. The most important gas-phase reaction leading to the oxidation of SO_2 is the addition of HO• radical, forming a reactive free radical which is eventually converted to a form of sulfate. $HO\bullet + SO_2 \rightarrow HOSO_2\bullet$

In all but relatively dry atmospheres, it is probable that sulfur dioxide is oxidized by reactions occurring inside water aerosol droplets. The overall process of sulfur dioxide oxidation in the aqueous phase is rather complicated. It involves the transport of gaseous SO_2 and oxidant to the aqueous phase, diffusion of species in the aqueous droplet, hydrolysis and ionization of SO_2, and oxidation of SO_2 by the following overall process, where {O} represents an oxidizing agent such as H_2O_2, HO•, or O_3 and S(IV) is $SO_2(aq)$, $HSO_3^-(aq)$, and $SO_3^{2-}(aq)$.

$$\{O\}(aq) + S\,(IV)\,(aq) \rightarrow 2H^+ + SO_4^{2-} \text{ (unbalanced)}$$

In the absence of catalytic species, the reaction with dissolved molecular O_2 is too slow to be significant. Hydrogen peroxide is an important oxidizing agent in the atmosphere.

$$1/2O_2\,(aq) + SO_2\,(aq) + H_2O \rightarrow H_2SO_4\,(aq)$$

It reacts with dissolved sulfur dioxide through the overall reaction, to produce sulfuric acid. The major reaction is thought to be between hydrogen peroxide and HSO_3^- ion with peroxymonosulfurous acid, $HOOSO_2$: SO_2 (*aq*) + H_2O_2 (*aq*) → H_2SO_4 (*aq*), as an intermediate. Ozone, O_3, oxidizes sulfur dioxide in water.

The fastest reaction is with sulfite ion; SO_3^{2-} (*aq*) + O_3 (*aq*) →SO_4^{2-}(*aq*) + O_2 reactions are slower with HSO_3^-(*aq*) and SO_2 (*aq*). The rate of oxidation of aqueous SO_2 species by ozone increases with increasing pH. The oxidation of sulfur dioxide in water droplets is faster in the presence of ammonia, which reacts with sulfur dioxide to produce bisulfite ion and sulfite ion in solution:

$$NH_3 + SO_2 + H_2O \rightarrow NH_4^+ + HSO_3^-$$

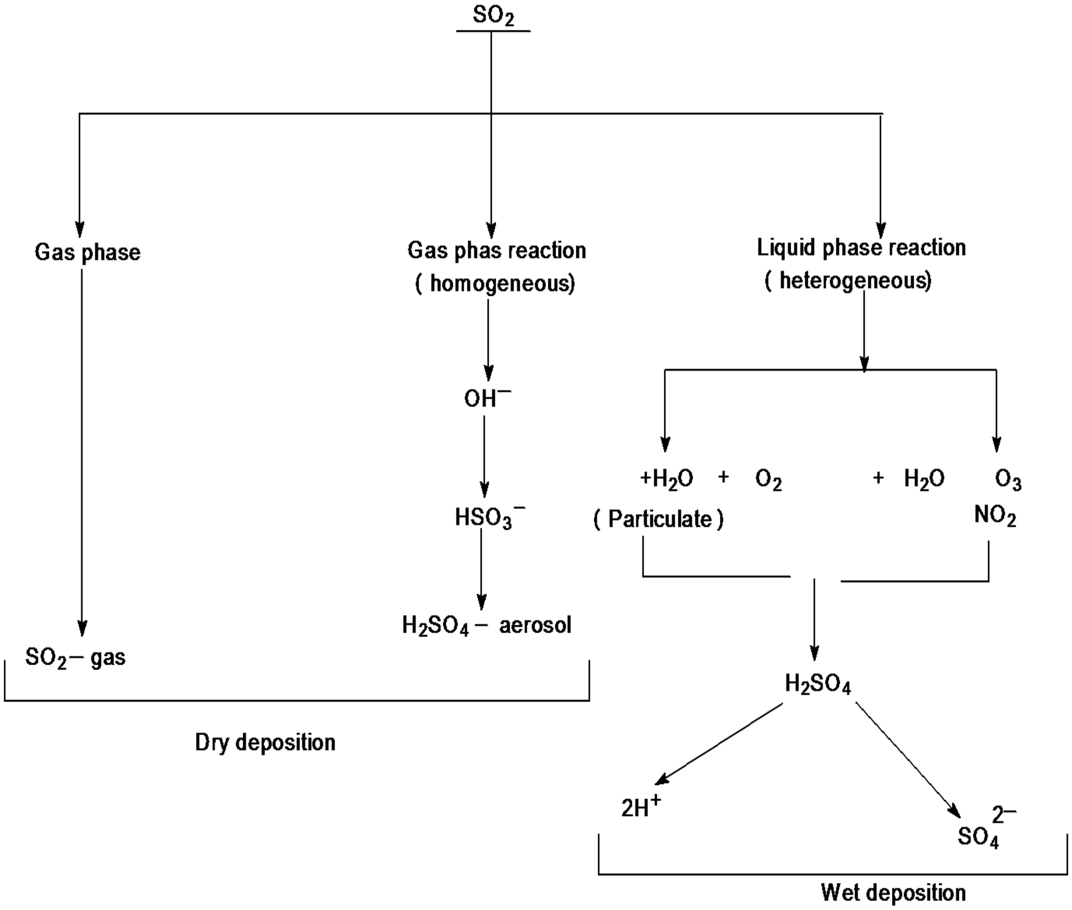


Figure 3.6.2.4 Acid deposition

ii) Effects of Atmospheric Sulfur Dioxide

Though not terribly toxic to most people, low levels of sulfur dioxide in air do have some health effects. Its primary effect is upon the respiratory tract, producing irritation and increasing airway resistance, especially to people with respiratory weaknesses and sensitized asthmatics. Therefore, exposure to the gas may increase the effort required to breathe. Mucus secretion is also stimulated by exposure to air contaminated by sulfur dioxide. Although SO_2 causes death in humans at 500 ppm, it has not been found to harm laboratory animals at 5 ppm.

Sulfur dioxide has been at least partially implicated in several acute incidents of air pollution. **For example,** in December 1930, a thermal inversion trapped waste products from a number of industrial sources in the narrow Meuse River Valley of Belgium. Sulfur dioxide levels reached 38 ppm. Approximately 60 people died in the episode, and some cattle were killed.

iii) Sulfur dioxide removal

A number of processes are being used to remove sulfur and sulfur oxides from fuel before combustion and from stack gas after combustion. Most of these efforts concentrate on coal, since it is the major source of sulfur oxides pollution. Physical separation techniques may be used to remove discrete particles of pyritic sulfur from coal. Chemical methods may also be employed for removal of sulfur from coal. Fluidized bed combustion of coal promises to eliminate SO_2 emissions at the point of combustion. The process consists of burning granular coal in a bed of finely divided limestone or dolomite maintained in a fluid-like condition by air injection. Heat calcines the limestone,

$CaCO_3 \rightarrow CaO + CO_2$ and the lime produced absorbs SO_2:

$CaO + SO_2 \rightarrow CaSO_3$ (Which may be oxidized to $CaSO_4$)

3.6.2.4 Nitrogen oxides in the atmosphere

Dear student, under this main content you learn about Nitrogen oxides in the atmosphere. Do you know some of the Atmospheric reactions of Nitrogen oxides, let warm up yourself with the following activities.

Learning task 3.6.2.4

a) Mention the common oxides of nitrogen
b) Describe the major oxides of nitrogen reactions in the atmosphere
c) Explain the harmful effects of nitrogen oxides
d) Explain the major factors that influence the atmospheric chemical reactions of nitrogen oxides
e) Explain how nitrogen oxides are controlled from the atmosphere

The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Nitrous oxide, a commonly used anesthetic known as “laughing gas,” is produced by microbiological processes and is a component of the unpolluted atmosphere at a level of approximately 0.3 ppm. This gas is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere. Its concentration decreases rapidly with altitude in the stratosphere due to the photochemical reaction

$$N_2O + h\nu \rightarrow N_2 + O$$

and some reaction with singlet atomic oxygen:

$$N_2O + O \rightarrow N_2 + O_2$$

$$N_2O + O \rightarrow 2NO$$

These reactions are significant in terms of depletion of the ozone layer. Increased global fixation of nitrogen, accompanied by increased microbial production of N_2O, could contribute to ozone layer depletion. Colorless, odorless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO_2) are very important in polluted air. Collectively designated NOx, these gases enter the atmosphere from natural sources, such as lightning and biological processes, and from pollutant sources. The latter are much more significant because of regionally high NO_2 concentrations which can cause severe air quality deterioration. Practically all anthropogenic NOx enters the atmosphere as a result of the combustion of fossil fuels in both stationary and mobile sources.

There are, of course, many other species present in the combustion mixture besides those shown. The oxygen atoms are especially reactive toward hydrocarbon fragments by reactions such as the following: **$RH + O \rightarrow R\bullet + HO\bullet$** where RH represents a hydrocarbon fragment with an extractable hydrogen atom. These fragments compete with N_2 for oxygen atoms. It is partly for this reason that the formation of NO is appreciably higher at air/fuel ratios exceeding the stoichiometric ratio.

The hydroxyl radical itself can participate in the formation of NO. The reaction is $N + HO\bullet \rightarrow NO + H\bullet$; Nitric oxide, NO, is a product of the combustion of coal and petroleum containing chemically bound nitrogen. Production of NO by this route occurs at much lower temperatures than those required for “thermal” NO, discussed previously.

i) Atmospheric Reactions of NOx

Atmospheric chemical reactions convert NOx to nitric acid, inorganic nitrate salts, organic nitrates, and peroxyacetyl nitrate. The principal reactive nitrogen oxide species in the troposphere are NO, NO_2, and HNO_3. Although NO is the primary form in which NOx is released to the atmosphere, the conversion of NO to NO_2 is relatively rapid in the troposphere. Principal reactions among NO, NO_2, and HNO_3 in the atmosphere is given below

$HOO\bullet + NO \rightarrow NO_2 + HO\bullet$

$ROO\bullet + NO \rightarrow NO_2 + RO\bullet$

$NO + O_3 \rightarrow NO_2 + O_2$

$O + NO \rightarrow hv + NO_2$

$HO\bullet + NO_2 \rightarrow HNO_3$

$NO_2 + HO\bullet \rightarrow hv + HNO_3$

ROO• represents an organic peroxyl radical, such as the methylperoxyl radical, $CH_3OO\bullet$. Nitrogen dioxide is a very reactive and significant species in the atmosphere. It absorbs light throughout the ultraviolet and visible spectrum penetrating the troposphere.

At wavelengths below 398 nm, photodissociation occurs, **$NO_2 + hv \rightarrow NO + O$** to produce ground state oxygen atoms. Above 430 nm, only excited molecules are formed, **$NO_2 + hv \rightarrow NO_2^*$** whereas at wavelengths between 398 nm and 430 nm, either process may occur. Photo dissociation at these wavelengths requires input of rotational energy from rotation of the NO_2 molecule. The tendency of NO_2 to photo dissociate is shown clearly by the fact that in direct sunlight the half-life of NO_2 is much shorter than that of any other common molecular atmospheric species. The photo dissociation of nitrogen dioxide can give rise to the following significant inorganic reactions in addition to a host of atmospheric reactions involving organic species:

$O + O_2 + M \text{ (third body)} \rightarrow O_3 + M$

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$O + NO_2 \rightarrow NO + O_2$

$O + NO_2 + M \rightarrow NO_3 + M$

$NO_2 + NO_3 \rightarrow N_2O_5$

$NO + NO_3 \rightarrow 2NO_2$

$O + NO + M \rightarrow NO_2 + M$

Nitrogen dioxide ultimately is removed from the atmosphere as nitric acid, nitrates, or (in atmospheres where photochemical smog is formed) as organic nitrogen. Dinitrogen pentoxide formed in the above reaction is the anhydride of nitric acid, which it forms by reacting with water:

$N_2O_5 + H_2O \rightarrow 2HNO_3$

In the stratosphere, nitrogen dioxide reacts with hydroxyl radicals to produce nitric acid:

$HO\bullet + NO_2 \rightarrow HNO_3$

In this region, the nitric acid can also be destroyed by hydroxyl radicals,

$HO\bullet + HNO_3 \rightarrow H_2O + NO_3$

or by a photochemical reaction,

$HNO_3 + h\text{v} \rightarrow HO\bullet + NO_2$

so that HNO_3 serves as a temporary sink for NO_2 in the stratosphere. Nitric acid produced from NO_2 is removed as precipitation, or reacts with bases (ammonia, particulate lime) to produce particulate nitrates.

ii) Harmful Effects of Nitrogen Oxides

Nitric oxide, NO, is less toxic than NO_2. Like carbon monoxide and nitrite, NO attaches to hemoglobin and reduces oxygen transport efficiency. However, in a polluted atmosphere, the concentration of nitric oxide normally is much lower than that of carbon monoxide so that the effect on hemoglobin is much less. Acute exposure to NO_2 can be quite harmful to human health. **For example**, for exposures ranging from several minutes to one hour, a level of 50-100 ppm of

NO_2 causes inflammation of lung tissue for a period of 6-8 weeks, after which time the subject normally recovers.

Exposure of the subject to 150-200 ppm of NO_2 causes *bronchiolitis fibrosa obliterans*, a condition fatal within 3-5 weeks after exposure. Death generally results within 2-10 days after exposure to 500 ppm or more of NO_2. “Silofiller’s disease,” caused by NO_2 generated by the fermentation of ensilage containing nitrate, is a particularly striking example of nitrogen dioxide poisoning. Deaths have resulted from the inhalation of NO_2-containing gases from burning celluloid and nitrocellulose film, and from spillage of NO_2 oxidant (used with liquid hydrazine fuel) from missile rocket motors.

Although extensive damage to plants is observed in areas receiving heavy exposure to NO_2, most of this damage probably comes from secondary products of nitrogen oxides, such as PAN formed in smog. Exposure of plants to several parts per million of NO_2 in the laboratory causes leaf spotting and breakdown of plant tissue. Exposure to 10 ppm of NO causes a reversible decrease in the rate of photosynthesis. The effect on plants of long-term exposure to a few tenths of a part per million of NO_2 is less certain.

Nitrogen oxides are known to cause fading of dyes and inks used in some textiles. This has been observed in gas clothes dryers and is due to NOx formed in the dryer flame. Much of the damage to materials caused by NOx comes from secondary nitrates and nitric acid. **For example**, stress-corrosion cracking of springs used in telephone relays occurs far below the yield strength of the nickel-brass spring metal because of the action of particulate nitrates and aerosol nitric acid formed from NOx.

In the upper stratosphere and in the mesosphere, molecular oxygen is photodissociated by ultraviolet light of less than 242-nm wavelength: $\mathbf{O_2 + \mathit{h}v \rightarrow O + O}$**; In** the presence of energy-absorbing third bodies, the atomic oxygen reacts with molecular oxygen to produce ozone:

$$\mathbf{O_2 + O + M \rightarrow O_3 + M}$$

Ozone can be destroyed by reaction with atomic oxygen, $\mathbf{O_3 + O \rightarrow O_2 + O_2}$; and its formation can be prevented by recombination of oxygen atoms: $\mathbf{O + O + M \rightarrow O_2 + M}$. Addition of the reaction of nitric oxide with ozone, $\mathbf{NO + O_3 \rightarrow NO_2 + O_2}$ to the reaction of nitrogen dioxide with atomic oxygen, results in a net reaction for the destruction of ozone:

$\mathbf{NO_2 + O \rightarrow NO + O_2}$

$\mathbf{O + O_3 \rightarrow O_2 + O_2}$

Along with NOx, water vapor is also emitted into the atmosphere by aircraft exhausts, which could accelerate ozone depletion by the following two reactions:

$O + H_2O \rightarrow HO\bullet + HO\bullet$

$HO\bullet + O_3 \rightarrow HOO\bullet + O_2$

However, there are many natural stratospheric buffering reactions which tend to mitigate the potential ozone destruction from those reactions outlined above. Atomic oxygen capable of regenerating ozone is produced by the photochemical reaction,

$NO_2 + h\nu \rightarrow NO + O$ ($\lambda < 420$ nm)

A competing reaction removing catalytic NO is $NO + HOO\bullet \rightarrow NO_2 + HO\bullet$

Current belief is that supersonic aircraft emissions will not cause nearly as much damage to the ozone layer as chlorofluorocarbons.

iii) Control of Nitrogen Oxides

The level of NOx emitted from stationary sources such as power plant furnaces generally falls within the range of 50-1000 ppm. NO production is favored both kinetically and thermodynamically by high temperatures and by high excess oxygen concentrations. These factors must be considered in reducing NO emissions from stationary sources. Reduction of flame temperature to prevent NO formation is accomplished by adding recirculated exhaust gas, cool air, or inert gases.

3.6.2.5 Ammonia in the atmosphere

Ammonia is present even in unpolluted air as a result of natural biochemical and chemical processes. Among the various sources of atmospheric ammonia are microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems. High concentrations of ammonia gas in the atmosphere are generally indicative of accidental release of the gas. Ammonia is removed from the atmosphere by its affinity for water and by its action as a base. It is a key species in the formation and neutralization of nitrate and sulfate aerosols in polluted atmospheres. Ammonia reacts with these acidic aerosols to form ammonium salts:

$NH_3 + HNO_3 \rightarrow NH_4NO_3$

$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$

Ammonium salts are among the more corrosive salts in atmospheric aerosols.

3.6.3 Gaseous organic air pollutants

Dear student, under this main content you learn about Gaseous organic air pollutants. Do you know some of the causes for Gaseous organic air pollutants, Let warm up yourself with the following activities.

Learning task 3.6.3

a) What are Gaseous organic air pollutants?
b) Mention some of organic compounds in the atmosphere
c) Explain how organic contaminants lost from the atmosphere
d) Mention some organic compounds that can be obtained from natural sources
e) Mention some of pollutant hydrocarbons
f) Explain the source and effects of organohalide compounds

3.6.3.1. Effect of Organic pollutants

Organic pollutants may have a strong effect upon atmospheric quality. The effects of organic pollutants in the atmosphere may be divided into two major categories. The first consists of **direct effects**, such as cancer caused by exposure to vinyl chloride. The second is the formation of **secondary pollutants**, especially photochemical smog. In the case of pollutant hydrocarbons in the atmosphere, the latter is the more important effect. In some localized situations, particularly the workplace, direct effects of organic air pollutants may be equally important.

3.6.3.2. Removal of Organic Substances from the Atmosphere

Organic contaminants are lost from the atmosphere by a number of routes. These include dissolution in precipitation (rainwater), dry deposition, photochemical reactions, formation of and incorporation into particulate matter, and uptake by plants. Reactions of organic atmospheric contaminants are particularly important in determining their manner and rates of loss from the atmosphere. **For example;** forest trees present a large surface area to the atmosphere and are particularly important in filtering organic contaminants from air.

On a global scale, it is likely that persistent organic pollutants undergo a cycle of distillation and fractionation in which they are vaporized into the atmosphere in warmer regions of the Earth and condense and are deposited in colder regions. The theory of this phenomenon holds that the distribution of such pollutants is governed by their physicochemical properties and the temperature conditions to which they are exposed.

As a result, the least volatile persistent organic pollutants are deposited near their sources, those of relatively high volatility are distilled into Polar Regions, and those of intermediate volatility are deposited predominantly at mid latitudes. This phenomenon has some important implications regarding the accumulation of persistent organic pollutants in environmentally fragile polar regions far from industrial sources.

3.6.3.3. Organic compounds from natural organic compounds

Natural sources are the most important contributors of organics in the atmosphere, and hydrocarbons generated and released by human activities constitute only about 1/7 of the total hydrocarbons in the atmosphere. This ratio is primarily the result of the huge quantities of methane produced by anaerobic bacteria in the decomposition of organic matter in water, sediments, and soil: $\mathbf{2\{CH_2O\}\ (bacterial\ action) \rightarrow CO_2\ (\mathit{g}) + CH_4\ (\mathit{g})}$

Methane is a natural constituent of the atmosphere and is present at a level of about 1.4 parts per million (ppm) in the troposphere. Methane in the troposphere contributes to the photochemical production of carbon monoxide and ozone. The photochemical oxidation of methane is a major source of water vapor in the stratosphere.

Atmospheric hydrocarbons produced by living sources are called **biogenic hydrocarbons**. Vegetation is the most important natural source of non-methane biogenic compounds. A compilation of organic compounds in the atmosphere documented a total of 367 different compounds that are released to the atmosphere from vegetation sources. Other natural sources include microorganisms, forest fires, animal wastes, and volcanoes.

One of the simplest organic compounds given off by plants is ethylene, C_2H_4. This compound is produced by a variety of plants and released to the atmosphere in its role as a messenger species regulating plant growth. Because of its double bond, ethylene is highly reactive with hydroxyl radical, HO•, and with oxidizing species in the atmosphere. Ethylene from vegetation sources should be considered as an active participant in atmospheric chemical processes. Most of the hydrocarbons emitted by plants are **terpenes**, which constitute a large class of organic compounds found in essential oils.

3.6.3.4 Hydrocarbons

Ethylene and terpenes, which were discussed in the preceding section, are **hydrocarbons**, organic compounds containing only hydrogen and carbon. The major classes of hydrocarbons are **alkanes** (formerly called paraffins), such as methane; **alkenes**, such as ethylene; **alkynes**, such as acetylene; and **aryl** (aromatic) **compounds**, such as naphthalene: Because of their widespread use in fuels, hydrocarbons predominate among organic atmospheric pollutants. Petroleum products, primarily gasoline, are the source of most of the anthropogenic (originating through human activities) pollutant hydrocarbons found in the atmosphere. Hydrocarbons may enter the atmosphere either directly or as by-products of the partial combustion of other hydrocarbons.

3.6.3.5 Aromatic hydrocarbons/Aryl compounds/

Aryl (**aromatic**) **hydrocarbons** may be divided into the two major classes of those that have only one benzene ring and those with multiple rings such as *polycyclic aryl hydrocarbons, PAH.* Aryl hydrocarbons with two rings, such as naphthalene, are intermediate in their behavior. Some typical aryl hydrocarbons are: Benzene 2,6-Dimethylnaphthalene Pyrene.

3.6.3.6 Carbonyl compounds /Aldehydes and Ketones/

Carbonyl compounds, consisting of aldehydes and ketones that have a carbonyl moiety, C=O, are often the first species formed, other than unstable reaction intermediates, in the photochemical oxidation of atmospheric hydrocarbons. **For example**, formaldehyde occurs in the atmosphere primarily in the gas phase. Photolytically excited formaldehyde, CH_2O^*, may dissociate in two ways. The first of these produces an H atom and HCO radical; the second produces chemically stable H_2 and CO.

3.6.3.7 Organohalide compounds

Organohalides consist of halogen-substituted hydrocarbon molecules, each of which contains at least one atom of F, Cl, Br, or I. They may be saturated (**alkyl halides**), unsaturated (**alkenyl halides**), or aryl (**aryl halides)**. The organohalides of environmental and toxicological concern exhibit a wide range of physical and chemical properties. Although most organohalide compounds of pollution concern are from anthropogenic sources, it is now known that a large variety of such compounds are generated by organisms, particularly those in marine environments.

i) Chloro carbon compound (Chlorinated hydrocarbons)

Volatile **chloromethane** (methyl chloride) is consumed in the manufacture of silicones. **Dichloromethane** is a volatile liquid with excellent solvent properties for nonpolar organic solutes. It has been used as a solvent for the decaffeination of coffee, in paint strippers, as a blowing agent in urethane polymer manufacture, and to depress vapor pressure in aerosol formulations.

Vinyl chloride is consumed in large quantities as a raw material to manufacture pipe, hose, wrapping, and other products fabricated from polyvinyl chloride plastic. This highly flammable, volatile, sweet-smelling gas is known to cause angiosarcoma, a rare form of liver cancer.

Trichloroethylene is a clear, colorless, nonflammable, volatile liquid. It is an excellent degreasing and dry-cleaning solvent, and has been used as a household solvent and for food extraction (for example, in decaffeination of coffee). **Allyl chloride** is an intermediate in the manufacture of allyl alcohol and other allyl compounds, including pharmaceuticals, insecticides, and thermosetting varnish and plastic resins.

ii) Chlorofluorocarbons

Dichlorodifluoromethane is one of the chlorofluorocarbon compounds once widely manufactured as a refrigerant and involved in stratospheric ozone depletion. One of the more common industrial chlorinated solvents is **1,1,1-trichloroethane**. Viewed as halogen-substituted derivatives of alkenes, the **alkenyl** or **olefinic organohalides** contain at least one halogen atom and at least one carbon-carbon double bond. The most significant of these are the lighter chlorinated compounds.

Chlorofluorocarbons (**CFC**s), such as dichlorodifluoromethane, commonly called Freons, are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon. These compounds are notably stable and nontoxic. They have been widely used in recent decades in the fabrication of flexible and rigid foams and as fluids for refrigeration and air conditioning. The most widely manufactured of these compounds are CCl_3F (CFC-11, bp 24°C), CCl_2F_2 (CFC-12, bp - 28°C), $C_2Cl_3F_3$ (CFC-113), $C_2Cl_2F_4$ (CFC-114), and C_2ClF_5 (CFC-115).

iii) Mixed Halo compounds (Halons)

Halons are related compounds that contain bromine and are used in fire extinguisher systems. The major commercial halons are $CBrClF_2$ (Halon-1211), $CBrF_3$ (Halon-1301), and $C_2Br_2F_4$ (Halon-2402), where the sequence of numbers denotes the number of carbon, fluorine, chlorine, and bromine atoms, respectively, per molecule. Halons are particularly effective fire extinguishing agents because of the way in which they stop combustion. Halons act by chain reactions that destroy hydrogen atoms which sustain combustion. The basic sequence of reactions involved is outlined below:

$$CBrClF_2 + H \rightarrow CClF_2\bullet + HBr$$

$$HBr + H\bullet \rightarrow Br\bullet + H_2$$

$$Br\bullet + H\bullet \rightarrow HBr$$

Although quite inert in the lower atmosphere, CFCs undergo photodecomposition by the action of high-energy ultraviolet radiation in the stratosphere, which is energetic enough to break their very strong C-Cl bonds through reactions such as, thereby releasing Cl atoms.

$Cl_2CF_2 + h\nu \rightarrow Cl\bullet + ClCF_2\bullet$

The Cl atoms are very reactive species. Under the rarefied conditions of the stratosphere, one of the most abundant reactive species available for them to react with is ozone, which they destroy through a process that generates ClO: $\mathbf{Cl + O_3 \rightarrow ClO + O_2}$

In the stratosphere, there is an appreciable concentration of atomic oxygen by virtue of the reaction: $\mathbf{O_3 + h\nu \rightarrow O_2 + O}$**; Nitric** oxide, NO, is also present. The ClO species may react with either O or NO, regenerating Cl atoms and resulting in chain reactions that cause the net destruction of ozone:

$ClO + O \rightarrow Cl + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$O_3 + O \rightarrow 2O_2$
$ClO + NO \rightarrow Cl + NO_2$
$O_3 + Cl \rightarrow ClO + O_2$
$O_3 + NO \rightarrow NO_2 + O_2$

Both ClO and Cl involved in the above chain reactions have been detected in the 25- 45-km altitude region. The effects of CFCs on the ozone layer may be the single greatest threat to the global atmosphere. **For example;** U. S. Environmental Protection Agency regulations, imposed in accordance with the 1986 Montreal Protocol on Substances that Deplete the Ozone Layer, curtailed production of CFCs and halocarbons in the U. S. starting in 1989.

3.6.4 The endangered global atmosphere

Dear student, under this main content you learn about the endangered global atmosphere. Do you know some of the causes for the endangered global atmosphere, let warm up yourself with the following activities.

Learning task 3.6.4

a) Mention the major anthropogenic change in the atmosphere
b) What do we mean the endangered global atmosphere?
c) Explain the basis for the ‘’Gaia hypothesis’’
d) Mention the major effects of human activities and the anthrosphere on the atmosphere

Anthropogenic change in the atmosphere

There is a very strong connection between life forms on earth and the nature of earth’s climate, which determines its suitability for life. As proposed by James Lovelock, a British chemist, this forms the basis of the Gaia hypothesis, which contends that the atmospheric O_2/CO_2 balance established and sustained by organisms determines and maintains earth’s climate and other environmental conditions.

Ever since life first appeared on earth, the atmosphere has been influenced by the metabolic processes of living organisms. When the first primitive life molecules were formed approximately 3.5 billion years ago, the atmosphere was very different from its present state. At that time it was chemically reducing and thought to contain nitrogen, methane, ammonia, water vapor, and hydrogen, but no elemental oxygen.

These gases and water in the sea were bombarded by intense, bond-breaking ultraviolet radiation which, along with lightning and radiation from radionuclides, provided the energy to bring about chemical reactions that resulted in the production of relatively complicated molecules, including even amino acids and sugars. From this rich chemical mixture, life molecules evolved. Initially, these very primitive life forms derived their energy from fermentation of organic matter formed by chemical and photochemical processes, but eventually they gained the capability to produce organic matter, “$\{CH_2O\}$,” by photosynthesis, and the stage was set for the massive biochemical transformation that resulted in the production of almost all the atmosphere’s oxygen.

$$\mathbf{CO_2 + H_2O + \mathit{h}v \rightarrow \{CH_2O\} + O_2\ (\mathit{g})}$$

The oxygen initially produced by photosynthesis was probably quite toxic to primitive life forms. However, much of this oxygen was converted to iron oxides by reaction with soluble iron (II):

$$\mathbf{4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+}$$

The enormous deposits of iron oxides thus formed provide convincing evidence for the liberation of free oxygen in the primitive atmosphere. Eventually enzyme systems developed that enabled organisms to mediate the reaction of waste-product oxygen with oxidizable organic matter in the sea. Later this mode of waste-product disposal was utilized by organisms to produce energy for respiration, which is now the mechanism by which nonphotosynthetic organisms obtain energy.

In time, oxygen accumulated in the atmosphere, providing an abundant source of O_2 for respiration. It had an additional benefit in that it enabled the formation of an ozone shield against solar ultraviolet radiation. With this shield in place, the earth became a much more hospitable environment for life, and life forms were enabled to move from the protective surroundings of the sea to the more exposed environment of the land.

Other instances of climatic change and regulation induced by organisms can be cited. An example is the maintenance of atmospheric carbon dioxide at low levels through the action of photosynthetic organisms. But, at an ever accelerating pace during the last 200 years, another organism, humankind, has engaged in a number of activities that are altering the atmosphere profoundly. As noted in Chapter 1, human influences are so strong that it is useful to invoke a fifth sphere of the environment, the anthrosphere.

The effects of human activities and the anthrosphere on the atmosphere are summarized below:

- Industrial activities, which emit a variety of atmospheric pollutants including SO_2, particulate matter, photochemically reactive hydrocarbons, chlorofluorocarbons, and inorganic substances (such as toxic heavy metals)
- Burning of large quantities of fossil fuel, which can introduce CO_2, CO, SO_2, NOx, hydrocarbons (including CH_4), and particulate soot, polycyclic aromatic hydrocarbons, and fly ash into the atmosphere
- Transportation practices, which emit CO_2, CO, NOx, photochemically reactive (smog forming) hydrocarbons, and polycyclic aromatic hydrocarbons

- Alteration of land surfaces, including deforestation
- Burning of biomass and vegetation, including tropical and subtropical forests and savanna grasses, which produces atmospheric CO_2, CO, NOx, and particulate soot and polycyclic aromatic hydrocarbons
- Agricultural practices, which produce methane (from the digestive tracts of domestic animals and from the cultivation of rice in waterlogged anaerobic soils) and N_2O from bacterial denitrification of nitrate-fertilized soils. These kinds of human activities have significantly altered the atmosphere, particularly in regard to its composition of minor constituents and trace gases.

- **Major effects have been the following:**
  - ✓ Increased acidity in the atmosphere
  - ✓ Production of pollutant oxidants in localized areas of the lower troposphere
  - ✓ Elevated levels of infrared-absorbing gases (greenhouse gases)
  - ✓ Threats to the ultraviolet-filtering ozone layer in the stratosphere
  - ✓ Increased corrosion of materials induced by atmospheric pollutants

3.6.4.1 Photochemical smog

Dear student, under this main content you learn about Photochemical smog. Do you know some of the causes for Photochemical smog, let warm up yourself with the following activities.

Learning task 3.6.4.1

a) What is Photochemical smog?
b) Mention the sources of Photochemical smog
c) Explain the effects of Photochemical smog
d) Explain how Photochemical smog is minimized

Dear student, photochemical smog is a major air pollution phenomenon. It occurs in urban areas where the combination of pollution-forming emissions and appropriate atmospheric conditions are right for its formation. In order for high levels of smog to form, relatively stagnant air must be subjected to sunlight under low humidity conditions in the presence of pollutant nitrogen oxides and hydrocarbons. Although the automobile is the major source of these pollutants, hydrocarbons may come from biogenic sources, of which a-pinene and isoprene from trees are the most abundant.

Stated briefly, “The urban atmosphere is a giant chemical reactor in which pollutant gases such as hydrocarbons and oxides of nitrogen and sulfur react under the influence of sunlight to create a variety of products.”Although not as great a threat to the global atmosphere as some of the other air pollutants discussed in this chapter, smog does pose significant hazards to living things and materials in local urban areas in which millions of people are exposed.

Ironically, ozone, which serves an essential protective function in the stratosphere, is the major cause in tropospheric smog. In fact, surface ozone levels are used as a measure of smog. Ozone’s phytotoxicity raises particular concern with respect to trees and crops. Ozone is the smog constituent responsible for most of the respiratory system distress and eye irritation characteristic of human exposure to smog. Breathing is impaired at ozone levels approaching only about 0.1 ppm. Ozone is the “criterion” air pollutant that has been most resistant to control measures. Because of its strongly oxidizing nature, ozone attacks unsaturated bonds in fatty acid constituents of cell membranes. Other oxidants, such as PAN, also contribute to the toxicity of smog, as do aldehydes produced as reactive intermediates in smog formation.

Smog is a secondary air pollutant that forms sometime after and some distance from the injection into the atmosphere of the primary pollutant nitrogen oxides and reactive hydrocarbons required for its formation. **For example,** the U.S. Environmental Protection Agency’s Empirical Kinetic Modeling Approach uses the concept of an air parcel to model smog formation. This model utilizes the concept of a “parcel” of relatively unpolluted air moving across an urban area in which it becomes contaminated with smog-forming gases.

When the upper boundary of this parcel is restricted to about 1000 meters by a temperature inversion and subjected to sunlight, the primary pollutants react to form smog in a system that involves photochemical reaction processes, transport, mixing, and dilution. As the hydrocarbons are consumed by photochemical oxidation processes in the air, and as nitrogen oxides are removed as nitrates and nitric acid (especially at nighttime), ozone levels reach a peak concentration at a time and place some distance removed from the source of pollutants.

The most visible manifestation of smog is the urban aerosol, which greatly reduces visibility in smoggy urban atmospheres. The urban aerosol also contains particle constituents that originate from processes other than smog formation. Oxidation of pollutant sulfur dioxide by the strongly oxidizing conditions of photochemical smog, $SO_2 + 1/2O_2 + H_2O \rightarrow H_2SO_4$ (overall process) produces sulfuric acid and sulfate particles. Nitric acid and nitrates are produced at night when sunlight is absent, a process that involves intermediate NO_3 radical:

$O_3 + NO_2 \rightarrow O_2 + NO_3$

$NO_3 + NO_2 + M$ (energy-absorbing third body) $\rightarrow N_2O_5 + M$

$N_2O_5 + H_2O \rightarrow 2HNO_3$

$HNO_3 + NH_3 \rightarrow NH_4NO_3$

As indicated by the last reaction above, ammonium salts are common constituents of urban aerosol particles; they tend to be particularly corrosive. Metals, which may contribute to the toxicity of urban aerosol particles and which may catalyze reactions on their surfaces, occur in the particles. Water is always present, even in low humidity atmospheres, and is usually present in urban aerosol particles.

Carbon and polycyclic aromatic hydrocarbons from partial combustion and diesel engine emissions are usually abundant constituents; elemental carbon is usually the particulate constituent most responsible for absorbing light in the urban aerosol. If the air parcel originates over the ocean, it contains sea salt particles consisting largely of NaCl, from which some of the chloride may be lost as volatile HCl by the action of less volatile strong acids produced by smog. This phenomenon is responsible for Na_2SO_4 and $NaNO_3$ found in the urban aerosol.

3.6.4.2 Greenhouse gases and global warming

Dear student, under this main content you learn about Greenhouse gases and global warming. Do you know some of the causes for Greenhouse gases and global warming, let warm up yourself with the following activities.

Learning task 3.6.4.2

a) Mention the major greenhouse gases
b) Mention the major effects of greenhouse gases
c) Explain how a greenhouse gases cause global warming
d) Explain how global warming can be minimized

Dear student, this section deals with infrared-absorbing trace gases (other than water vapor) in the atmosphere that contribute to global warming.

These gases produce a ***"greenhouse effect"*** by allowing incoming solar radiant energy to penetrate to the earth's surface while reabsorbing infrared radiation emanating from it. Levels of these "greenhouse gases" have increased at a rapid rate during recent decades and are continuing to do so. Concern over this phenomenon has intensified since about 1980.

In general, the 1990s continued the warming trend. For example; all months in 1998 except for October (which missed by about 0.1°C) set record monthly temperature highs, and 1998 was the warmest year on record as of 1999. In addition to being a scientific issue, greenhouse warming of the atmosphere has also become a major policy, political, and economic issue. The analysis of fossil ice provides evidence of past variations in temperature. One characteristic of ice that indicates the temperature at which it was deposited is conductivity, which declines with declining temperature of ice formation.

There are many uncertainties surrounding the issue of greenhouse warming. However, several things about the phenomenon are certain. It is known that CO_2 and other greenhouse gases, such as CH_4, absorb infrared radiation by which earth loses heat. The levels of these gases have increased markedly since about 1850 as nations have become industrialized and as forest lands and grasslands have been converted to agriculture.

The phenomenon has been the subject of much computer modeling. Most models predict global warming of at least 3.0° and up to 5.5°C occurring over a period of just a few decades. These estimates are sobering because they correspond to the approximate temperature increase since the last ice age 18,000 years past, which took place at a much slower pace of only about 1 or 2°C per 1,000 years. Such warming would have profound effects on rainfall, plant growth, and sea levels, which might rise as much as 0.5-1.5 meters.

Carbon dioxide is the gas most commonly thought of as a greenhouse gas; it is responsible for about half of the atmospheric heat retained by trace gases. It is produced primarily by the burning of fossil fuels, and deforestation accompanied by burning and biodegradation of biomass. On a molecule-for-molecule basis, methane, CH_4, is 20–30 times more effective in trapping heat than is CO_2. Other trace gases that contribute are chlorofluorocarbons and N_2O.

Both positive and negative feedback mechanisms may be involved in determining the rates at which carbon dioxide and methane build up in the atmosphere. Laboratory studies indicate that increased CO_2 levels in the atmosphere cause accelerated uptake of this gas by plants undergoing photosynthesis, which tends to slow the buildup of atmospheric CO_2. Given adequate rainfall, plants living in a warmer climate that would result from the greenhouse effect would grow faster and take up more CO_2. This could be an especially significant effect of forests, which have a high CO_2-fixing ability.

However, the projected rate of increase in carbon dioxide levels is so rapid that forests would lag behind in their ability to fix additional CO_2. Similarly, higher atmospheric CO_2 concentrations will result in accelerated sorption of the gas by oceans.

A concern with increased levels of CO_2 in the oceans is the lowering of ocean water pH that will result. Even though such an effect will be slight, of the order of one tenth to several tenths of a pH unit, it has the potential to strongly impact organisms that live in ocean water. Severe drought conditions resulting from climatic warming could cut down substantially on CO_2 uptake by plants. Warmer conditions would accelerate release of both CO_2 and CH_4 by microbial degradation of organic matter. Global warming might speed up the rates at which biodegradation adds these gases to the atmosphere.

It is certain that atmospheric CO_2 levels will continue to increase significantly. The degree to which this occurs depends upon future levels of CO_2 production and the fraction of that production that remains in the atmosphere. Given plausible projections of CO_2 production and a reasonable estimate that half of that amount will remain in the atmosphere, projections can be made that indicate that sometime during the middle part of the next century the concentration of this gas will reach 600 ppm in the atmosphere. This is well over twice the levels estimated for preindustrial times. Much less certain are the effects that this change will have on climate.

It is virtually impossible for the elaborate computer models used to estimate these effects to accurately take account of all variables, such as the degree and nature of cloud cover. Clouds both reflect incoming light radiation and absorb outgoing infrared radiation, with the former effect tending to predominate. The magnitudes of these effects depend upon the degree of cloud cover, brightness, altitude, and thickness. In the case of clouds, too, feedback phenomena occur; for example, warming induces formation of more clouds, which reflect more incoming energy.

Drought is one of the most serious problems that could arise from major climatic change resulting from greenhouse warming. Typically, a three-degree warming would be accompanied by a ten percent decrease in precipitation. Water shortages would be aggravated, not just from decreased rainfall, but from increased evaporation as well. Increased evaporation results in decreased runoff, thereby reducing water available for agricultural, municipal, and industrial use. Water shortages, in turn, lead to increased demand for irrigation and to the production of lower quality, higher salinity runoff water and wastewater.

A variety of other problems, some of them unforeseen as of now, could result from global warming. An example is the effect of warming on plant and animal pests —insects, weeds, diseases, and rodents. Many of these would certainly thrive much better under warmer conditions. Interestingly, another air pollutant, acid-rain-forming sulfur dioxide, may have a counteracting effect on greenhouse gases. This is because sulfur dioxide is oxidized in the atmosphere to sulfuric acid, forming a light-reflecting haze. Furthermore, the sulfuric acid and resulting sulfates act as condensation nuclei upon which atmospheric water vapor condenses, thereby increasing the extent, density, and brightness of light-reflecting cloud cover.

For example; sulfate aerosols are particularly effective in counteracting greenhouse warming in central Europe and the eastern United States during the summer. Some evidence of the effects of global warming may have been manifested by the powerful **El Niño phenomenon** that occurred during the late months of 1997 and early months of 1998. El Niño is the name given to the warming of surface water in the eastern Pacific Ocean that commonly takes place around Christmas time. The 1997/98 El Niño was particularly powerful and caused many marked weather phenomena. It also increased confidence in global climate models because of the generally accurate forecasts of its effect on climate.

3.6.4.3 The Nuclear winter

Dear student, under this main content you learn about the Nuclear winter. Do you know some of the causes for Nuclear winter, let warm up yourself with the following activities

Learning task 3.6.4.3

a) What is Nuclear winter
b) Explain the source of Nuclear winter
c) Describe the effects of Nuclear winter
d) Explain how global warming can be minimized

Dear student, Nuclear winter is a term used to describe a catastrophic atmospheric effect that might occur after a massive exchange of nuclear firepower between major powers. The heat from the nuclear blasts and from resulting fires would cause powerful updrafts carrying sooty combustion products to stratospheric regions. This would result in several years of much lower temperatures and freezing temperatures even during summertime.

There are several reasons for such an effect. First of all, the highly absorbent, largely black particulate matter would absorb solar radiation high in the atmosphere so that it would not reach earth's surface. ***Cooling would also occur from a phenomenon opposite to that of the greenhouse effect***. That is because outgoing infrared radiation from particles high in the atmosphere would have to penetrate relatively much less of the atmosphere and, therefore, would be exposed to much less infrared-absorbing water vapor and carbon dioxide gas.

This would deprive the lower atmosphere of the warming effect of outgoing infrared radiation and would mean that less infrared would be re-radiated from the atmosphere back to earth's surface. The cooling would also inhibit the evaporation of water, thereby reducing the amount of infrared-absorbing water vapor in the atmosphere and slowing the process by which particulate matter is scavenged from the atmosphere by rain.

For example, conditions similar to those of a nuclear winter occurred in 1816, "the year without a summer," following the amazingly massive Tambora, Indonesia volcanic explosion of 1815. Brutally cold years around 210 B.C. that followed a similar volcanic incident in Iceland were recorded in ancient China. The Hiroshima fission bomb had the explosive force of 12 kilotons of TNT explosive. Its blast, fireball, and instantaneous emissions of neutrons and gamma radiation, followed by fires and exposure to radioactive fission products, killed about 100,000 people and destroyed the city on which it was dropped.

As a result, unimaginable quantities of soot from the partial combustion of wood, plastics, paving asphalt, petroleum, forests, and other combustibles would be carried to the stratosphere. At such high altitudes, tropospheric removal mechanisms for particles are not effective because there is not enough water in the stratosphere to produce rainfall to wash particles from the air, and convection processes are very limited.

3.6.4.4 Acid rain

Dear student, under this main content you learn about the Acid rain. Do you know some of the causes for Acid rain? Let warm up yourself with the following activities

Learning task 3.6.4.4

a) What is Acid rain?
b) Explain the source of Acid rain.
c) Describe the effects of Acid rain.
d) Explain whether acid rain is local, regional or global pollution problem
e) Explain how Acid rain can be minimized

As discussed in this chapter, much of the sulfur and nitrogen oxides entering the atmosphere are converted to sulfuric and nitric acids, respectively. When combined with hydrochloric acid arising from hydrogen chloride emissions, these acids cause acidic precipitation (acid rain) that is now a major pollution problem in some areas. Headwater streams and high-altitude lakes are especially susceptible to the effects of acid rain and may sustain loss of fish and other aquatic life.
Other effects of acid rain include reductions in forest and crop productivity; leaching of nutrient cations and heavy metals from soils, rocks, and the sediments of lakes and streams; dissolution of metals such as lead and copper from water distribution pipes; corrosion of exposed metal; and dissolution of the surfaces of limestone buildings and monuments. As a result of its widespread distribution and effects, acid rain is an air pollutant that may pose a threat to the global atmosphere.

Precipitation made acidic by the presence of acids stronger than CO_2 (*aq*) is commonly called acid rain; the term applies to all kinds of acidic aqueous precipitation, including fog, dew, snow, and sleet. In a more general sense, acid deposition refers to the deposition on the earth’s surface of aqueous acids, acid gases (such as SO_2), and acidic salts (such as NH_4HSO_4). According to this definition, deposition in solution form is *acid precipitation*, and deposition of dry gases and compounds is *dry deposition*. Although carbon dioxide is present at higher levels in the atmosphere, sulfur dioxide, SO_2, contributes more to the acidity of precipitation for two reasons.

The first of these is that sulfur dioxide is significantly more soluble in water than is carbon dioxide, is more than four orders of magnitude higher than the value of 4.45×10^{-7} for CO_2. Although acid rain can originate from the direct emission of strong acids, such as HCl gas or sulfuric acid mist, most of it is a secondary air pollutant produced by the atmospheric oxidation of acid-forming gases such as the following:

$SO_2 + 1/2O_2 + H_2O$; Overall reaction consisting of several steps $\{2H^+ + SO_4^{2-\}}$ $^{(}$*aq*)

$2NO_2 + 1/2O_2 + H_2O$; Overall reaction consisting of several steps $2\{H^+ + NO_3^{\ -}\}$ (*aq*)

Chemical reactions such as these play a dominant role in determining the nature, transport, and fate of acid precipitation. As the result of such reactions the chemical properties (acidity, ability to react with other substances) and physical properties (volatility, solubility) of acidic atmospheric pollutants are altered drastically. **For example**, even the small fraction of NO that does dissolve in water does not react significantly. However, its ultimate oxidation product, HNO_3, though volatile, is highly water-soluble, strongly acidic, and very reactive with other materials. Therefore, it tends to be removed readily from the atmosphere and to do a great deal of harm to plants, corrodible materials, and other things that it contacts.

Although emissions from industrial operations and fossil fuel combustion are the major sources of acid-forming gases, acid rain has also been encountered in areas far from such sources. This is due in part to the fact that acid-forming gases are oxidized to acidic constituents and deposited over several days, during which time the air mass containing the gas may have moved as much as several thousand kilometers. It is likely that the burning of biomass, such as is employed in “slash-and-burn” agriculture evolves the gases that lead to acid formation in more remote areas. In arid regions, dry acid gases or acids sorbed to particles may be deposited with effects similar to those of acid rain deposition.

Acid rain spreads out over areas of several hundred to several thousand kilometers. This classifies it as a ***regional air pollution problem*** compared to a *local* air pollution problem for smog and a *global* one for ozone-destroying chlorofluorocarbons and greenhouse gases. Other examples of regional air pollution problems are those caused by soot, smoke, and fly ash from combustion sources and fires (forest fires). Nuclear fallout from weapons testing or from reactor fires (of which, fortunately, there has been only one major one to date—the one at Chernobyl in the Soviet Union) may also be regarded as a regional phenomenon.

Dear student, the major effects of acid rain is summarized as follows:

- Direct phytotoxicity to plants from excessive acid concentrations.
- Phytotoxicity from acid-forming gases, particularly SO_2 and NO_2 that accompany acid rain
- Indirect phytotoxicity, such as from Al^{3+} liberated from soil
- Destruction of sensitive forests
- Respiratory effects on humans and other animals
- Acidification of lake water with toxic effects to Lake Flora and fauna, especially fish fingerlings
- Corrosion of exposed structures, electrical relays, equipment, and ornamental materials. Because of the effect of hydrogen ion, $2H^+ + CaCO_3(s) \rightarrow Ca^{2+} + CO_2\ (g) + H_2O$ limestone, $CaCO_3$, is especially susceptible to damage from acid rain
- Associated effects, such as reduction of visibility by sulfate aerosols and the influence of sulfate aerosols on physical and optical properties of clouds. A significant association exists between acidic sulfate in the atmosphere and haziness. Soil sensitivity to acid precipitation can be estimated from cation exchange capacity.

3.6.4.5 What is to be done?

Dear student, under this main content you learn about the possible solution that can be used to keep the global atmosphere from danger. Do you know some possible solution that can be used to keep the global atmosphere from danger? Let warm up yourself with the following activities

Learning task 3.6.4.5

a) Explain the measures to be taken to keep the global atmosphere from danger
b) Mention some of the International protocols and treaty that were contributed for keeping the atmosphere from danger

Dear student, of all environmental hazards, there is little doubt that major disruptions in the atmosphere and climate have the greatest potential for catastrophic and irreversible environmental damage. If levels of greenhouse gases and reactive trace gases continue to increase at present rates, major environmental effects are virtually certain. On a hopeful note, the bulk of these emissions arise from industrialized nations which, in principle, can apply the resources needed to reduce them substantially.

The best example to date has been the 1987 “Montreal Protocol on substances that Deplete the Ozone Layer,” an international treaty through which a large number of nations agreed to cut chlorofluorocarbon emissions by 50% by the year 2000. This agreement and subsequent ones, particularly the Copenhagen Amendment of 1992, may pave the way for more encompassing agreements covering carbon dioxide and other trace gases.

Therefore, what is to be done? First of all, it is important to keep in mind that the atmosphere has a strong ability to cleanse itself of pollutant species. The measures to be taken in dealing with this problem fall into ***the three following categories:***
i) Minimization by reducing emissions of greenhouse gases, switching to alternate energy sources, increasing energy conservation, and reversing deforestation. It is especially sensible to use measures that have major benefits in addition to reduction of greenhouse warming. Such measures include, as examples, reforestation, and restoration of grasslands, increased energy conservation, and a massive shift to solar energy sources.

ii) Counteracting measures, such as injecting light-reflecting particles into the upper atmosphere.
iii) Adaptation, particularly through increased efficiency and flexibility of the distribution and use of water, which might be in very short supply in many parts of the world as a consequence of greenhouse warming. Important examples are implementation of more efficient irrigation practices and changes in agriculture to grow crops that require less irrigation. Emphasis on adaptation is favored by those who contend that not enough is known about the types and severity of global warming to justify massive expenditures on minimization and counteractive measures.

In any case, adaptation will certainly have to be employed as a means of coping with global warming. Potentially, tax strategy can be very effective in reducing use of carbonaceous fuels and greenhouse CO_2 emissions. This is the rationale behind the carbon tax, which is tied with the carbon content of various fuels. Another option is to dispose of carbon dioxide to a sink other than the atmosphere. The most obvious such sink is the ocean; other possibilities are deep subterranean aquifers and exhausted oil and gas wells.

The **"tie-in strategy"** has been proposed as a sensible approach to dealing with the kinds of global environmental problems discussed in this chapter. This approach was first enunciated in 1980. It advocates taking measures consisting of "high leverage actions" which are designed to prevent problems from occurring and which have substantial merit even if the major problems that they are designed to avoid do not materialize. An example is implementation of environmentally sound substitutes for fossil fuels to lower atmospheric CO_2 output and prevent greenhouse warming.

Definite economic and political benefits would also accrue from lessened dependence on uncertain, volatile petroleum supplies. Increased energy efficiency would diminish both greenhouse gas and acid rain production, while lowering costs of production and reducing the need for expensive and environmentally disruptive new power plants.

Chapter Summary

- The atmosphere consists of the thin layer of mixed gases covering the earth's surface
- The most significant feature of atmospheric chemistry is the occurrence of photochemical reactions resulting from the absorption by molecules of light photons, designated *h*v.
- Oxides of carbon, sulfur, and nitrogen are important constituents of the atmosphere and are pollutants at higher levels.
- The most abundant hydrocarbon in the atmosphere is methane, CH_4, released from underground sources as natural gas and produced by the fermentation of organic matter
- The atmosphere is a protective blanket which nurtures life on the Earth and protects it from the hostile environment of outer space.
- The atmosphere is the source of carbon dioxide for plant photosynthesis and of oxygen for respiration.
- It provides the nitrogen that nitrogen-fixing bacteria and ammonia-manufacturing plants use to produce chemically-bound nitrogen, an essential component of life molecules
- Atmospheric science deals with the movement of air masses in the atmosphere, atmospheric heat balance, and atmospheric chemical composition and reactions.
- In order to understand atmospheric chemistry and air pollution, it is important to have an overall appreciation of the atmosphere, its composition, and physical characteristics.
- The characteristics of the atmosphere vary widely with altitude, time (season), location (latitude), and even solar activity.
- At very high altitudes, normally reactive species such as atomic oxygen, O, persist for long periods of time. That occurs because the pressure is very low at these altitudes such that the distance traveled by a reactive species
- The atmosphere is stratified on the basis of the temperature/density relationships resulting from interactions between physical and photochemical (light-induced chemical phenomena) processes in air; these layers are Troposphere, Stratosphere, Mesosphere, and Thermosphere

- Atmospheric chemistry involves the unpolluted atmosphere, highly polluted atmospheres, and a wide range of gradations in between.
- Photochemical reactions, which are induced by intense solar radiation, play a very important role in determining the nature and ultimate fate of a chemical species in the atmosphere.
- The reactions that occur following absorption of a photon of light to produce an electronically excited species are largely determined by the way in which the excited species loses its excess energy.
- The main reactions in troposphere takes place are: Acid – base reactions, photochemical smog formation, acid rain formation , redox reaction, complexation reaction , precipitation and others
- Stratospheric ozone, O_3, serves as a shield to absorb harmful ultraviolet radiation in the stratosphere, protecting living beings on the earth from the effects of excessive amounts of such radiation
- The major cause in ozone depletion consists of chlorofluorocarbon (CFC) compounds, commonly known as “Freons.”
- The most prominent instance of ozone layer destruction is the so-called *“Antarctic ozone hole”* that has shown up in recent years.
- Cold T^o is responsible for the formation of Polar Stratospheric Cloud (PSC) and Polar winter are responsible for Polar Vortex. Isolation of polar vortex results for growth of PSC sink to lower altitudes and gave rise for Spring sunlight
- But in the polar stratosphere, the low sun elevation results in essentially no photo–dissociation of O_2. O_3 destruction in the Antarctica couldn’t be explained by ClOx destruction mechanism alone Stratospheric O_3 destruction reactions
- CH_4 is stable in the troposphere, however, if it crosses the tropopause it under goes oxidation to give CO_2 and H_2O that subsequently undergoes photo-ionization to generate OH and H that degrades O_3
- HO_x, ClO_x & NO_x are the cause for ozone depletion in the stratosphere
- The oxygen cycle is critically important in atmospheric chemistry, geochemical transformations, and life processes.

- Thermosphere is one of the stratification of atmosphere. It is rich in Oxygen atom; hence two types of reactions are common in Thermosphere; these are photo-dissociation and photo-ionization
- Atmospheric (air) pollution occurs when the concentration of certain substances become high enough to toxify the atmospheric environment.
- The main atmospheric pollutants are: Particles in the atmosphere, Gaseous inorganic pollutants, Gaseous organic pollutants, Photochemical smog, Green house and Global warming, the Nuclear winter, Acid rain
- Particles in the atmosphere, which range in size from about one-half millimeter down to molecular dimensions, are made up of an amazing variety of materials and discrete objects that may consist of either solids or liquid droplets.
- Particles in the atmosphere can be formed by both physical and Chemical processes
- Particles can be formed from water, inorganic substances, organic substances, toxic heavy metals, Radioactive particulates
- Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility.
- The removal of particulate matter from gas streams is the most widely practiced means of air pollution control. A number of devices have been developed for this purpose which differs widely in effectiveness, complexity, and cost
- A number of gaseous inorganic pollutants enter the atmosphere as the result of human activities. Those added in the greatest quantities are CO, SO_2, NO, and NO_2 (these quantities are relatively small compared to the amount of CO_2 in the atmosphere).
- Other inorganic pollutant gases include NH_3, N_2O, N_2O_5, H_2S, Cl_2, HCl, and HF. substantial quantities of some of these gases are added to the atmosphere each year by human activities.
- Organic pollutants may have a strong effect upon atmospheric quality. The effects of organic pollutants in the atmosphere may be divided into two major categories.
- The first consists of direct effects, such as cancer caused by exposure to vinyl chloride.
- The second is the formation of secondary pollutants, especially photochemical smog. In the case of pollutant hydrocarbons in the atmosphere, the latter is the more important

effect. In some localized situations, particularly the workplace, direct effects of organic air pollutants may be equally important.

- Organic contaminants are lost from the atmosphere by a number of routes. These include dissolution in precipitation (rainwater), dry deposition, photochemical reactions, formation of and incorporation into particulate matter, and uptake by plants.
- Organohalides consist of halogen-substituted hydrocarbon molecules, each of which contains at least one atom of F, Cl, Br, or I.
- They may be saturated (alkyl halides), unsaturated (alkenyl halides), or aryl (aryl halides).
- The organohalides of environmental and toxicological concern exhibit a wide range of physical and chemical properties.
- Although most organohalide compounds of pollution concern are from anthropogenic sources, it is now known that a large variety of such compounds are generated by organisms, particularly those in marine environments.
- Anthropogenic change in the atmosphere; There is a very strong connection between life forms on earth and the nature of earth's climate, which determines its suitability for life.
- Major effects have been the following:
    - ✓ Increased acidity in the atmosphere
    - ✓ Production of pollutant oxidants in localized areas of the lower troposphere
    - ✓ Elevated levels of infrared-absorbing gases (greenhouse gases)
    - ✓ Threats to the ultraviolet-filtering ozone layer in the stratosphere
    - ✓ Increased corrosion of materials induced by atmospheric pollutants
- Photochemical smog is a major air pollution phenomenon. It occurs in urban areas where the combination of pollution-forming emissions and appropriate atmospheric conditions are right for its formation.
- Greenhouse gases produce a *"greenhouse effect"* by allowing incoming solar radiant energy to penetrate to the earth's surface while reabsorbing infrared radiation emanating from it.
- In addition to being a scientific issue, greenhouse warming of the atmosphere has also become a major policy, political, and economic issue.
- Greenhouse gases are the cause for global warming

- Nuclear winter is a term used to describe a catastrophic atmospheric effect that might occur after a massive exchange of nuclear firepower between major powers.
- The heat from the nuclear blasts and from resulting fires would cause powerful updrafts carrying sooty combustion products to stratospheric regions.
- This would result in several years of much lower temperatures and freezing temperatures even during summertime.
- Cooling would also occur from a phenomenon opposite to that of the greenhouse effect.
- Acid rain is acidic precipitation that is caused by much of the sulfur and nitrogen oxides entering the atmosphere are converted to sulfuric and nitric acids, that is now a major pollution problem in some areas.
- Acid rain spreads out over areas of several hundred to several thousand kilometers.
- This classifies it as a *regional air pollution problem* compared to a *local* air pollution problem for smog and a *global* one for ozone-destroying chlorofluorocarbons and greenhouse gases.
- The measures to be taken to keep the global atmosphere from danger are:
  - ✓ **Minimization** by reducing emissions of greenhouse gases, switching to alternate energy sources, increasing energy conservation, and reversing deforestation.
  - ✓ **Counteracting measures**, such as injecting light-reflecting particles into the upper atmosphere.
  - ✓ **Adaptation**, particularly through increased efficiency and flexibility of the distribution and use of water, which might be in very short supply in many parts of the world as a consequence of greenhouse warming.

Self test exercises

1. What phenomenon is responsible for the temperature maximum at the boundary of the stratosphere and the mesosphere?
2. Describe the strata of atmosphere
3. What function does a third body serve in an atmospheric chemical reaction?
4. Of the gases neon, sulfur dioxide, helium, oxygen, and nitrogen, which shows the most variation in its atmospheric concentration?
5. What is the distinction between chemiluminescence and luminescence caused when light is absorbed by a molecule or atom?
6. State two factors that make the stratosphere particularly important in terms of acting as a region where atmospheric trace contaminants are converted to other, chemically less reactive, forms.
7. What two chemical species are most generally responsible for the removal of hydroxyl radical from the unpolluted troposphere.
8. What is the distinction between the symbols * and • in discussing chemically active species in the atmosphere?
9. O_3 is one component of the atmosphere. Describe all its reactions and the functions and effects in the atmosphere.
10. How does the extreme cold of stratospheric clouds in Antarctic regions contribute to the Antarctic ozone hole?
11. What type of process results in the formation of very small aerosol particles?
12. . What is the settling velocity of a particle having a Stokes diameter of 10 µm and a density of 1 g/cm^3 in air at 1.00 atm pressure and 0°C temperature? (The viscosity of air at 0°C is 170.8 micropoise. The density of air under these conditions is 1.29 g/L.)
13. How do modern transportation problems contribute to the kinds of atmospheric problems?

14. Some atmospheric chemical reactions are abstraction reactions and others are addition reactions. Which of these applies to the reaction of hydroxyl radical with propane? With propene (propylene)?
15. How does the oxidizing nature of ozone from smog contribute to the damage that it does to cell membranes?
16. What is the main species responsible for the oxidation of NO to NO_2 in a smoggy atmosphere?
17. What the distinction between reactivity and instability is as applied to some of the chemically active species in a smog-forming atmosphere?
18. Why are hydrocarbon emissions from uncontrolled automobile exhaust particularly reactive?
19. In the sequence of reactions leading to the oxidation of hydrocarbons in the atmosphere, what is the first stable class of compounds generally produced?
20. . Give a sequence of reactions leading to the formation of acetaldehyde from ethane starting with the reaction of hydroxyl radical.
21. What important photochemical property do carbonyl compounds share with NO_2?
22. Which unstable, reactive species is responsible for the removal of CO from the atmosphere?
23. In what major respect is NO_2 a more significant species than SO_2 in terms of participation in atmospheric chemical reactions?
24. Analysis of particulate matter collected in the atmosphere near seashore shows considerably more Na than Cl on a molar basis. What does this indicate?
25. What is the rationale for classifying most acid rain as a secondary pollutant?
26. What is the basis for “nuclear winter”?
27. What is meant by a “tie-in strategy”?

Chapter
4

SOIL CHEMISTRY

Unit Introduction

Dear student, this chapter deals with Soil Chemistry. It deals with soil and agriculture, nature and compositions of soil, nutrients in soil, reactions in soil and wastes and pollutants in soil which provide you the basic concept of soil Chemistry.

Learning objective of the unit

Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:-

- Define terms such as soil and nutrient
- Explain the nature and the composition of soil in the environment
- Discuss about organic and inorganic nutrients in the soil
- Discuss the reaction that takes place in the soil
- Explain the wastes and pollutants in the soil

4.1. Soil and Agriculture

Dear student under this main content you learn about soil and the agricultural activities in the soil. Do you know the effect of agricultural practices upon the soil? Warm up yourself with the following activities.

Learning task 4.1

a) Define agriculture
b) Define soil
c) Describe the effect of Agricultural practices in the soil

Soil and agricultural practices are strongly tied with the environment. Cultivation of land and agricultural practices can influence both the atmosphere and the hydrosphere. Although this chapter deals primarily with soil, the topic of agriculture in general is introduced for perspective.

Agriculture

Dear student, can you define agriculture?

Agriculture is the production of food by growing crops and livestock that provides for the most basic of human needs. No other industry impacts as much as agriculture does on the environment. Agriculture is absolutely essential to the maintenance of the huge human populations now on earth. The displacement of native plants, destruction of wildlife habitat, erosion, pesticide pollution and other environmental aspects of agriculture have enormous potential for environmental damage. Survival of humankind on earth demands that agricultural practice become as environmentally friendly as possible. On the other hand, growth of domestic crops removes (at least temporarily) greenhouse gas carbon dioxide from the atmosphere and provides potential sources of renewable resources of energy and fiber that can substitute for petroleum-derived fuels and materials.

Soil

Soil, consists of a finely divided layer of weathered minerals and organic matter upon which plants grow. It is the most fundamental requirement for agriculture. To humans and most terrestrial organisms, soil is the most important part of the geosphere. Though only a tissue-thin layer compared with the earth’s total diameter, soil is the medium that produces most of the food required by most living things. Good soil and a climate conducive to its productivity is the most valuable asset a nation can have. In addition being the site of most food production, soil is the receptor of large quantities of pollutants, such as particulate matter from power plant smokestacks, fertilizers, pesticides and some other materials applied to soil often contribute to water and air pollution.

Therefore, soil is a key component of environmental chemical cycles. Soils are formed by the weathering of parent rocks as the result of interactive geological, hydrological and biological processes. Soils are porous and are vertically stratified into horizons as the result of downward-percolating water and biological processes, including the production and decay of biomass. Soils are open systems that undergo continual exchange of matter and energy with the atmosphere, hydrosphere, and biosphere.

4.2. Nature and composition of soil

Dear student under this main content you learn about nature and compositions of soil. Do you know the nature and composition of the soil? Warm up yourself with the following activities.

Learning task 4.2

a) Explain the relationship between the nature and composition of soil
b) List the organic constituents of the soil
c) List the inorganic constituents of the soil
d) Describe how the composition affects the nature of the soil

Soil is a variable mixture of minerals, organic matter, and water capable of supporting plant life on the earth’s surface. It is the final product of the weathering action of physical, chemical and biological processes on rocks, which largely produces clay minerals. The organic portion of soil consists of plant biomass in various stages of decay. High populations of bacteria, fungi, and animals such as earthworms can be found in soil. Soil contains air spaces and generally has a loose texture.

The solid fraction of typical productive soil is approximately 5% organic matter and 95% inorganic matter. Some soils, such as peat soils, may contain as much as 95% organic material. Other soils contain as little as 1% organic matter. Typical soils exhibit distinctive layers with increasing depth. These layers are called horizons. Horizons form as the result of complex interactions among processes that occur during weathering. Rainwater percolating through soil carries dissolved and colloidal solids to lower horizons where they are deposited. A biological process, such as bacterial decay of residual plant biomass, produces slightly acidic CO_2, organic acids and complexing compounds that are carried by rainwater to lower horizons, where they interact with clays and other minerals, altering the properties of the minerals.

The top layer of soil, typically several inches in thickness, is known as the A horizon, or **topsoil**. This is the layer of maximum biological activity in the soil and 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.

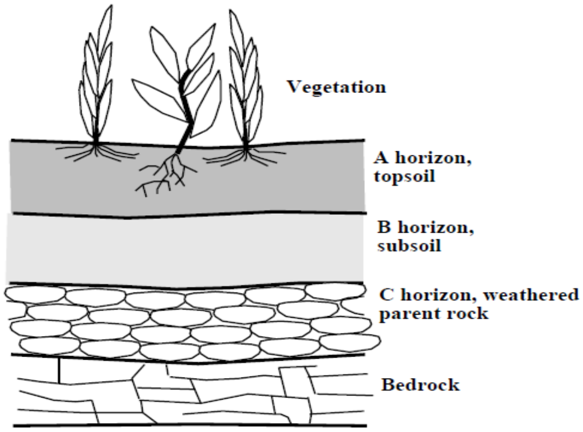


Figure 4.2 Soil profile showing soil horizons.

Soils exhibit a large variety of characteristics that are used for their classification for various purposes, including crop production, road construction and waste disposal. The parent rocks from which soils are formed obviously play a strong role in determining the composition of soils. Other soil characteristics include strength, workability, soil particle size, permeability and degree of maturity. One of the more important classes of productive soils is the pod-zol type of soil formed under relatively high rainfall conditions in temperate zones of the world. These generally rich soils tend to be acidic (pH 3.5–4.5) such that alkali and alkaline earth metals and, to a lesser extent aluminum and iron, are leached from their A horizons, leaving kaolinite as the predominant clay mineral.

At somewhat higher pH in the B horizons, hydrated iron oxides and clays are redeposited. From the engineering standpoint, especially, the mechanical properties of soil are emphasized. These properties, which may have important environmental implications in areas such as waste disposal, are largely determined by particle size. According to the United Classification System (UCS), the four major categories of soil particle sizes are the following: **Gravels** (2–60 mm) > **sands** (0.06–2 mm) > **silts** (0.06-0.006 mm) > **clays** (less than 0.002 mm).

4.2.1. Water and Air in Soil

Is water and air the composition of the soil?

Large quantities of water are required for the production of most plant materials. For example, several hundred kilo grams of water are required to produce one kilogram of dry hay. Water is part of the three-phase, solid-liquid-gas system making up soil. It is the basic transport medium for carrying essential plant nutrients from solid soil particles into plant roots and to the farthest reaches of the plant's leaf structure. The water enters the atmosphere from the plant's leaves, a process called **transpiration**. Normally, because of the small size of soil particles and the presence of small capillaries and pores in the soil, the water phase is not totally independent of soil solid matter.

The availability of water to plants is governed by gradients arising from capillary and gravitational forces. The availability of nutrient solutes in water depends upon concentration gradients and electrical potential gradients. Water present in larger spaces in soil is relatively more available to plants and readily drains away. Water held in smaller pores or between the unit layers of clay particles is held much more strongly. Soils high in organic matter may hold appreciably more water than other soils, but it is relatively less available to plants because of physical and chemical sorption of the water by the organic matter.

There is a very strong interaction between clays and water in soil. Water is absorbed on the surfaces of clay particles. Because of the high surface-volume ratio of colloidal clay particles, a great deal of water can be bound in this manner. Water is also held between the unit layers of the expanding clays, such as the montmorillonite clays.

As soil becomes waterlogged (water-saturated) it undergoes drastic changes in physical, chemical, and biological properties. Oxygen in such soil is rapidly used up by the respiration of microorganisms that degrade soil organic matter. In such soils, the bonds holding soil colloidal particles together are broken, which causes disruption of soil structure. Thus, the excess water in such soils is detrimental to plant growth, and the soil does not contain the air required by most plant roots. Most useful crops, with the notable exception of rice, cannot grow on waterlogged soils.

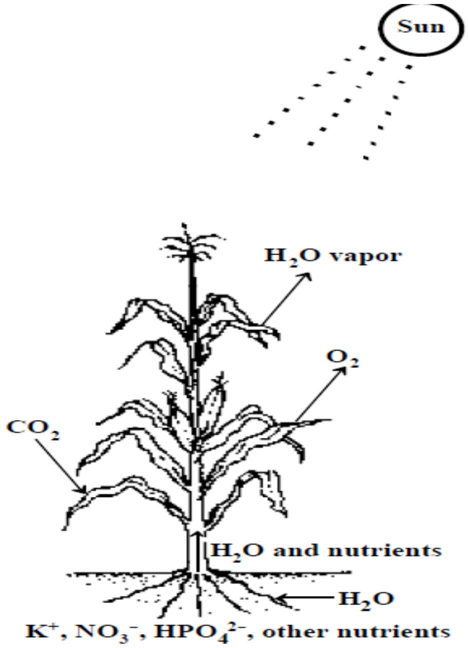


Figure 4.2.1 Plants transport water from the soil to the atmosphere by transpiration.

Nutrients are also carried from the soil to the plant extremities by this process. Plants remove CO_2 from the atmosphere and add O_2 by photosynthesis. The reverse occurs during plant respiration.

One of the most marked chemical effects of water logging is a reduction of pE by the action of organic reducing agents acting through bacterial catalysts. Thus, the redox condition of the soil becomes much more reducing, and the soil pE may drop from that of water in equilibrium with air (+ 13.6 at pH 7) to 1 or less.

One of the more significant results of this change is the mobilization of iron and manganese as soluble iron (II) and manganese (II) through reduction of their insoluble higher oxides:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

$$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$$

Although soluble manganese generally is found in soil as Mn^{2+} ion, soluble iron(II) frequently occurs as negatively charged iron-organic chelates. Strong chelation of iron (II) by soil fulvic acids apparently enables reduction of iron (III) oxides at more positive pE values than would otherwise be possible. This causes an upward shift in the Fe (II) -Fe $(OH)_3$ boundary. Some soluble metal ions such as Fe^{2+} and Mn^{2+} are toxic to plants at high levels .Their oxidation to insoluble oxides may cause formation of deposits of $Fe_2O_3$and MnO_2, which clog tile drains in fields.

Roughly 35% of the volume of typical soil is composed of air-filled pores. Whereas the normal dry atmosphere at sea level contains 21% O_2 and 0.03% CO_2 by volume, these percentages may be quite different in soil air because of the decay of organic matter:

$$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$$

This process consumes oxygen and produces CO_2. As a result, the oxygen content of air in soil may be as low as 15%, and the carbon dioxide content may be several percent. Thus, the decay of organic matter in soil increases the equilibrium level of dissolved CO_2 in groundwater. This lowers the pH and contributes to weathering of carbonate minerals, particularly calcium carbonate. CO_2 also shifts the equilibrium of the process by which roots absorb metal ions from soil.

4.2.2 The Inorganic Components of Soil

Dear student, do you know the inorganic components of the soil?

The weathering of parent rocks and minerals to form the inorganic soil components results ultimately in the formation of inorganic colloids. These colloids are repositories of water and plant nutrients, which may be made available to plants as needed. Inorganic soil colloids often absorb toxic substances in soil, thus playing a role in detoxification of substances that otherwise would harm plants. The abundance and nature of inorganic colloidal material in soil are obviously important factors in determining soil productivity.

The uptake of plant nutrients by roots often involves complex interactions with the water and inorganic phases. For example, a nutrient held by inorganic colloidal material has to traverse the mineral/water interface and then the water/root interface. This process is often strongly influenced by the ionic structure of soil inorganic matter.

The most common elements in the earth's crust are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. Therefore, minerals composed of these elements particularly silicon and oxygen constitute most of the mineral fraction of the soil. Common soil mineral constituents are finely divided **quartz** (SiO_2), **orthoclase** ($KAlSi_3O_8$), **albite** ($NaAlSi_3O_8$),**epidote** ($4CaO\bullet 3(AlFe)_2O_3\bullet 6SiO_2\bullet H_2O$),**goethite** ($FeO(OH)$), **magnetite** ($Fe_3O_4$), **calcium and magnesium carbonates** ($CaCO_3$, $CaCO_3\bullet MgCO_3$), and oxides of manganese and titanium.

4.2.3 The organic components of Soil

Dear student, do you know the organic components of the soil?

Though typically composing less than 5% of a productive soil, organic matter largely determines soil productivity. It serves as a source of food for micro-organisms, undergoes chemical reactions such as ion exchange, and influences the physical properties of soil. Some organic compounds even contribute to the weathering of mineral matter, the process by which soil is formed. For example, $C_2O_4^{2-}$, oxalate ion, produced as a soil fungi metabolite, occurs in soil as the calcium salts whewellite and weddelite.

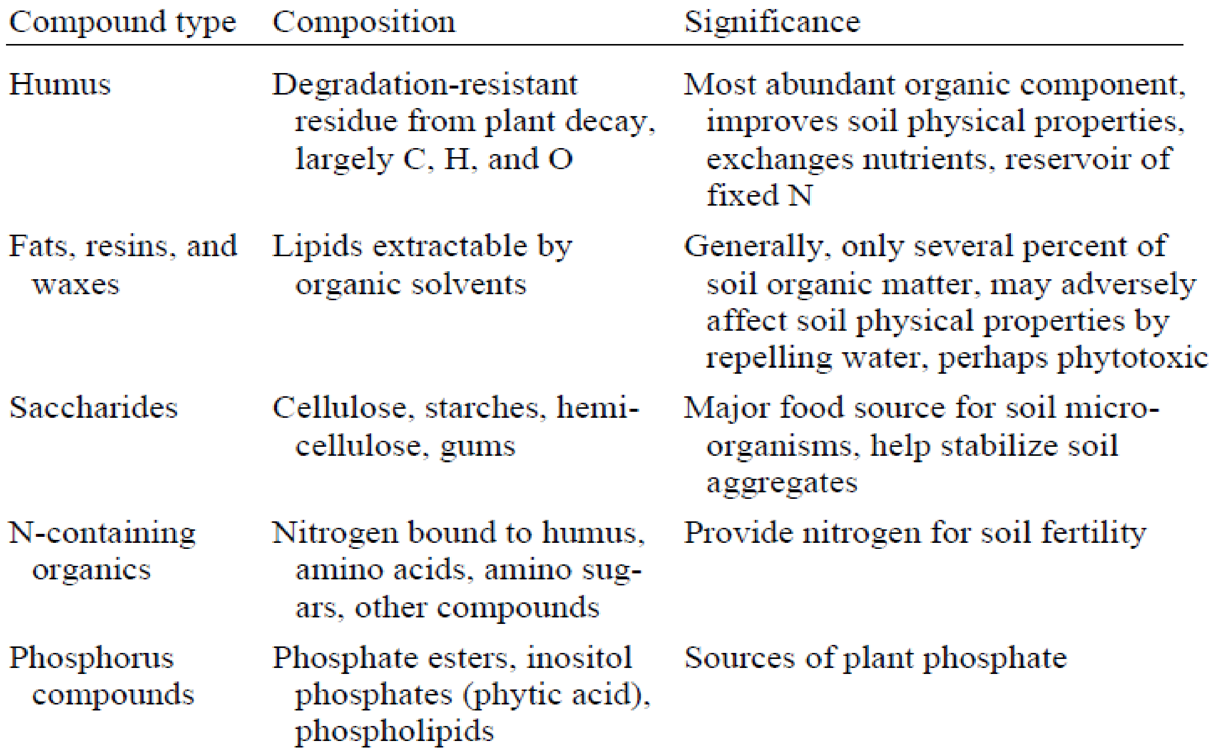
Oxalate in soil water dissolves minerals, thus speeding the weathering process and increasing the availability of nutrient ion species. This weathering process involves oxalate complexation of iron or aluminum in minerals, represented by the following reaction in which M is Al or Fe.

$$3H^{+} + M(OH)_3(s) + 2CaC_2O_4(s) \rightarrow M(C_2O_4)_2^{-}(aq) + 2Ca^{2+}(aq) + 3H_2O$$

Some soil fungi produce citric acid and other chelating organic acids that react with silicate minerals and release potassium and other nutrient metal ions held by these minerals. The strong chelating agent 2- ketogluconic acid is produced by some soil bacteria. By solubilizing metal ions, it may contribute to the weathering of minerals. It may also be involved in the release of phosphate from insoluble phosphate compounds.

Biologically active components of the organic soil fraction include polysaccharides, amino sugars, nucleotides, and organic sulfur and phosphorus compounds. Humus, a water-insoluble material that biodegrades very slowly, makes up the bulk of soil organic matter. The organic compounds in soil are summarized in the table below.

Table 4.2.3 Major Classes of Organic Compounds in Soil



Compound type	Composition	Significance
Humus	Degradation-resistant residue from plant decay, largely C, H, and O	Most abundant organic component, improves soil physical properties, exchanges nutrients, reservoir of fixed N
Fats, resins, and waxes	Lipids extractable by organic solvents	Generally, only several percent of soil organic matter, may adversely affect soil physical properties by repelling water, perhaps phytotoxic
Saccharides	Cellulose, starches, hemi-cellulose, gums	Major food source for soil micro-organisms, help stabilize soil aggregates
N-containing organics	Nitrogen bound to humus, amino acids, amino sugars, other compounds	Provide nitrogen for soil fertility
Phosphorus compounds	Phosphate esters, inositol phosphates (phytic acid), phospholipids	Sources of plant phosphate

The accumulation of organic matter in soil is strongly influenced by temperature and by the availability of oxygen. Since the rate of biodegradation decreases with decreasing temperature, organic matter does not degrade rapidly in colder climates and tends to build up in soil. In water and in waterlogged soils, decaying vegetation does not have easy access to oxygen, and organic matter accumulates. The organic content may reach 90% in areas where plants grow and decay in soil saturated with water.

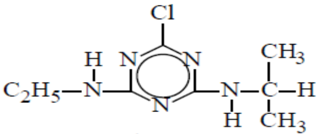
The presence of naturally occurring poly-nuclear aromatic (PAH) compounds is an interesting feature of soil organic matter. PAH compounds found in soil include fluoranthene, pyrene, and chrysene. PAH compounds in soil result in part from combustion from both natural sources (grass fires) and pollutant sources. Terpenes also occur in soil organic matter. Extraction of soil with ether and alcohol yields the pigments β-carotene, chlorophyll, and xanthophyll.

Soil humus is by far the most significant. Humus, composed of a base-soluble fraction called **humic** and **fulvic acids**, and an **insoluble fraction** called **humin**, is the residue left when bacteria and fungi biodegrade plant material. The bulk of plant biomass consists of relatively degradable cellulose and degradation-resistant lignin, which is a polymeric substance with higher carbon content than cellulose. Among lignin's prominent chemical components are aromatic rings connected by alkyl chains, methoxyl groups, and hydroxyl groups. These structural artifacts occur in soil humus and give it many of its characteristic properties. The process by which humus is formed is called **humification**.

Soil humus is similar to its lignin precursors, but has more carboxylic acid groups. Part of each molecule of humic substance is non-polar and hydrophobic, and part is polar and hydrophilic. Such molecules are called amphiphiles, and they form micelles, in which the non-polar parts compose the inside of small colloidal particles and the polar functional groups are on the outside. Amphiphilic humic substances probably also form bilayer surface coatings on mineral grains in soil.

An increase in nitrogen-carbon ratio is a significant feature of the transformation of plant biomass to humus through the humification process. This ratio starts at approximately 1/100 in fresh plant biomass. During humification, microorganisms convert organic carbon to CO_2 to obtain energy. Simultaneously, the bacterial action incorporates bound nitrogen with the compounds produced by the decay processes. The result is a nitrogen-carbon ratio of about 1/10 upon completion of humification. As a general rule, therefore, humus is relatively rich in organically bound nitrogen. Humic substances influence soil properties to a degree out of proportion to their small percentage in soil. They strongly bind metals, and serve to hold micronutrient metal ions in soil. Because of their acid-base character, humic substances serve as buffers in soil.

The water-holding capacity of soil is significantly increased by humic substances. These materials also stabilize aggregates of soil particles, and increase the sorption of organic compounds by soil. Humic materials in soil strongly sorb many solutes in soil water and have a particular affinity for heavy polyvalent cations. Soil humic substances may contain levels of uranium more than 104 times that of the water with which they are in equilibrium. Thus, water becomes depleted of its cations (or purified) in passing through humic-rich soils. Humic substances in soils also have a strong affinity for organic compounds with low water solubility, such as DDT or Atrazine, herbicide widely used to kill weeds in corn fields.



Atrazine

In some cases, there is a strong interaction between the organic and inorganic portions of soil. This is especially true of the strong complexes formed between clays and humic (fulvic) acid compounds. In many soils, 50–100% of soil carbon is complexed with clay. These complexes play a role in determining the physical properties of soil, soil fertility and stabilization of soil organic matter.

One of the mechanisms for the chemical binding between clay colloidal particles and humic organic particles is probably of the flocculation types in which anionic organic molecules with carboxylic acid functional groups serve as bridges in combination with cations to bind clay colloidal particles together as a floc. Support is given to this hypothesis by the known ability of NH_4^+, Al^{3+}, Ca^{2+}, and Fe^{3+} cations to stimulate clay-organic complex formation. The synthesis, chemical reactions, and biodegradation of humic materials are affected by interaction with clays.

The Soil Solution

The soil solution is the aqueous portion of soil that contains dissolved matter from soil chemical and biochemical processes in soil and from exchange with the hydrosphere and biosphere. This medium transports chemical species to and from soil particles and provides intimate contact between the solutes and the soil particles.

In addition to providing water for plant growth, it is an essential pathway for the exchange of plant nutrients between roots and solid soil. Obtaining a sample of soil solution is often very difficult because the most significant part of it is bound in capillaries and as surface films. The most straightforward means is collection of drainage water. Soil solution can be isolated from moist solid soil by displacement with a water immiscible fluid, mechanical separation by centrifugation, or pressure or vacuum treatment.

Dissolved mineral matter in soil is largely present as ions. Prominent among the cations are H^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, and usually very low levels of Fe^{2+}, Mn^{2+}, and Al^{3+}. The last three cations may be present in partially hydrolyzed form, such as $FeOH^+$, or complexed by organic humic substance ligands.

Anions that may be present are HCO_3^-, CO_3^{2-}, HSO_4^-, SO_4^{2-}, Cl^-, and F^-. In addition to being bound to H^+ in species such as bicarbonate, anions may be complexed with metal ions, such as in AlF^{2+}. Multivalent cations and anions form ion pairs with each other in soil solutions. Examples of these are $CaSO_4$ and $FeSO_4$.

4.3. Nutrients in the soil

4.3.1. Macronutrients in soil

Dear student, under this main content you will learn about nutrients in the soil Environment. Do you know the processes of nutrients in the soil? Try to attempt the following activities by yourself.

Learning task 4.3.1

a) Describe nutrients in the soil
b) List some of the macro and micro nutrients in the soil
c) Explain the uses of Nitrogen and Phosphorus in soil

One of the most important functions of soil in supporting plant growth is to provide essential plant nutrients are macronutrients and micronutrients. Macronutrients are those elements that occur in substantial levels in plant materials or in fluids in the plant. Micronutrients are elements that are essential only at very low levels and generally are required for the functioning of essential enzymes.

The elements generally recognized as essential macronutrients for plants are carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur. Carbon, hydrogen, and oxygen are obtained from the atmosphere. The other essential macronutrients must be obtained from soil. Of these, nitrogen, phosphorus, and potassium are the most likely to be lacking and are commonly added to soil as fertilizers.

Calcium deficient soils are relatively uncommon. Application of lime, a process used to treat acid soils, provides a more than adequate calcium supply for plants. However, calcium uptake by plants and leaching by carbonic acid may produce a calcium deficiency in soil. Acid soils may still contain an appreciable level of calcium which, because of competition by hydrogen ion, is not available to plants.

Treatment of acid soil to restore the pH to near neutrality generally remedies the calcium deficiency. In alkaline soils, the presence of high levels of sodium, magnesium, and potassium sometimes produces calcium deficiency because these ions compete with calcium for availability to plants. Most of the 2.1% of magnesium in earth’s crust is rather strongly bound in minerals. Exchangeable magnesium held by ion-exchanging organic matter or clays is considered available to plants. The availability of magnesium to plants depends upon the calcium/magnesium ratio. If this ratio is too high, magnesium may not be available to plants and magnesium deficiency results. Similarly, excessive levels of potassium or sodium may cause magnesium deficiency.

Sulfur is assimilated by plants as the sulfate ion, SO_4^{2-}. In addition, in areas where the atmosphere is contaminated with SO_2, sulfur may be absorbed as sulfur dioxide by plant leaves. Atmospheric sulfur dioxide levels have been high enough to kill vegetation in some areas. However, some experiments designed to show SO_2 toxicity to plants have resulted in increased plant growth where there was an unexpected sulfur deficiency in the soil used for the experiment.

Soils deficient in sulfur do not support plant growth well, largely because sulfur is a component of some essential amino acids and of thiamin and biotin. Sulfate ion is generally present in the soil as immobilized insoluble sulfate minerals, or as soluble salts that are readily leached from the soil and lost as soil water runoff. Unlike the case of nutrient cations such as K^+, little sulfate is adsorbed to the soil (i.e., bound by ion exchange binding) where it is resistant to leaching while still available for assimilation by plant roots.

Soil sulfur deficiencies have been found in a number of regions of the world. Whereas most fertilizers used to contain sulfur, its use in commercial fertilizers has declined. With continued use of sulfur deficient fertilizers, it is possible that sulfur will become a limiting nutrient in more cases. The reaction of FeS_2 with acid in acid sulfate soils may release H_2S, which is very toxic to plants and which also kills many beneficial microorganisms. Toxic hydrogen sulfide can also be produced by reduction of sulfate ion through microorganism mediated reactions with organic matter. Production of hydrogen sulfide in flooded soils may be inhibited by treatment with oxidizing compounds, one of the most effective of which is KNO_3.

Nitrogen and phosphorus in the soil

Nitrogen, phosphorus, and potassium are plant nutrients that are obtained from soil. They are so important for crop productivity that they are commonly added to soil as fertilizers.

Nitrogen

In most soils, over 90% of the nitrogen content is organic. This organic nitrogen is primarily the product of the biodegradation of dead plants and animals. It is eventually hydrolyzed to NH_4^+, which can be oxidized to NO_3^- by the action of bacteria in the soil.

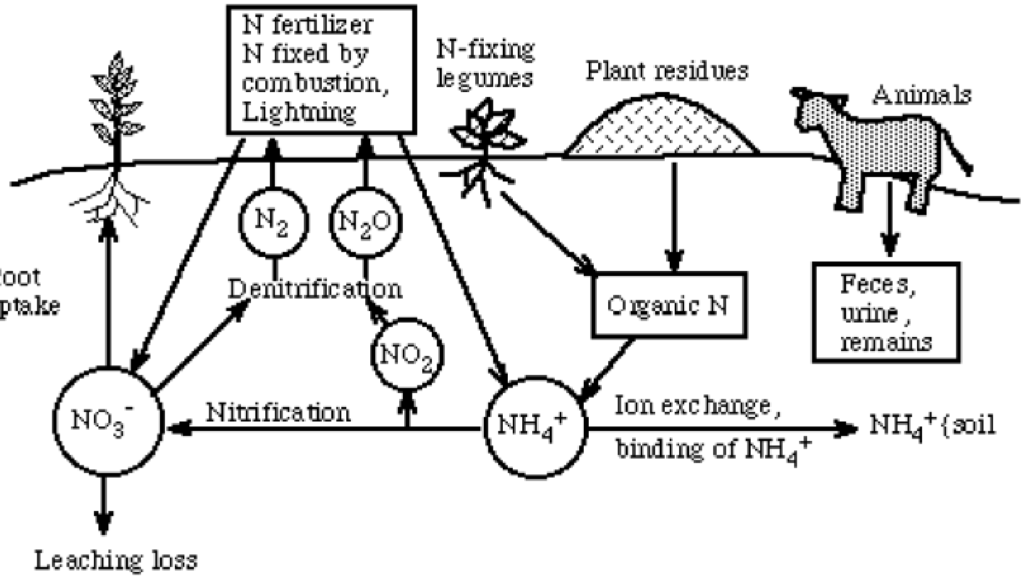


Figure 4.3.1 Nitrogen sinks and path way in soil

Nitrogen bound to soil humus is especially important in maintaining soil fertility. Unlike potassium or phosphate, nitrogen is not a significant product of mineral weathering. Nitrogen-fixing organisms ordinarily cannot supply sufficient nitrogen to meet peak demand. Inorganic nitrogen from fertilizers and rainwater is often largely lost by leaching. Soil humus, however, serves as a reservoir of nitrogen required by plants. It has the additional advantage that its rate of decay, hence its rate of nitrogen release to plants, roughly parallels plant growth rapid during the warm growing season, slow during the winter months. Nitrogen is an essential component of proteins and other constituents of living matter.

Plants and cereals grown on nitrogen-rich soils not only provide higher yields, but are often substantially richer in protein and, therefore, more nutritious. Nitrogen is most generally available to plants as nitrate ion, NO_3^-. Some plants such as rice may utilize ammonium nitrogen; however, other plants are poisoned by this form of nitrogen. When nitrogen is applied to soils in the ammonium form, nitrifying bacteria perform an essential function in converting it to available nitrate ion. Plants may absorb excessive amounts of nitrate nitrogen from soil. This phenomenon occurs particularly in heavily fertilized soils under drought conditions. Forage crops containing excessive amounts of nitrate can poison ruminant animals such as cattle or sheep.

Plants having excessive levels of nitrate can endanger people when used for ensilage, an animal food consisting of finely chopped plant material such as partially matured whole corn plants, fermented in a structure called a silo. Under the reducing conditions of fermentation, nitrate in ensilage may be reduced to toxic NO_2 gas, which can accumulate to high levels in enclosed silos.

There have been many cases reported of persons being killed by accumulated NO_2 in silos. Nitrogen fixation is the process by which atmospheric N_2 is converted to nitrogen compounds available to plants. Human activities are resulting in the fixation. Of a great deal more nitrogen than would otherwise be the case. Artificial sources now account for 30-40% of all nitrogen fixed. These include chemical fertilizer manufacture, nitrogen fixed during fuel combustion, combustion of nitrogen containing fuels, and the increased cultivation of nitrogen-fixing legumes.

A major concern with this increased fixation of nitrogen is the possible effect upon the atmospheric ozone layer by N_2O released during denitrification of fixed nitrogen. Before the widespread introduction of nitrogen fertilizers, soil nitrogen was provided primarily by legumes. These are plants such as soybeans, alfalfa, and clover, which contain on their root structures bacteria capable of fixing atmospheric nitrogen.

Leguminous plants have a symbiotic (mutually advantageous) relationship with the bacteria that provide their nitrogen. Legumes may add significant quantities of nitrogen to soil, up to 10 pounds per acre per year, which is comparable to amounts commonly added as synthetic fertilizers. Soil fertility with respect to nitrogen can be maintained by rotating plantings of nitrogen-consuming plants with plantings of legumes, a fact recognized by agriculturists as far back as the Roman era. The nitrogen-fixing bacteria in legumes exist in special structures on the roots called root nodules. The rod-shaped bacteria that fix nitrogen are members of a special genus, Rhizobium. These bacteria can exist independently, but cannot fix nitrogen except in symbiotic combination with plants. Although all species of Rhizobium appear to be very similar, they exhibit a great deal of specificity in their choice of host plants. Curiously, legume root nodules also contain a form of hemoglobin, which must somehow be involved in the nitrogen fixation process.

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$$

The origin of most nitrates produced from feedlot wastes is amino nitrogen present in nitrogen-containing waste products. Approximately one-half of the nitrogen excreted by cattle is contained in the urine. Part of this nitrogen is protein aceous and the other part is in the form of urea, NH_2CONH_2. As a first step in the degradation process, the amino nitrogen is probably hydrolyzed to ammonia, or ammonium ion:

$$RNH_2 + H_2O \rightarrow R\text{-}OH + NH_3\ (NH_4^+)$$

This product is then oxidized through microorganism-catalyzed reactions to nitrate ion:

$$NH_3 + 2O_2 \rightarrow H^+ + NO_3^- + H_2O$$

Under some conditions, an appreciable amount of the nitrogen originating from the degradation of feedlot wastes is present as ammonium ion. Ammonium ion is rather strongly bound to soil, and a small fraction is fixed as non-exchangeable ammonium ion in the crystal lattice of clay minerals. Because nitrate ion is not strongly bound to soil, it is readily carried through soil formations by water. Many factors, including soil type, moisture, and level of organic matter, affect the production of ammonia and nitrate ion originating from feedlot wastes, and a marked variation is found in the levels and distributions of these materials in feed lot areas.

Phosphorus

Although the percentage of phosphorus in plant material is relatively low, it is an essential component of plants. Phosphorus, like nitrogen, must be present in a simple inorganic form before it can be taken up by plants. In the case of phosphorus, the utilizable species is some form of orthophosphate ion. In the pH range that is present in most soils, $H_2PO_4^-$ and HPO_2^- are the predominant orthophosphate species.

Orthophosphate is most available to plants at pH values near neutrality. It is believed that in relatively acidic soils, orthophosphate ions are precipitated or sorbed by species of Al (III) and Fe (III). In alkaline soils, orthophosphate may react with calcium carbonate to form relatively insoluble hydroxyapatite:

$$3HPO_4^{2-} + 5CaCO_3(s) + 2H_2O \rightarrow Ca_5(PO_4)_3(OH)(s) + 5HCO_3^- + OH^-$$

In general, because of these reactions, little phosphorus applied as fertilizer leaches from the soil. This is important from the standpoint of both water pollution and utilization of phosphate fertilizers.

4.3.2. Micronutrients in soil

Dear student, under this main content you will learn about micronutrients in the soil Environment. Do you know the processes of micronutrients in the soil? Try to attempt the following activities by yourself.

Learning task 4.3.2

a) List some of the micro nutrients in the soil
b) Describe the source of the micro nutrients in the soil
c) Explain the use of micro nutrients in the soil

Boron, chlorine, copper, iron, manganese, molybdenum (for N-fixation), and zinc are considered essential plant micronutrients. These elements are needed by plants only at very low levels and frequently are toxic at higher levels. There is some chance that other elements will be added to this list as techniques for growing plants in environments free of specific elements improve. Most of these elements function as components of essential enzymes. Manganese, iron, chlorine, and zinc may be involved in photosynthesis. Though not established for all plants; it is possible that sodium, silicon, and cobalt may also be essential plant nutrients. Iron and manganese occur in a number of soil minerals. Sodium and chlorine (as chloride) occur naturally in soil and are transported as atmospheric particulate matter from marine sprays.

Some of the other micronutrients and trace elements are found in primary (unweathered) minerals that occur in soil. Boron is substituted isomorphically for Si in some micas and is present in tourmaline, a mineral with the formula $NaMg_3Al_6B_3Si_6O_{27}(OH, F)_4$. Copper is isomorphically substituted for other elements in feldspars, amphiboles, olivines, pyroxenes, and micas; it also occurs as trace levels of copper sulfides in silicate minerals. Molybdenum occurs as molybdenite

(MoS_2). Vanadium is isomorphically substituted for Fe or Al in oxides, pyroxenes, amphiboles, and micas. Zinc is present as the result of isomorphic substitution for Mg, Fe and Mn in oxides, amphiboles, olivines, and pyroxenes and as trace zinc sulfide in silicates.

Other trace elements that occur as specific minerals, sulfide inclusions, or by isomorphic substitution for other elements in minerals are chromium, cobalt, arsenic, selenium, nickel, lead, and cadmium. The trace elements listed above may be coprecipitated with secondary minerals that are involved in soil formation. Such secondary minerals include oxides of aluminum, iron, and manganese; calcium and magnesium carbonates; smectites; vermiculites; and illites.

Some plants accumulate extremely high levels of specific trace metals. Those accumulating more than 1.00 mg/g of dry weight are called **hyperaccumulater**. Nickel and copper both undergo hyper accumulation in some plant species. As an example of a metal hyperaccumulater, Aeolanthus biformifolius deWild, growing in copper-rich regions of Shaba Province, Zaire, contains up to 1.3% copper (dry weight) and is known as a “copper flower.” The hyperaccumulation of metals by some plants has led to the idea of **phytoremediation** in which plants growing on contaminated ground accumulate metals, which are then removed with the plant biomass.

4.4. Reactions in soil

Dear student, under this main content you will learn about reactions in soil. Do you know some of the reactions in soil? Try to attempt the following activities by yourself.

Learning task 4.4

a) Describe how reaction takes place in the soil.
b) Explain how the reaction in the soil will affect the nature of the soil.
c) Explain how Soil Acidity can be Adjusted
d) Discuss acid-base and ion exchange reactions in soil

Dear student, what does it mean by acid-base and ion exchange reactions in soil?

One of the more important chemical functions of soils is the exchange of cations. The ability of a sediment or soil to exchange cations is expressed as the cation-exchange capacity (CEC), the number of milliequivalents (meq) of monovalent cations that can be exchanged per 100 g of soil (on a dry weight basis). The CEC should be looked upon as a conditional constant since it can vary with soil conditions such as pE and pH. Both the mineral and organic portions of soils exchange cations. Clay minerals exchange cations because of the presence of negatively charged sites on the mineral, resulting from the substitution of an atom of lower oxidation number for one of higher number, for example, and magnesium for aluminum.

Organic materials exchange cations because of the presence of the carboxylate group and other basic functional groups. Humus typically has a very high cation-exchange capacity. The cation-exchange capacity of peat can range from 300–400 meq/100 g. Values of cation-exchange capacity for soils with more typical levels of organic matter are around 10–30 meq/100 g. Cation exchange in soil is the mechanism by which potassium, calcium, magnesium, and essential trace-level metals are made available to plants. When nutrient metal ions are taken up by plant roots, hydrogen ion is exchanged for the metal ions. This process, plus the leaching of calcium, magnesium, and other metal ions from the soil by water containing carbonic acid, tends to make the soil acidic:

$$\text{Soil}\}\text{Ca}^{2+} + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Soil}\}(\text{H}^+)_2 + \text{Ca}^{2+}(\text{root}) + 2\text{HCO}_3^-$$

Soil acts as a buffer and resists changes in pH. The buffering capacity depends upon:

The type of soil

Production of mineral acid in soil

The oxidation of pyrite in soil causes formation of acid-sulfate soils sometimes called “cat clays”:

Cat clay soils can have pH values as low as 3.0. These soils are formed when neutral or basic marine sediments containing FeS_2 become acidic upon oxidation of pyrite when exposed to air.

$$\text{FeS}_2 + {}^7\!/_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{H}^+ + 2\text{SO}_4^{2-}$$

For example, soil reclaimed from marshlands and used for citrus groves has developed high acidity detrimental to plant growth. In addition, H_2S released by reaction of FeS_2 with acid is very toxic to citrus roots. Soils are tested for potential acid-sulfate formation using a peroxide test. This test consists of oxidizing FeS_2 in the soil with 30% H_2O_2, then testing for acidity and sulfate.

$$FeS_2 + {}^{15}/_2H_2O_2 \rightarrow Fe^{3+} + H^+ + 2SO_4^{2-} + 7H_2O$$

Appreciable levels of sulfate and a pH below 3.0 indicate potential to form acid-sulfate soils. If the pH is above 3.0, either little FeS_2 is present or sufficient $CaCO_3$ is in the soil to neutralize the H_2SO_4 and acidic Fe^{3+}. Pyrite-containing mine spoils (residue left over from mining) also form soils similar to acid-sulfate soils of marine origin. In addition to high acidity and toxic H_2S, a major chemical species limiting plant growth on such soils is Al (III). Aluminum ion liberated in acidic soils is very toxic to plants.

Adjustment of Soil Acidity

Most common plants grow best in soil with a pH near neutrality. If the soil becomes too acidic for optimum plant growth, it may be restored to productivity by liming, ordinarily through the addition of calcium carbonate:

$$\mathrm{Soil}\}(H^+)_2 + CaCO_3 \rightarrow \mathrm{Soil}\}Ca^{2+} + CO_2 + H_2O$$

In areas of low rainfall, soils may become too basic (alkaline) due to the presence of basic salts such as Na_2CO_3. Alkaline soils can be treated with aluminum or iron sulfate, which release acid on hydrolysis:

$$2Fe^{3+} + 3SO_4^{2-} + 6H_2O \rightarrow 2Fe(OH)_3(s) + 6H^+ + 3SO_4^{2-}$$

Sulfur added to soils is oxidized by bacterially mediated reactions to sulfuric acid:

$$S + {}^{3}/_2O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}$$

and sulfur is used, therefore, to acidify alkaline soils. The huge quantities of sulfur now being removed from fossil fuels to prevent air pollution by sulfur dioxide may make the treatment of alkaline soils by sulfur much more attractive economically.

Ion Exchange Equilibria in Soil

Competition of different cations for cation exchange sites on soil cation exchangers may be described semi quantitatively by exchange constants. For example, soil reclaimed from an area flooded with seawater will have most of its cation exchange sites occupied by Na^+, and restoration of fertility requires binding of nutrient cations such as K^+:

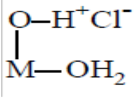
$$\mathrm{Soil\}Na^+ + K^+ \rightleftharpoons Soil\}K^+ + Na^+}$$

The exchange constant is given by

$$K_c = \frac{N_K[Na^+]}{N_{Na}[K^+]}$$

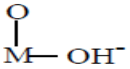
This expresses the relative tendency of soil to retain K^+ and Na^+. In this equation, N_K and N_{Na} are the equivalent ionic fractions of potassium and sodium, respectively, bound to soil, and $[Na^+]$ and $[K^+]$ are the concentrations of these ions in the surrounding soil water. For example, a soil with all cation exchange sites occupied by Na^+ would have a value of 1.00 for N_{Na}; with one-half of the cation exchange sites occupied by Na^+, N_{Na} is 0.5; etc. The exchange of anions by soil is not nearly as clearly defined as is the exchange of cations. In many cases, the exchange of anions does not involve a simple ion-exchange process. This is true of the strong retention of orthophosphate species by soil.

Anion exchange can be visualized as occurring at the surfaces of oxides in the mineral portion of soil. A mechanism for the acquisition of surface charge by metal oxides like MnO_2 is an example. At low pH, a metal oxide surface may have a net positive charge enabling it to hold anions, such as chloride, by electrostatic attraction as shown below where m represents a metal:



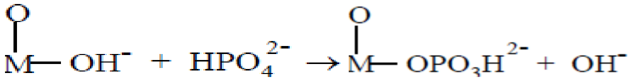
$$\begin{array}{l} \mathrm{O{-}H^+Cl^-} \\ | \\ \mathrm{M{-}OH_2} \end{array}$$

At higher pH values, the metal oxide surface has a net negative charge due to the formation of OH- ion on the surface caused by loss of H^+ from the water molecules bound to the surface: In such cases, it is possible for anions such as $HPO_4{}^{2-}$ bond directly to the oxide surface.



$$\begin{array}{l} \mathrm{O} \\ | \\ \mathrm{M{-}OH^-} \end{array}$$

In such cases, it is possible for anions such as $HPO4^{2-}$ to displace hydroxide ion and bond directly to the oxide surface:



$$\begin{array}{l} \mathrm{O} \\ | \\ \mathrm{M{-}OH^-} \end{array} + \mathrm{HPO_4^{2-}} \rightarrow \begin{array}{l} \mathrm{O} \\ | \\ \mathrm{M{-}OPO_3H^{2-}} \end{array} + \mathrm{OH^-}$$

4.5. Wastes and pollutants in soil

Dear student, under this main content you will learn about wastes and pollutants in soil. Do you know some of the wastes and pollutant in the soil? Try to attempt the following activities by yourself.

Learning task 4.5

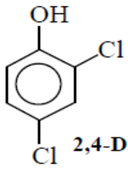
a) Explain the source of wastes and pollutants in the soil
b) Explain how wastes and pollutants affect the nature of the soil
c) Discuss how soil loss and degradation can occur

In some cases, land farming of degradable hazardous organic wastes is practiced as a means of disposal and degradation. The degradable material is worked into the soil, and soil microbial processes bring about its degradation. Sewage and fertilizer-rich sewage sludge can be applied to soil.

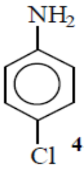
Much of the sulfur dioxide emitted in the burning of sulfur-containing fuels ends up as soil sulfate. Atmospheric nitrogen oxides are converted to nitrates in the atmosphere, and the nitrates eventually are deposited on soil. Soil sorbs NO and NO_2, and these gases are oxidized to nitrate in the soil. Carbon monoxide is converted to CO_2 and possibly to biomass by soil bacteria and fungi. Particulate lead from automobile exhausts is found at elevated levels in soil along heavily traveled highways. Elevated levels of lead from lead mines and smelters are found on soil near such facilities.

Volatile organic compounds (VOC) such as benzene, toluene, xylenes, dichloro-methane, trichloroethane, and trichloroethylene, may contaminate soil in industrialized and commercialized areas, particularly in countries in which enforcement of regulations is not very stringent. One of the more common sources of these contaminants is leaking underground storage tanks. Landfills built before current stringent regulations were enforced, and improperly discarded solvents are also significant sources of soil VOCs.

Some pollutant organic compounds are believed to become bound with humus during the humification process that occurs in soil. This largely immobilizes and detoxifies the compounds. Binding of pollutant compounds by humus is particularly likely to occur with compounds that have structural similarities to humic substances, such as phenolic and anilinic compounds, illustrated by the following two examples:



2,4-Dichlorophenol



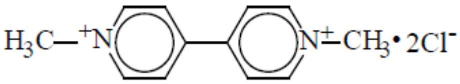
4-Chloroaniline

Such compounds can become covalently bonded to humic substance molecules, largely through the action of microbial enzymes. After binding they are known as **bound residues** and are highly resistant to extraction with solvents by procedures that would remove unbound parent compounds. Compounds in the bound residue are resistant to biological and chemical attack.

Soil receives enormous quantities of pesticides as an inevitable result of their application to crops. The degradation and eventual fate of these pesticides on soil largely determines their ultimate environmental effects. Among the factors to be considered are the sorption of the pesticide by soil; leaching of the pesticide into water, as related to its potential for water pollution; effects of the pesticide on microorganisms and animal life in the soil; and possible production of relatively more toxic degradation products.

Adsorption by soil is a key aspect of pesticide degradation and plays a strong role in the speed and degree of degradation. The degree of adsorption and the speed and extent of ultimate degradation are influenced by a number of other factors. Some of these, including solubility, volatility, charge, polarity, and molecular structure and size, are properties of the medium. Adsorption of a pesticide by soil components may have several effects. Under some circumstances, it retards degradation by separating the pesticide from the microbial enzymes that degrade it, whereas under other circumstances the reverse is true.

Purely chemical degradation reactions may be catalyzed by adsorption. Loss of the pesticide by volatilization or leaching is diminished. The toxicity of a herbicide to plants may be reduced by sorption on soil. The forces holding a pesticide to soil particles may be of several types. Physical adsorption involves vander Waals forces arising from dipole-dipole interactions between the pesticide molecule and charged soil particles. Ion exchange is especially effective in holding cationic organic compounds, such as the herbicide paraquat, to anionic soil particles.

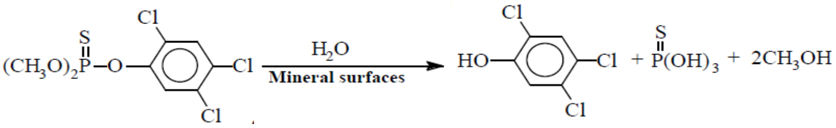


Paraquat

Some neutral pesticides become cationic by protonation and are bound as the protonated positive form. Hydrogen bonding is another mechanism by which some pesticides are held to soil. In some cases, a pesticide may act as a ligand coordinating to metals in soil mineral matter.

The three primary ways in which pesticides are degraded in or on soil are chemical degradation, photochemical reactions, and, most important, biodegradation. Various combinations of these processes may operate in the degradation of a pesticide.

Chemical degradation of pesticides has been observed experimentally in soils and clays sterilized to remove all microbial activity. For example, clays have been shown to catalyze the hydrolysis of o,o-dimethyl-o-2,4,5-trichlorophenyl thio-phosphate (also called Trolene, Ronnel, Etrolene, or trichlorometafos), an effect attributed to -OH groups on the mineral surface:



Many other purely chemical hydrolytic reactions of pesticides occur in soil. A number of pesticides have been shown to undergo photochemical reactions, that is, chemical reactions brought about by the absorption of light. Frequently, isomers of the pesticides are formed as products. Many of the studies reported apply to pesticides in water or on thin films, and the photochemical reactions of pesticides on soil and plant surfaces remain largely a matter of speculation.

Biodegradation and the Rhizosphere

Although insects, earthworms, and plants may play roles in the biodegradation of pesticides and other pollutant organic chemicals, microorganisms have the most important role. The **rhizosphere,** the layer of soil in which plant roots are especially active, is a particularly important part of soil with respect to biodegradation of wastes. It is a zone of increased biomass and is strongly influenced by the plant root system and the microorganisms associated with plant roots.

The rhizosphere may have more than ten times the microbial biomass per unit volume than non-rhizospheric zones of soil. This population varies with soil characteristics, plant and root characteristics, moisture content, and exposure to oxygen. If this zone is exposed to pollutant compounds, microorganisms adapted to their biodegradation may also be present. Plants and microorganisms exhibit a strong synergistic relationship in the rhizosphere, which benefits the plant and enables highly elevated populations of rhizospheric microorganisms to exist. Epidermal cells sloughed from the root as it grows and carbohydrates, amino acids, and root-growth-lubricant mucigel secreted from the roots all provide nutrients for microorganism growth. Root hairs provide a hospitable biological surface for colonization by microorganisms.

The biodegradation of a number of synthetic organic compounds has been demonstrated in the rhizosphere. Understandably, studies in this area have focused on herbicides and insecticides that are widely used on crops. Among the organic species for which enhanced biodegradation in the rhizosphere has been demonstrated are the following (associated plant or crop shown in parentheses): 2,4-D herbicide (wheat, African clover, sugarcane, flax), parathion (rice, bush bean), carbofuran (rice), atrazine (corn), diazinon (wheat, corn, peas), volatile aromatic alkyl and aryl hydrocarbons and chlorocarbons (reeds), and surfactants (corn, soybean, cattails).

It is interesting to note that enhanced biodegradation of polycyclic aromatic hydrocarbons (PAH) was observed in the rhizospheric zones of prairie grasses. This observation is consistent with the fact that in nature such grasses burn regularly and significant quantities of PAH compounds are deposited on soil as a result.

Soil loss and degradation

Dear student, do you know what soil loss and degradation mean?

Soil is a fragile resource that can be lost by erosion or become so degraded that it is no longer useful to support crops. The physical properties of soil and, hence, its susceptibility to erosion, are strongly affected by the cultivation practices to which the soil is subjected.

Desertification refers to the process associated with drought and loss of fertility by which soil becomes unable to grow significant amounts of plant life. Desertification caused by human activities is a common problem globally, occurring in diverse locations. It is a very old problem dating back many centuries to the introduction of domesticated grazing animals to areas where rainfall and groundcover were marginal.

The most notable example is desertification aggravated by domesticated goats in the Sahara region. Desertification involves a number of interrelated factors, including erosion, climate variations, water availability, loss of fertility, loss of soil humus, and deterioration of soil chemical properties. A related problem is deforestation, loss of forests. The problem is particularly acute in tropical regions, where the forests contain most of the existing plant and animal species. In addition to extinction of these species, deforestation can cause devastating deterioration of soil through erosion and loss of nutrients.

The practice of planting corn and soybeans year after year without intervening plantings of soil restoring clover or grass became widespread. The problem of decreased productivity due to soil erosion has been masked somewhat by increased use of chemical fertilizers.

Wind erosion, such as occurs on the generally dry, high plains soils of eastern Colorado, poses another threat. After the Dust Bowl days of the 1930s, much of this land was allowed to revert to grassland, and the topsoil was held in place by the strong root systems of the grass cover. However, in an effort to grow more wheat and improve the sale value of the land, much of it was later returned to cultivation.

The preservation of soil from erosion is commonly termed soil conservation. There are a number of solutions to the soil erosion problem. Some are old, well known agricultural practices such as terracing, contour plowing, and periodically planting fields with cover crops such as clover. For some crops, no-till agriculture, now commonly called conservation tillage, greatly reduces erosion. This practice consists of planting a crop among the residue of the previous year's crop without plowing. Weeds are killed in the newly planted crop row by application of a herbicide prior to planting. The surface residue of plant material left on top of the soil prevents erosion.

Another, more experimental, solution to the soil erosion problem is the cultivation of perennial plants that develop large root systems and come up each spring after being harvested the previous fall. For example, a perennial corn plant has been developed by crossing corn with a distant wild relative, teosinte, which grows in Central America. Unfortunately, the resulting plant does not give outstanding grain yields.

It should be noted that an annual plant’s ability to propagate depends upon producing large quantities of seeds, whereas a perennial plant must develop a strong root system with bulbous growths called rhizomes that store food for the coming year. However, it is possible that the application of genetic engineering may result in the development of perennial crops with good seed yields. The cultivation of such a crop would cut down on a great deal of soil erosion. The best known perennial plants are trees, which are very effective in stopping soil erosion. Wood from trees can be used as biomass fuel, as a source of raw materials, and as food. There is a tremendous unrealized potential for an increase in the production of biomass from trees.

Chapter Summary

- Soil can be defined as a finely divided layer of weathered minerals and organic matter upon which plants grow formed by the weathering of parent rocks as the result of interactive geological, hydrological, and biological processes.
- Agriculture is defined as the production of food by growing crops and livestock. It can be divided into the two main categories of crop farming and livestock farming.
- The top layer of soil, typically several inches in thickness, is known as the A horizon, or topsoil and the next layer is the B horizon, or subsoil. This is the layer of maximum biological activity in the soil and contains most of the soil organic matter
- Transpiration is a process entering the water from the plant’s leaves to the atmosphere.
- Organic matter component of the soil serves as a source of food for micro-organisms, undergoes chemical reactions such as ion exchange, and influences the physical properties of soil.
- Soil humus is composed of a base-soluble fraction called humic and fulvic acids, and an insoluble fraction called humin (a residue left when bacteria and fungi biodegrade plant material) ; the process by which humus is formed is called humification.
- Some plants accumulate extremely high levels of specific trace metals. Those accumulating more than 1.00 mg/g of dry weight are called hyperaccumulater.
- Phytoremediation is a means to remove metals from contaminated soil by growing plants on contaminated ground accumulate metals.
- Micronutrients are elements that are essential only at very low levels and generally are required for the functioning of essential enzymes. They are toxic at higher levels.

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- The ability of a sediment or soil to exchange cations is expressed as the cation-exchange capacity (CEC),
- Organic matter largely determines soil productivity. It serves as a source of food for micro-organisms, undergoes chemical reactions such as ion exchange, and influences the physical properties of soil. Some organic compounds even contribute to the weathering of mineral matter, the process by which soil is formed
- The buffering capacity of a soil depends upon the type of soil, production of mineral acid in soil and the oxidation of pyrite in soil causes formation of acid-sulfate soils sometimes called “cat clays”:
- Most plants grow best in soil with a pH near neutrality.
- Acidic soils can be restored to productivity by liming, ordinarily through the addition of calcium carbonate:

Self test exercises

1. Give two examples of reactions involving manganese and iron compounds that might occur in waterlogged soil.
2. What temperature and moisture conditions favor the buildup of organic matter in soils?
3. "Cat clays" are soils containing a high level of iron pyrite, FeS_2. Hydrogen peroxide, H_2O_2, is added as a test for such soils, producing sulfate cat clays. Explain the rationale behind and suggest the chemical reaction involved in this test.
4. What effect upon soil acidity would result from heavy fertilization with ammonium nitrate accompanied by exposure of the soil to air and the action of aerobic bacteria?
5. How many moles of H^+ ion are consumed when 200 kilograms of $NaNO_3$ undergo denitrification in soil?
6. What is the primary mechanism by which organic material in soil exchanges cations?
7. Prolonged water logging of soil doesn't

   (a) Increase NO_3^- production (b) Increase Mn^{2+} concentration,

   (c) Increase Fe^{2+} concentration (d) Have harmful effects upon most plants,

   (e) Increase production of NH_4^+ from NO_3^-.

8. Of the following phenomena, the one that eventually makes soil more basic is

   (a) Removal of metal cations by roots (b) Leaching of soil with CO_2-saturated water,

   (c) Oxidation of soil pyrite (d) Fertilization with $(NH_4)_2SO_4$,

   (e) Fertilization with KNO_3.

9. How are the chelating agents that are produced from soil microorganisms involved in soil formation?

10. What specific compound is both a particular animal waste product and a major fertilizer?

11. What happens to the nitrogen/carbon ratio as organic matter degrades in soil?

12. Explain why plants grown on either excessively acidic or excessively basic soils may suffer from calcium deficiency.

13. What are two mechanisms by which anions may be held by soil mineral matter?

14. What are the three major ways in which pesticides are degraded in or on soil?

15. What are the processes occurring in soil that operate to reduce the harmful effects of pollutants?

16. Under what conditions do the following reactions occur in soil? Name two detrimental effects that can result from these reactions.

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

and

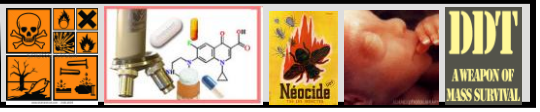
$$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$$

17. List the four important effects of organic matter in soil?

18. How might irrigation with water treated with fertilizer containing potassium and ammonia become depleted of these nutrients in passing through humus-rich soil?

Chapter 5

ENVIRONMENTAL TOXICITY AND TOXICOLOGY



Chapter Introduction

Dear student, this chapter deals with introduction to Environmental Toxicity and Toxicology. It deals with definition of some basic terms, which provide you the basic concept of Environmental Toxicity and Toxicology. You will also discuss further about organic and inorganic pollutants, agricultural and pharmaceutical contaminants, pesticides, PCB's (poly chlorinated biphenyl), Chlorofluro compounds, nitrogen and phosphorous compounds, toxic heavy metals and Organo-metallic compounds.

Learning objective of the unit

Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:-

- Define Environmental Toxicity and Toxicology
- Compare and contrast organic and inorganic pollutants
- Explain agricultural and pharmaceutical contaminants
- Discuss the effect of pesticides upon the Environment
- Describe the effect of PCB's and Chlorofluro compounds upon the Environment
- Discuss about nitrogen and phosphorous compounds
- Explain about some of the heavy metals and Organo-metallic compounds

5.1. Introduction to Toxicity and Toxicology

Dear student, under this main content you learn about Toxicity and Toxicology. Do you know some of the causes for Toxicity and Toxicology, let warm up yourself with the following activities.

Learning task 5.1

a) Define the following terms: Toxicant, Toxicity and Toxicology
b) Explain the relationship among dose, concentration and frequency of toxic Substances
c) Compare and contrast acute effects and chronic effects
d) Compare and contrast chronic systemic exposure, chronic local exposure, acute local exposure and acute systemic exposure

5.1.1 Toxicity

Toxicity is of the highest concern in dealing with hazardous substances. This includes both long-term chronic effects from continual or periodic exposures to low levels of toxicants and acute effects from a single large exposure. Ultimately, most pollutants and hazardous substances are of concern because of their toxic effects. To understand toxicological chemistry, it is essential to have some understanding of biochemistry, the science that deals with chemical processes and materials in living systems.

Not surprisingly, the management of chemicals discharged to the environment has become a major focus for Environmental Chemistry. Many of the topics in Environmental Chemistry are concerned with chemical pollutants in the environment. However, it is not only concerned with pollutants but also with the behavior of natural chemicals in the natural systems. Environmental chemistry is basically concerned with developing and understanding of the chemistry of the world in which we live.

5.1.2 Toxicology

Dear student, Toxicology is the science of poisons. A poison, or toxicant, is a substance that is harmful to living organisms because of its detrimental effects on tissues, organs, or biological processes.. Toxicants to which subjects are exposed in the environment or occupationally may be in several different physical forms, such as vapors or dusts that are inhaled, liquids that can be absorbed through the skin or solids ingested orally. A substance with which the toxicant may be associated (the solvent in which it is dissolved or the solid medium in which it is dispersed) is called the matrix. The matrix may have a strong effect upon the toxicity of the toxicant.

There are numerous variables related to the ways in which organisms are exposed to toxic substances. One of the most crucial is dose. Another important factor is the toxicant concentration, which may range from the pure substance (100%) down to a very dilute solution of a highly potent poison. Both the duration of exposure per incident and the frequency of exposure are important. The rate of exposure and the total time period over which the organism is exposed are both important situational variables. The exposure site and route also affect toxicity.

It is possible to classify exposures on the basis of four general categories. Acute local exposure occurs at a specific location over a time period of a few seconds to a few hours and may affect the exposure site, particularly the skin, eyes, or mucous membranes. The same parts of the body can be affected by chronic local exposure, for which the time span may be as long as several years. Acute systemic exposure is a brief exposure or exposure to a single dose and occurs with toxicants that can enter the body and affect organs that are remote from the entry site. Chronic systemic exposure differs in that the exposure occurs over a prolonged time period.

In discussing exposure sites for toxicants it is useful to consider the major routes and sites of exposure, distribution, and elimination of toxicants in the body. The major routes of accidental or intentional exposure to toxicants in humans and other animals are the skin (percutaneous route), the lungs (inhalation, respiration, pulmonary route), and the mouth (oral route). The pulmonary system is most likely to take in toxic gases or very fine, respirable solid or liquid particles. In other than a respirable form, a solid usually enters the body orally. Absorption through the skin is most likely for liquids, solutes in solution, and semisolids, such as sludges.

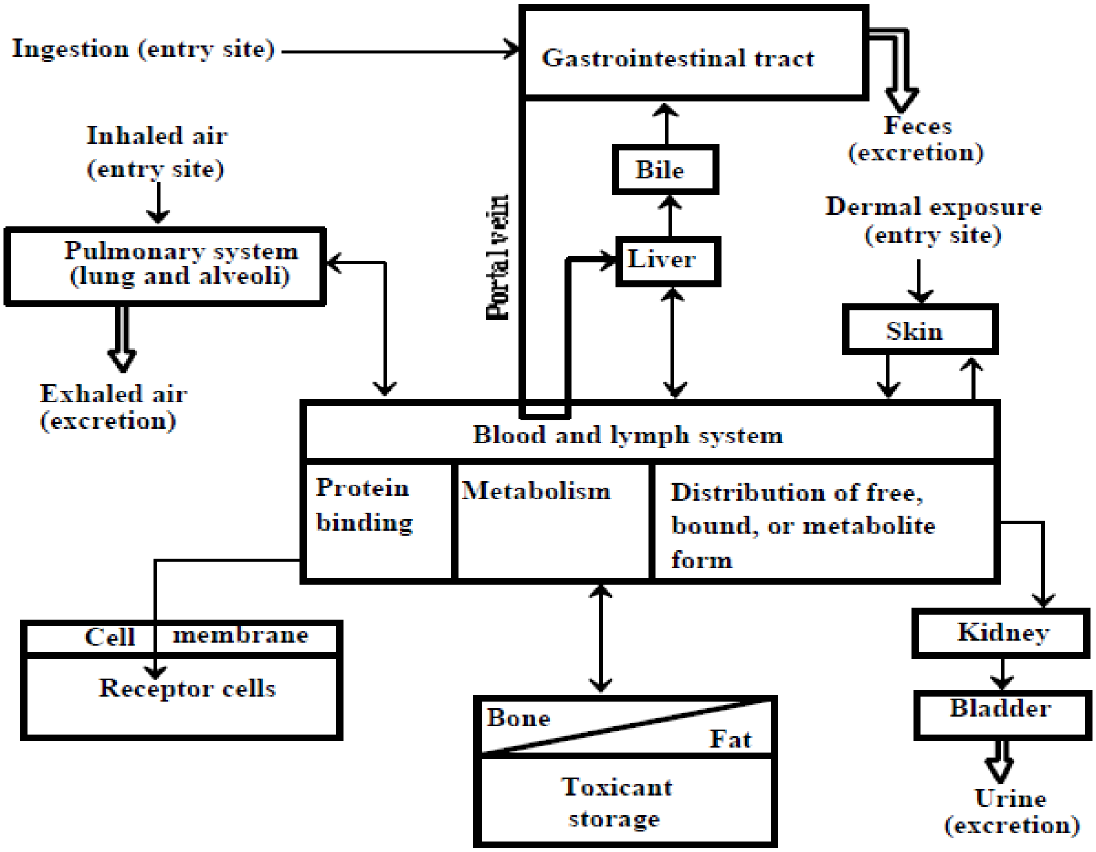


Figure 5.1 Major sites of exposure, metabolism and storage, routes of distribution and elimination of toxic substances in the body

The defensive barriers that a toxicant may encounter vary with the route of exposure. An interesting historical example of the importance of the route of exposure to toxicants is provided by cancer caused by contact of coal tar with skin. The permeability of skin is inversely proportional to the thickness of the skin's stratum corneum layer, which varies by location on the body in the following order: soles and palms > abdomen, back, legs, arms > genital (perineal) area. The cancer-causing agent was coal tar condensed in chimneys. This material was more readily absorbed through the skin in the genital areas than elsewhere, leading to a high incidence of scrotal cancer. Organisms can serve as indicators of various kinds of pollutants, thus serving as **biomonitors**. For example, higher plants, fungi, lichens, and mosses can be important biomonitors for heavy-metal pollutants in the environment.

5.1.3 Synergism, Potentiation, and Antagonism

Dear student, under this main content you learn about Synergism, Potentiation, and Antagonism. Do you know meanings of Synergism, Potentiation, and Antagonism, let warm up yourself with the following activities.

Learning task 5.1 .3

a) Define the following terms: Synergism, Potentiation, and Antagonism
b) Compare and contrast Synergism, Potentiation, and Antagonism
c) Explain Dose-response relationships
d) Describe Relative toxicities
e) Explain the difference between Hypersensitivity and Hyposensitivity

The biological effects of two or more toxic substances can be different in kind and degree from those of one of the substances alone. Chemical interaction between substances may affect their toxicities. Both substances may act upon the same physiologic function, or two substances may compete for binding to the same receptor (molecule or other entity acted upon by a toxicant).

When substances have the same physiologic function, their effects may be simply additive or they may be synergistic (the total effect is greater than the sum of the effects of each separately). Potentiation occurs when an inactive substance enhances the action of an active one, and antagonism when an active substance decreases the effect of another active one.

5.1.3.1 Dose-response relationships

Dear ***student, do you know dose-response relationships?***

Toxicants have widely varying effects upon organisms. Quantitatively, these variations include minimum levels at which the onset of an effect is observed, the sensitivity of the organism to small increments of toxicant, and levels at which the ultimate effect (particularly death) occurs in most exposed organisms. Some essential substances, such as nutrient minerals, have optimum ranges above and below which detrimental effects are observed.

Factors such as those just outlined are taken into account by the ***dose-response relationship***, which is one of the key concepts of toxicology. Dose is the amount, usually per unit body mass, of a toxicant to which an organism is exposed. Response is the effect upon an organism resulting from exposure to a toxicant. To define a dose-response relationship, it is necessary to specify a particular response, such as death of the organism, as well as the conditions under which the response is obtained, such as the length of time from administration of the dose.

Consider a specific response for a population of the same kinds of organisms. At relatively low doses, none of the organisms exhibits the response (for example, all live), whereas at higher doses all of the organisms exhibit the response (for example, all die). In between, there is a range of doses over which some of the organisms respond in the specified manner and others do not, thereby defining a dose-response curve.

Dose- response relationships differ among different kinds and strains of organisms, types of tissues, and populations of cells. The dose corresponding to the mid-point (inflection point) of the resulting S-shaped curve is the statistical estimate of the dose that would kill 50 % of the subjects. It is designated as LD_{50} and is commonly used to express toxicities.

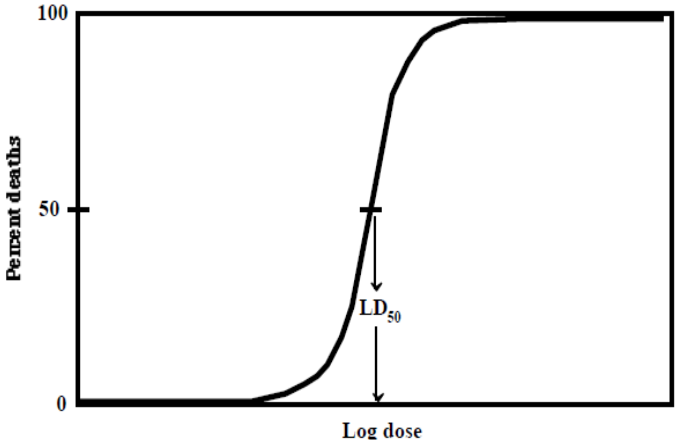


Figure 5.2 Illustration **of dose – response curve in which the response is the death of the organism. The cumulative percentage of deaths of organisms is plotted on the Y axis.**

i) Relative toxicities

When there is a substantial difference between LD_{50} values of two different substances, the one with the lower value is said to be the more **potent**. Such a comparison must assume that the dose-response curves for the two substances being compared have similar slopes.

ii) Nonlethal Effects

So far, toxicities have been described primarily in terms of the ultimate effect death of organisms, or lethality. This is obviously an irreversible consequence of exposure. In many, and perhaps most, cases, **sublethal** and **reversible** effects are of greater importance. The **margin of safety** is used in connection with drugs to express the difference between the dose that gives a desired therapeutic effect and a harmful, potentially lethal, effect. This term applies to other substances, such as pesticides, for which it is desirable to have a large difference between the dose that kills a target species and that which harms a desirable species.

iii) Reversibility and sensitivity

Sub lethal doses of most toxic substances are eventually eliminated from an organism's system. If there is no lasting effect from the exposure, it is said to be reversible. In cases where the effect is permanent, it is termed irreversible. Irreversible effects of exposure remain after the toxic substance is eliminated from the organism. For various chemicals and different subjects, toxic effects can range from the totally reversible to the totally irreversible.

iv) Hypersensitivity and Hyposensitivity

Some subjects are very sensitive to a particular poison, whereas others are very resistant to the same substance. These two kinds of responses illustrate hypersensitivity and hyposensitivity, respectively; subjects in the mid-range of the dose-response curve are termed normals. These variations in response tend to complicate toxicology in that there is no specific dose guaranteed to yield a particular response, even in a homogeneous population.

In some cases, hypersensitivity is an induced response to exposure to a substance. After one or more doses of a chemical, a subject may develop an extreme reaction to it. This occurs with penicillin, for example, in cases where people develop such a severe allergic response to the antibiotic that exposure is fatal if countermeasures are not taken.

5.2. Organic and Inorganic Pollutants

Dear student, in the previous content, you have introduced about toxicity and toxicology. Now you learn about organic and inorganic pollutants. Let warm up yourself with the following activities.

Learning task 5.2

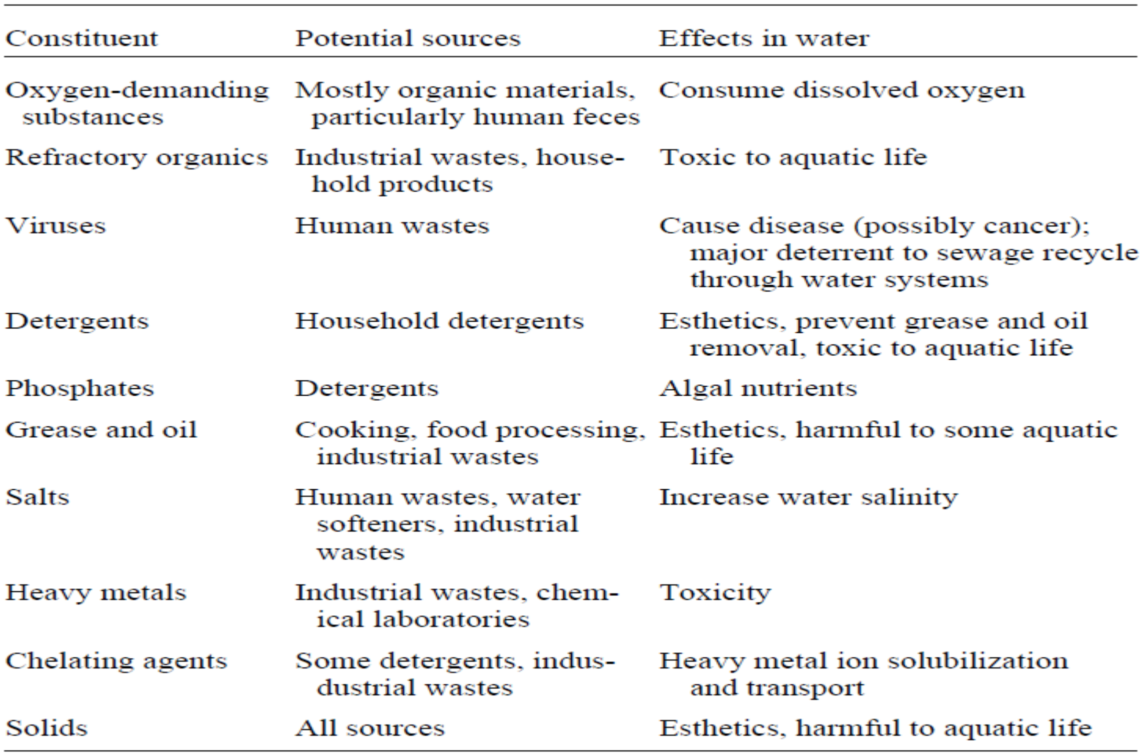
a) Define pollutants
b) Compare and contrast organic and inorganic pollutants
c) Explain how Soaps, detergents, and associated chemicals are potential sources of organic pollutants.
d) Explain the source and effects of sewage on some of the primary constituents of sewage from a city Sewage system

5.2.1. Organic pollutants

Sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants, including organic pollutants. Some of these pollutants, particularly oxygen demanding substances oil, grease and solids are removed by primary and secondary sewage treatment processes. Others, such as salts, heavy metals, and refractory (degradation-resistant) organics, are not efficiently removed.

Disposal of inadequately treated sewage can cause severe problems. For example, offshore disposal of sewage, once commonly practiced by coastal cities, results in the formation of beds of sewage residues. Municipal sewage typically contains about 0.1% solids, even after treatment, and these settle out in the ocean in a typical pattern. The warm sewage water rises in the cold hypolimnion and is carried laterally by tides or currents. Rising to the thermocline, it spreads out as a cloud from which the solids rain down on the ocean floor. Aggregation of sewage colloids is aided by dissolved salts in seawater, thus promoting the formation of sludge-containing sediment.

Table 5.2.1 some of the primary constituents of sewage from a city sewage system



Constituent	Potential sources	Effects in water
Oxygen-demanding substances	Mostly organic materials, particularly human feces	Consume dissolved oxygen
Refractory organics	Industrial wastes, household products	Toxic to aquatic life
Viruses	Human wastes	Cause disease (possibly cancer); major deterrent to sewage recycle through water systems
Detergents	Household detergents	Esthetics, prevent grease and oil removal, toxic to aquatic life
Phosphates	Detergents	Algal nutrients
Grease and oil	Cooking, food processing, industrial wastes	Esthetics, harmful to some aquatic life
Salts	Human wastes, water softeners, industrial wastes	Increase water salinity
Heavy metals	Industrial wastes, chemical laboratories	Toxicity
Chelating agents	Some detergents, indusdustrial wastes	Heavy metal ion solubilization and transport
Solids	All sources	Esthetics, harmful to aquatic life

Careful control of sewage sources is needed to minimize sewage pollution problems. Particularly, heavy metals and refractory organic compounds need to be controlled at the source to enable use of sewage, or treated sewage effluents, for irrigation, recycling to the water system, or groundwater recharge. Soaps, detergents, and associated chemicals are potential sources of organic pollutants.

5.2.1.1 Soaps, Detergents, and Detergent Builders

i) Soaps

Dear student, can you explain what soaps are?

Soaps are salts of higher fatty acids, such as sodium stearate, $C_{17}H_{35}COO\text{-}Na^{+}$. Soap's cleaning action results largely from its emulsifying power and its ability to lower the surface tension of water. This concept can be understood by considering the dual nature of the soap anion. An examination of its structure shows that the stearate ion consists of an ionic carboxyl “head” and a long hydrocarbon “tail”:

In the presence of oils, fats, and other water-insoluble organic materials, the tendency is for the “tail” of the anion to dissolve in the organic matter, whereas the “head” remains in aquatic solution. Thus, the soap emulsifies, or suspends, organic material in water. In the process, the anions form colloidal soap micelles in which the hydrocarbon “tails” of the soap anion are clustered inside the small colloidal particle and the carboxylate anion “heads” are located on the surface of the colloidal particle. The primary disadvantage of soap as a cleaning agent comes from its reaction with divalent cations to form insoluble salts of fatty acids:

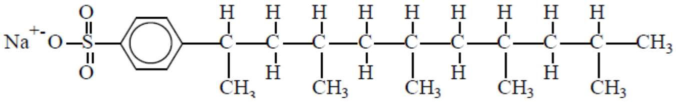
$$2C_{17}H_{35}COO^{-}Na^{+} + Ca^{2+} \rightarrow Ca(C_{17}H_{35}CO_2)_2(s) + 2Na^{+}$$

ii) Detergents

Dear student, can you define detergents?

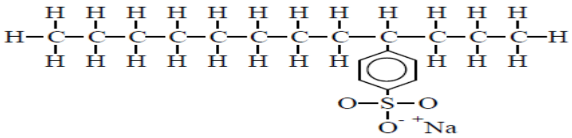
Detergents are synthetic cleansing agents that have good cleaning properties and do not form insoluble salts with “hardness ions” such as calcium and magnesium. Such synthetic detergents have the additional advantage of being the salts of relatively strong acids and, therefore, they do not precipitate out of acidic waters as insoluble acids, an undesirable characteristic of soaps. The potential of detergents to contaminate water is high because of their heavy use throughout the consumer, institutional, and industrial markets.

The key ingredient of detergents is the **surfactant** or surface-active agent, which acts in effect to make water “wetter” and a better cleaning agent. Surfactants concentrate at interfaces of water with gases (air), solids (dirt), and immiscible liquids (oil). They do so because of their **amphiphilic structure**, meaning that one part of the molecule is a polar or ionic group (head) with a strong affinity for water, and the other part is a hydrocarbon group (tail) with an aversion to water. This kind of structure is illustrated below for the structure of alkyl benzene sulfonate (ABS) surfactant:



Until the early 1960s, ABS was the most common surfactant used in detergent formulations. However, it suffered the distinct disadvantage of being only very slowly biodegradable because of its branched-chain structure, which is particularly difficult for microorganisms to metabolize.

Among the other undesirable effects of persistent detergents upon waste-treatment processes were lowered surface tension of water; deflocculation of colloids; flotation of solids; emulsification of grease and oil; and destruction of useful bacteria. Consequently, ABS was replaced by a biodegradable surfactant known as linear alkyl sulfonate LAS. LAS, β–benzenesulfonate, has the following general structure where the benzene ring may be attached at any point on the alkyl chain except at the ends.



LAS is more biodegradable than ABS because the alkyl portion of LAS is not branched and does not contain the tertiary carbon that is so detrimental to biodegradability. Since LAS has replaced ABS in detergents, the problems arising from the surface-active agent in the detergents (such as toxicity to fish fingerlings) have greatly diminished and the levels of surface-active agents found in water have decreased markedly.

Most of the environmental problems currently attributed to detergents do not arise from the surface-active agents, which basically improve the wetting qualities of water. The **builders** added to detergents continued to cause environmental problems for a longer time, however. Builders bind to hardness ions, making the detergent solution alkaline and greatly improving the action of the detergent surfactant. A commercial solid detergent contains only 10–30 % surfactant.

In addition, some detergents still contain polyphosphates added to complex calcium and to function as builders. Other ingredients include ion exchangers, alkalies (sodium carbonate), anti-corrosive sodium silicates, amide foam stabilizers, soil-suspending carboxymethyl cellulose, bleaches, fabric softeners, enzymes, optical brighteners, fragrances, dyes, and diluent sodium sulfate. Of these materials, the polyphosphates have caused the most concern as environmental pollutants, although these problems have largely been resolved.

Increasing demands on the performance of detergents have led to a growing use of enzymes in detergent formulations destined for both domestic and commercial applications. To a degree, enzymes can take the place of chlorine and phosphates, both of which can have detrimental environmental consequences.

5.2.1.2 Bio-refractory Organic Pollutants

Dear student, can you explain bio-refractory Organic Pollutants?

Bio-refractory organics are the organic compounds of most concern in waste water, particularly when they are found in sources of drinking water. These are poorly biodegradable substances, prominent among which are aromatic or chlorinated hydrocarbons.

The most common bio refractory organic industrial wastes are benzene, bornyl alcohol, bromobenzene, bromochlorobenzene, butyl benzene, camphor chloroethyl ether, chloroform, chloromethylethyl ether, chloronitrobenzene, chloropyridine, dibromobenzene, dichlorobenzene, chloroethyl ether, dinitrotoluene, ethylbenzene, ethylene dichloride, 2-ethylhexanol, isocyanic acid, isopropyl-benzene, methylbiphenyl, methyl chloride, nitrobenzene, styrene, tetrachloroethylene, trichloroethane, toluene, 1,2-dimethoxybenzene and methyl tert-butyl ether (MTBE). Many of these compounds have been found in drinking water, and some are known to cause taste and odor problems in water.

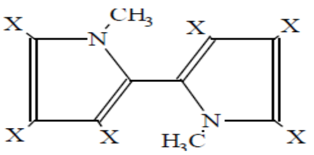
Bio refractory compounds are not completely removed by biological treatment, and water contaminated with these compounds must be treated by physical and chemical means, including air stripping, solvent extraction, ozonation, and carbon adsorption.

5.2.1.3 Naturally Occurring Chlorinated and Brominated Compounds

Dear student, can you mention some of naturally occurring chlorinated and brominated Compounds?

Although halogenated organic compounds in water are normally considered to be from anthropogenic sources, approximately 2400 such compounds have been identified from natural sources. These are produced largely by marine species, especially some kinds of red algae, probably as chemical defense agents. Some marine microorganisms, worms, sponges, and tunicates are also known to produce organochlorine and organobromine compounds.

An interesting observation has been made of the possible bio-accumulation of a class of compounds with the formula $C_{10}H_6N_2Br_4Cl_2$ in several species of sea birds from the Pacific Ocean region. Although the structural formula of the compound could not be determined with certainty, mass spectral data indicate that it is 1,1'-dimethyl-tetrabromodichloro-2,2'-bipyrrole.



X is Br (4) and Cl (2)

5.2.2. Inorganic pollutants

Dear student, in the previous content, you have introduced about Inorganic pollutants. Now you learn about Inorganic pollutants. Let warm up yourself with the following activities.

Learning task 5.2.2

a) Define inorganic pollutants
b) Mention some of the major inorganic pollutants
c) Explain the source of inorganic pollutants
d) Explain the source of Algal nutrients and Eutrophication
e) Explain how of inorganic pollutants contributes acidity, alkalinity, and salinity to water

Some important inorganic water pollutants are trace elements. Inorganic pollutant contributes to acidity, alkalinity, or salinity to water. Still another class is that of algal nutrients. Some important inorganic pollutant species are cyanide ion, ammonia, carbon dioxide, hydrogen sulfide, nitrite, and sulfite.

i) Cyanide (CN^-)

Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid, K_a of $6x10^{-10}$. The cyanide ion has a strong affinity for many metal ions, forming relatively less-toxic ferrocyanide, $Fe\ (CN)_6^{4-}$, with iron (II), for example. Volatile HCN is very toxic and has been used in gas chamber executions.

Cyanide is widely used in industry, especially for metal cleaning and electro- plating. It is also one of the main gas and coke scrubber effluent pollutants from gas works and coke ovens. Cyanide is widely used in certain mineral-processing operations.

ii) Ammonia (NH_3)

Excessive levels of ammoniacal nitrogen cause water-quality problems. **Ammonia** is the initial product of the decay of nitrogenous organic wastes, and its presence frequently indicates the presence of such wastes. It is a normal constituent of low-pE ground waters and is sometimes added to drinking water, where it reacts with chlorine to provide residual chlorine. Since the pK_a of ammonium ion, NH_4^+, is 9.26, most ammonia in water is present as NH_4^+ rather than as NH_3.

iii) Hydrogen sulfide (H_2S)

Hydrogen sulfide is a product of the anaerobic decay of organic matter containing sulfur. It is also produced in the anaerobic reduction of sulfate by microorganisms and is evolved as a gaseous pollutant from geothermal waters. Wastes from chemical plants, paper mills, textile mills, and tanneries may also contain H_2S. Its presence is easily detected by its characteristic rotten-egg odor. In water, H_2S is a weak diprotic acid with $pK_{a1}$of 6.99 and pK_{a2} of 12.92; S^{2-} is not present in normal natural waters. The sulfide ion has tremendous affinity for many heavy metals, and precipitation of metallic sulfides often accompanies production of H_2S.

iv) Carbon dioxide (CO_2)

Carbon dioxide is frequently present in water at high levels due to decay of organic matter. It is also added to softened water during water treatment as part of a recarbonation process. Excessive carbon dioxide levels may make water more corrosive, therefore, damaging to water distribution systems, and may be harmful to aquatic life.

V) Nitrite ion (NO_2^-)

Nitrite ion (NO_2^-) occurs in water as an intermediate oxidation state of nitrogen over a relatively narrow pE range. Nitrite is added to some industrial process water as a corrosion inhibitor. However, it rarely occurs in drinking water at levels over 0.1 mg/L.

vi) Sulfite ion ($SO_3^{2-)}$

Sulfite ion ($SO_3^{2-)}$ is found in some industrial wastewaters. Sodium sulfite is commonly added to boiler feed waters as an oxygen scavenger where it reacts to remove potentially corrosive dissolved molecular oxygen from the water:

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$

Since pK_{a1} of sulfurous acid is 1.76 and pK_{a2} is 7.20, sulfite exists as either HSO_3 or $SO_3\ ^{2-}$ in natural waters, depending upon pH.

vii) Asbestos

The toxicity of inhaled asbestos is well established. The fibers scar lung tissue and cancer eventually develops often 20 or 30 years after exposure. It is not known for sure whether asbestos is toxic in drinking water. This has been a matter of considerable concern because of the dumping of taconite (iron ore tailings) containing asbestos-like fibers into Lake Superior. The fibers have been found in drinking waters of cities around the lake.

Algal nutrients and Eutrophication

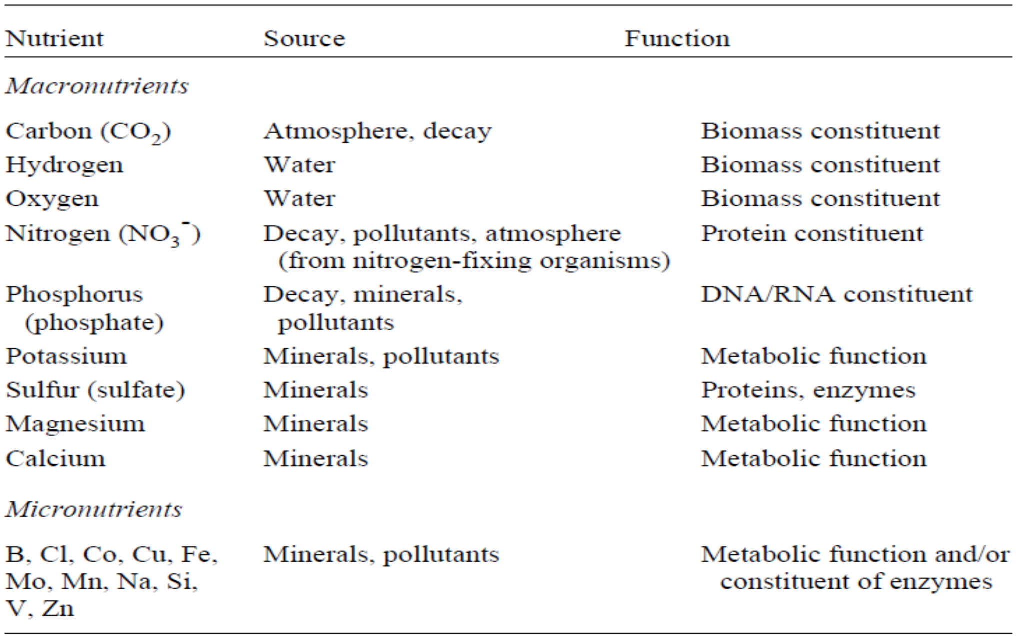
Dear student, can you define Eutrophication?

The term **eutrophication**, derived from the Greek word meaning “well- nourished,” describes a condition of lakes or reservoirs involving excess algal growth. Although some algal productivity is necessary to support the food chain in an aquatic ecosystem, excess growth under eutrophic conditions may eventually lead to severe deterioration of the body of water. The first step in eutrophication of a body of water is an input of plant nutrients from watershed runoff or sewage.

The nutrient-rich body of water then produces a great deal of plant biomass by photosynthesis, along with a smaller amount of animal biomass. Dead biomass accumulates in the bottom of the lake, where it undergoes partial mineralization, recycling nutrient carbon dioxide, phosphorus, nitrogen, and potassium. If the lake is not too deep, bottom-rooted plants begin to grow, accelerating the accumulation of solid material in the basin. Eventually, a marsh is formed that finally fills in to produce a meadow or forest.

Eutrophication is often a natural phenomenon; for instance, it is basically responsible for the formation of huge deposits of coal and peat. However, human activity can greatly accelerate the process. Most of these are present at levels more than sufficient to support plant life in the average lake or reservoir. Hydrogen and oxygen come from the water itself. Carbon is provided by CO_2 from the atmosphere or from decaying vegetation.

Table 5.2.2 Essential plant Nutrients: sources and Functions



Nutrient	Source	Function
Macronutrients		
Carbon (CO_2)	Atmosphere, decay	Biomass constituent
Hydrogen	Water	Biomass constituent
Oxygen	Water	Biomass constituent
Nitrogen (NO_3^-)	Decay, pollutants, atmosphere (from nitrogen-fixing organisms)	Protein constituent
Phosphorus (phosphate)	Decay, minerals, pollutants	DNA/RNA constituent
Potassium	Minerals, pollutants	Metabolic function
Sulfur (sulfate)	Minerals	Proteins, enzymes
Magnesium	Minerals	Metabolic function
Calcium	Minerals	Metabolic function
Micronutrients		
B, Cl, Co, Cu, Fe, Mo, Mn, Na, Si, V, Zn	Minerals, pollutants	Metabolic function and/or constituent of enzymes

Sulfate, magnesium, and calcium are normally present in abundance from mineral strata in contact with the water. The micronutrients are required at only very low. Therefore, the nutrients most likely to be limiting are the “fertilizer” elements: nitrogen, phosphorus, and potassium. These are all present in sewage and are, of course, found in runoff from heavily fertilized fields. They are also constituents of various kinds of industrial wastes. Each of these elements can also come from natural sources phosphorus and potassium from mineral formations, and nitrogen fixed by bacteria, cyanobacteria, or discharge of lightning in the atmosphere.

In most cases, the single plant nutrient most likely to be limiting is phosphorus, and it is generally named as the culprit in excessive eutrophication. Household detergents are a common source of phosphate in wastewater, and eutrophication control has concentrated upon eliminating phosphates from detergents, removing phosphate at the sewage treatment plant, and preventing phosphate-laden sewage effluents from entering bodies of water.

In some cases, nitrogen or even carbon may be limiting nutrients. This is particularly true of nitrogen in seawater. The whole eutrophication picture is a complex one, and continued research is needed to solve the problem. It is indeed ironic that in a food-poor world, nutrient- rich wastes from over fertilized fields or from sewage are causing excessive plant growth in many lakes and reservoirs. This illustrates a point that, in many cases, pollutants are resources (in this case, plant nutrients) gone to waste.

Acidity, alkalinity, and salinity

Dear student, can you define Acidity, alkalinity, and salinity?

Aquatic biota is sensitive to extremes of pH. Largely because of osmotic effects, they cannot live in a medium having a salinity to which they are not adapted. Thus, a freshwater fish soon succumbs in the ocean, and sea fish normally cannot live in fresh water. Excess salinity soon kills plants not adapted to it. There are, of course, ranges in salinity and pH in which organisms live. As shown in Figure 12.2, these ranges frequently can be represented by a reasonably symmetrical curve, along the fringes of which an organism may live without really thriving.

The most common source of **pollutant acid** in water is acid mine drainage. Acid mine water results from the presence of sulfuric acid produced by the oxidation of pyrite, FeS2. Microorganisms are closely involved in the overall process, which consists of several reactions. The first of these reactions is the bacterially mediated oxidation of pyrite:

$$2FeS_2(s) + 2H_2O + 7O_2 \rightarrow 4H^+ + 4SO_4^{2-} + 2Fe^{2+}$$

The next step is the oxidation of iron (II) ion to iron (III) ion,

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

a process that occurs very slowly by purely chemical processes at the low pH values found in acid mine waters, but is accelerated by the action of bacteria. Below pH 3.5, the iron oxidation is catalyzed by the iron bacterium Thiobacillus ferrooxidans, and in the pH range 3.5-4.5 it may be catalyzed by a variety of Metallogenium, a filamentous iron acterium. Other bacteria that may be involved in acid mine water formation are Thiobacillus thiooxidansand Ferrobacillus ferrooxidans. The Fe3+ ion further dissolves pyrite,

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

$Fe(H_2O)_6^{3+}$ is an acidic ion and at pH values much above 3, the iron (III) precipitates as the hydrated iron (III) oxide:

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+$$

The beds of streams afflicted with acid mine drainage often are covered with “yellow boy,” an unsightly deposit of amorphous, semi gelatinous $Fe(OH)_3$. The most damaging component of acid mine water is sulfuric acid. It is directly toxic and has other undesirable effects. The values of pH encountered in acid polluted water may fall below 3, a condition deadly to most forms of aquatic life except the culprit bacteria mediating the pyrite and iron (II) oxidation, which thrive under very low pH conditions.

Industrial wastes frequently have the potential to contribute strong acid to water. Sulfuric acid produced by the air oxidation of pollutant sulfur dioxide enters natural waters as acidic rainfall. In cases where the water does not have contact with a basic mineral, such as limestone, the water pH may become dangerously low.

Excess **alkalinity** and frequently accompanying high pH, generally are not introduced directly into water from anthropogenic sources. However, in many geographic areas, the soil and mineral strata are alkaline and impart a high alkalinity to water. Human activity can aggravate the situation-for example, by exposure of alkaline overburden from strip mining to surface water or groundwater. Excess alkalinity in water is manifested by a characteristic fringe of white salts at the edges of a body of water or on the banks of a stream.

Water salinity may be increased by a number of human activities. Water passing through a municipal water system inevitably picks up salt from a number of processes; for example, recharging water softeners with sodium chloride is a major contributor to salinity in municipal wastewater. Salts can leach from spoil piles. One of the major environmental constraints on the production of shale oil, for example, is the high percentage of leachable sodium sulfate in piles of spent shale. Careful control of these wastes is necessary to prevent further saline pollution of water in areas where salinity is already a problem.

5.3. Agricultural and Pharmaceutical Contaminants

Dear student, in the previous content, you have introduced about organic and inorganic pollutants. Now you learn about Agricultural and Pharmaceutical Contaminants. Let warm up yourself with the following activities.

Learning task 5.3

a) Define contaminant
b) Explain the source and effects of Agricultural contaminants
c) Mention the common Agricultural contaminants
d) Explain the source and effects of Pharmaceutical contaminants
e) Mention the common Pharmaceutical contaminants

5.3.1 Agricultural Contaminants

5.3.1.1 Fertilizers

One of the common Agricultural contaminants is fertilizers. Crop fertilizers contain nitrogen, phosphorus and potassium as major components. Magnesium, sulfate and micronutrients may also be added. Fertilizers are designated by numbers, such as 6-12-8, showing the respective percentages of nitrogen expressed as N (in this case 6%), phosphorus as P_2O_5 (12%), and potassium as K_2O (8%).

Farm manure corresponds to an approximately 0.5-0.24-0.5 fertilizer. The organic fertilizers such as manure must undergo biodegradation to release the simple inorganic species (NO_3^-, $H_xPO_4^{x-3}$, K^+) assimilable by plants.

i) **Nitrogen fertilizers**

Most modern nitrogen fertilizers are made by the Haber process, in which N_2 and H_2 are combined over a catalyst at temperatures of approximately 500˚C and pressures up to 1000 atm:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The anhydrous ammonia product has a very high nitrogen content of 82%. It can be added directly to the soil, for which it has a strong affinity because of its water solubility and formation of ammonium ion:

$$NH_3(g)\ \text{(water)} \rightarrow NH_3(aq)$$

$$NH_3(aq) + H_2O \rightarrow NH_4^+ + OH^-$$

Special equipment is required, however, because of the toxicity of ammonia gas. Aqua ammonia, a 30% solution of NH_3 in water, can be used with much greater safety. It is sometimes added directly to irrigation water. It should be pointed out that ammonia vapor is toxic and NH_3 is reactive with some substances. Improperly discarded or stored ammonia can be a hazardous waste.

Ammonium nitrate, NH_4NO_3, is a common solid nitrogen fertilizer. It is made by oxidizing ammonia over a platinum catalyst, converting the nitric oxide product to nitric acid and reacting the nitric acid with ammonia. Ammonium nitrate contains 33.5% nitrogen. Although convenient to apply to soil, it requires considerable care during manufacture storage and use because it is explosive and toxic. It is mixed with fuel oil to form an explosive that serves as a substitute for dynamite in quarry blasting and construction.

Urea is another nitrogen fertilizer which is easier to manufacture and handle than ammonium nitrate. It is now the favored solid nitrogen-containing fertilizer. The overall reaction for urea synthesis is:

$$CO_2 + 2NH_3 \rightarrow CO(NH_2)_2 + H_2O$$

involving a rather complicated process in which ammonium carbamate, chemical formula $NH_2CO_2NH_4$, is an intermediate. Other compounds used as nitrogen fertilizers include sodium nitrate, calcium nitrate, potassium nitrate, and ammonium phosphates. Ammonium sulfate, a by-product of coke ovens, used to be widely applied as fertilizer. The alkali metal nitrates tend to make soil alkaline, whereas ammonium sulfate leaves an acidic residue.

ii) **Phosphorous fertilizers**

The principal mineral is fluorapatite, $Ca_5(PO_4)_3F$. The phosphate from fluorapatite is relatively unavailable to plants, and fluorapatite is frequently treated with phosphoric or sulfuric acids to produce superphosphates:

$$2Ca_5(PO4)_3F(s) + 14H_3PO_4 + 10H_2O \rightarrow 2HF(g) + 10Ca(H_2PO_4)_2 \bullet H_2O$$

$$2Ca_5(PO_4)_3F(s) + 7H_2SO_4 + 3H_2O \rightarrow 2HF(g) + 3Ca(H_2PO_4)2 \bullet H_2O + 7CaSO_4$$

The superphosphate products are much more soluble than the parent phosphate minerals. The HF produced as a byproduct of superphosphate production can create air pollution problems.

Phosphate minerals are rich in trace elements required for plant growth, such as boron, copper, manganese, molybdenum, and zinc. Ironically, these elements are lost to a large extent when the phosphate minerals are processed to make fertilizer.

Ammonium phosphates are excellent, highly soluble phosphate fertilizers. Liquid ammonium polyphosphate fertilizers consisting of ammonium salts of pyrophosphate, triphosphate, and small quantities of higher polymeric phosphate anions in aqueous solution work very well as phosphate fertilizers. The polyphosphates are believed to have the additional advantage of chelating iron and other micronutrient metal ions, thus making the metals more available to plants.

iii) Potassium fertilizer

Potassium fertilizer components consist of potassium salts, generally KCl. Such salts are found as deposits in the ground or can be obtained from some brine. Very large deposits are found in Saskatchewan, Canada. These salts are all quite soluble in water. One problem encountered with potassium fertilizers is the luxury uptake of potassium by some crops, which absorb more potassium than is really needed for their maximum growth. In a crop where only the grain is harvested, leaving the rest of the plant in the field, luxury uptake does not create much of a problem because most of the potassium is returned to the soil with the dead plant. However, when hay or forage is harvested, potassium contained in the plant as a consequence of luxury uptake is lost from the soil.

5.3.1.2 Agricultural pesticides/ insectcides

Dear student, do you know about pesticides?

Pesticides are designed chemical substances to kill one or more types of living organisms. Give at least few examples of these compounds. There is always concern about the risk that they pose to other, non-target, organisms. The extent of the risk that a pesticide poses to the environment and human health depends, in large measure, on what happens to that pesticide after application. Two key factors are the length of time the pesticide remains in an active form in the environment, and the likelihood of the pesticide to move from the point of application.

An ideal pesticide would be one that would remain in the environment just long enough to accomplish its intended purpose, and then quickly break down into harmless compounds. In reality, pesticides vary greatly in their potential for causing damage. Some pose little risk to either the environment or to human health. Others can represent a significant hazard if they are not managed carefully.

i) Pesticides affecting pesticides environmental processes

Dear student, do you know how Environmental processes affecting pesticides?

After application in a field, pesticides are subjected to three main types of processes:

- **Adsorption -** pesticides can become attached to particles of soil or organic matter
- **Transfer -** they can be moved from the point to which they were applied
- **Degradation -** they can be broken down into less complex compounds.

The extent to which each of these processes act upon a pesticide varies depending on: the properties of the pesticide, the soil, the weather and the crop

Adsorption

Dear student, can you define adsorption?

Some pesticides are strongly attracted to soil particles and are held tightly by them. Pesticide held in this way is no longer active for controlling pests or causing damage to the environment. Adsorbed pesticides are also not prone to leaching, and therefore pose a low risk of groundwater contamination.

Transfer

Dear student, can you define transfer?

Pesticides can be moved from the point to which they were applied in a variety of ways:

- **volatilization** (evaporation)
- **runoff -** movement in water across the surface of land
- **leaching -** movement through the soil towards groundwater
- **plant uptake-** Pesticides are applied either to the soil or to the foliage. In either case, some pesticide is likely to taken into the plant through either the roots or leaves

Volatilization is the conversion of a solid or liquid into a gas and movement into the atmosphere. Once in the air, pesticide vapours move wherever they are taken by the wind and other air currents. Clearly, this is not desirable either for effective pest control or for environmental protection. Many pesticides are not volatile and thus are no cause for concern in this regard. Those that are prone to volatilization are formulated to minimize their volatility as much as possible, and are applied in ways designed to reduce the risk. For example, some highly volatile pesticides are worked into the soil at application to minimize their exposure to the atmosphere.

Runoff is the movement of water over the soil surface when rain falls faster than it can be absorbed by the soil. Pesticides can move from a field in runoff water (also called surface water), either dissolved in the water itself or attached to soil particles being eroded from the field. The amount of runoff depends on many factors:

- the type of soil (greater on clay than on sand)
- the slope of the land (the steeper the slope, the greater the potential for runoff)
- the condition of the soil surface (more runoff from bare soil than from fields covered with living crops or crop residues)
- the amount and intensity of rainfall following application

- the moisture content of the soil (the wetter the soil to begin with, the less rain it can absorb)
- the length of time after application before rain (the greater the time between application and rainfall, the less pesticide there will be in the runoff)

Leaching refers to the movement of materials down through the soil with water. The risk of a product being leached depends on its solubility in water, its tendency to be bound to soil particles and its persistence. To be leached, a pesticide must first be dissolved in the soil water. The longer the pesticide remains in its active form in the soil water, the greater the risk of it leaching into the groundwater. Most pesticides are either adsorbed by the soil or degraded before they can be leached. Few pesticides have the combination of properties that make them prone to leaching in quantities that pose a significant risk to groundwater quality. Leaching also depends on the characteristics of the field: it is more likely to occur in sandy or gravelly soils, in soils that are low in organic matter, and on flat rather than sloping land.

Plant uptake

Pesticides are applied either to the soil or to the foliage. In either case, some pesticide is likely to taken into the plant through either the roots or leaves. Pesticide taken up by plants is protected against runoff or leaching. Once within crop plants, pesticides are degraded through chemical reactions.

Degradation

Dear student, can you define degradation?

With the possible exception of pesticides that have leached into the groundwater, all pesticides are eventually degraded into harmless components in a variety of ways:

- Microbial breakdown: the pesticide is broken down (i.e., ‘eaten’) by fungi, bacteria or other micro-organisms living in the soil, on the surface of plants or in surface water.
- Chemical degradation: the pesticide reacts with other compounds in the soil, especially water, to form non-toxic compounds.
- Photo-decomposition: some pesticides are broken down by sunlight.

5.3.2 Pharmaceutical Contaminants

Dear student what are Pharmaceutical contaminants? What are the source and effects of Pharmaceutical contaminants? Can you mention the common Pharmaceutical Contaminants?

Pharmaceutical agents are greatly increasing in numbers and kinds, with greater likelihood of releases into the environment. Certain pharmaceuticals are now attracting attention as a potentially new class of water pollutants. Such drugs are: antibiotics, anti-depressants, anti-cancer drugs, pain killers, cholesterol-lowering agents, steroids, caffeine and reproductive hormones have been detected in various water sources. The presence of pharmaceuticals in our water ways and drinking water has gained national attention among lawmakers, regulators, and the public.

Pharmaceutical Contaminants come from different sources. The main ones are: Pharmaceutical industries, hospitals and other medical facilities are obvious sources, but households also contribute a significant share. People often dispose of unused medicines by flushing them down toilets, and human excreta can contain varied incompletely metabolized medicines. These drugs can pass intact through conventional sewage treatment facilities, into waterways, lakes and even aquifers. Further, discarded pharmaceuticals often end up at dumps and landfills, posing a threat to underlying groundwater.

Permanent developmental abnormalities have also been suspected from low-level exposures in other species, with mounting evidence that the contamination of waterways is causing interest fish in our nation’s rivers and drinking water sources. Identifying the Major sources of contamination there are many paths for pharmaceuticals to reach our water systems, with some releases being intentional and others unintentional. Much of the identified waste stems from agricultural uses, human excretion, and improper disposal of drugs by households and medical facilities, and drug manufacturing processes.

5.4. Pesticides

Dear student, in the previous content, you have introduced about Agricultural and Pharmaceutical Contaminants. Now you learn about pesticides. Let warm up yourself with the following activities.

Learning task 5.4

a) Define pesticides and Insecticides
b) Compare and contrast organochlorine pesticides and organophosphate pesticides
c) Define Herbicides and give examples of Herbicide
d) Explain the effect of pesticides in the Environment

Pesticides

A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest. A pesticide may be a chemical substance, biological agent (such as a virus or bacterium), antimicrobial, disinfectant or device used against any pest. The introduction of DDT during World War II marked the beginning of a period of very rapid growth in pesticide use.

Pesticides are employed for many different purposes. Chemicals used in the control of invertebrates include insecticides, molluscicides for the control of snails and slugs, and nematicides for the control of microscopic roundworms. Vertebrates are controlled by rodenticides, which kill rodents, avicides used to repel birds, and piscicides used in fish control.

Herbicides are used to kill plants. Plant growth regulators, defoliants, and plant desiccants are used for various purposes in the cultivation of plants. Fungicides are used against fungi, bactericides against bacteria, slimicides against slime-causing organisms in water, and algicides against algae. Herbicide production has increased as chemicals have increasingly replaced cultivation of land in the control of weeds and now accounts for the majority of agricultural pesticides. The potential exists for large quantities of pesticides to enter water either directly, in applications such as mosquito control or indirectly, primarily from drainage of agricultural lands.

5.4.1 Insecticides from natural source product, Pyrethrins and Pyrethroids

Dear student, can you define natural Product Insecticides, pyrethrins and pyrethroids?

Several significant classes of insecticides are derived from plants. These include nicotine from tobacco, rotenone extracted from certain legume roots, and pyrethrins. Because of the ways that they are applied and their biodegradabilities, these substances are unlikely to be significant water pollutants. Pyrethrins and their synthetic analogs represent both the oldest and newest of insecticides.

Pyrethrins have several advantages as insecticides, including facile enzymatic degradation, which makes them relatively safe for mammals; ability to rapidly paralyze (“knock down”) flying insects; and good biodegradability characteristics. Synthetic analogs of the pyrethrins, pyrethroids, have been widely produced as insecticides during recent years. The first of these was allethrin, and another common example is fenvalerate.

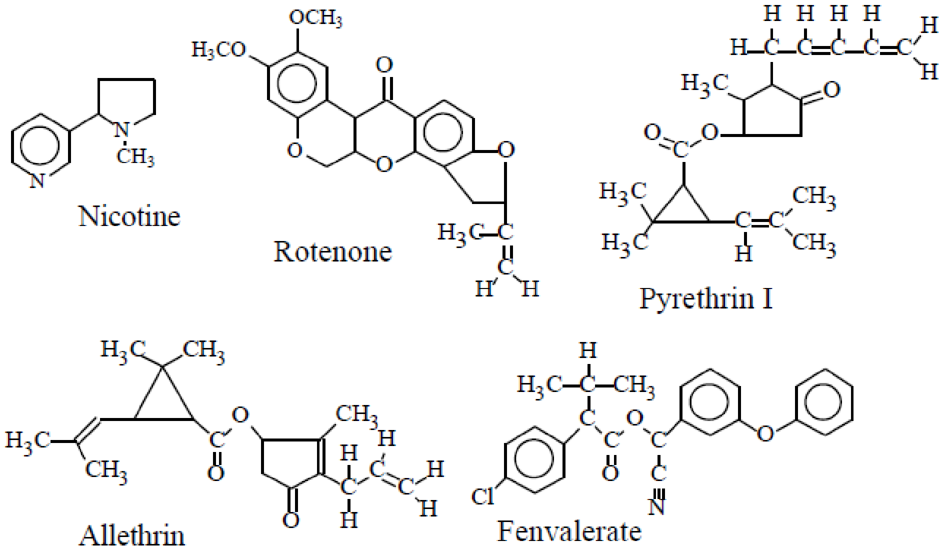


Figure 5.4 Common botanical insecticides and synthetic analogs of the pyrethrins

5.4.2 DDT and other Organochlorine Insecticides

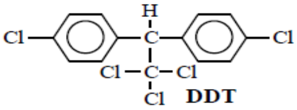
Dear student, what do you know about DDT and other Organochlorine Insecticides?

Chlorinated hydrocarbon or organochlorine insecticides are hydrocarbon compounds in which various numbers of hydrogen atoms have been replaced by Cl atoms. The structural formulas of several chlorinated hydrocarbon insecticides. It can be seen that the structural formulas of many of these insecticides are very similar; dieldrin and endrin are stereoisomers. The most commonly used insecticides in the 1960s; these compounds have been largely phased out of general use because of their toxicities, and particularly their accumulation and persistence in food chains. They are discussed briefly here, largely because of their historical interest, and because their residues in soils and sediments still contribute to water pollution.

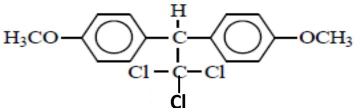
Among the organochlorine insecticides, the most notable has been **DDT**(dichlorodiphenyl-trichloroethane or 1, 1, 1-trichloro-2, 2-bis (4-chlorophenyl) ethane), which was used in massive quantities following World War II. It has a low acute toxicity to mammals, although there is some evidence that it might be carcinogenic. It is a very persistent insecticide and accumulates in food chains. It has been banned in the U.S. since 1972. For some time, **methoxychlor** was a popular DDT substitute, reasonably biodegradable, and with a low toxicity to mammals.

Structurally similar **chlordane**, **aldrin**, **dieldrin/endrin**, and **heptachlor**, all now banned for application in the U.S., share common characteristics of high persistence and suspicions of potential carcinogenicity. **Toxaphene** is a mixture of up to 177 individual compounds produced by chlorination of camphene, a terpene isolated from pine trees, to give a material that contains about 68% Cl and has an empirical formula of $C_{10}H_{10}Cl_8$. This compound had the widest use of any agricultural insecticide, particularly on cotton. It was employed to augment other insecticides, especially DDT, and in later years methyl parathion.

A mixture of five isomers, 1, 2, 3, 4, 5, 6-hexachlorocyclohexane has been widely produced for insecticidal use. Only the gamma isomer is effective as an insecticide, whereas the other isomers give the product a musty odor and tend to undergo bioaccumulation. A formulation of the essentially pure gamma isomer has been marketed as the insecticide called **lindane**.

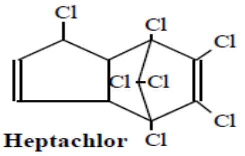


DDT



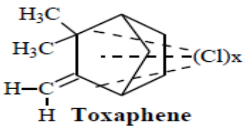
Methoxychlor

Dieldrin/Endrin



Heptachlor

Chlordane



Toxaphene

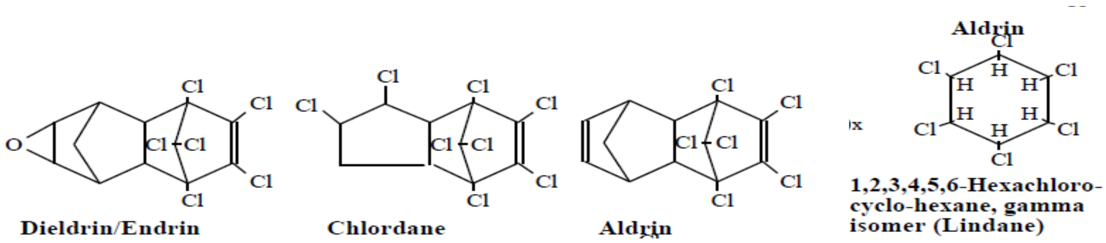


Figure 5.4.2 Common Organochlorine insecticides

5.4.3 Organophosphate insecticide

Dear student, what are Organophosphate insecticides?

An organophosphate insecticide is insecticidal organic compounds that contain phosphorus, some of which are organic esters of orthophosphoric acid, such as paraoxon. More commonly, insecticidal phosphorus compounds are phosphorothionate compounds, such as parathion or chlorpyrifos, which have an =S group rather than an =O group bonded to P.

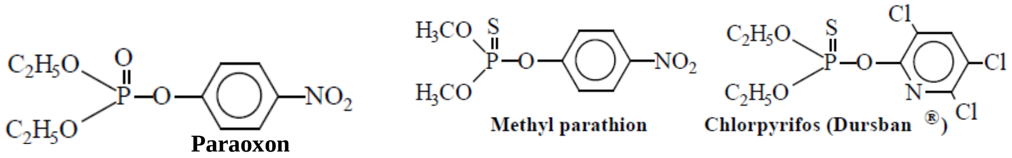
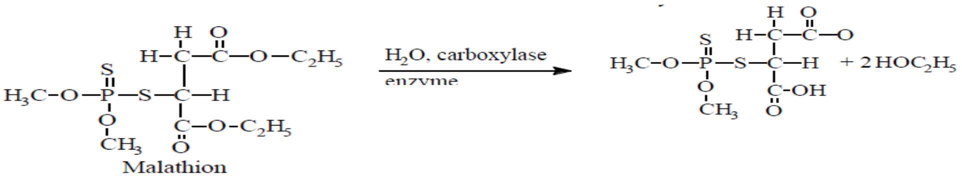


Figure 5.4.3 Common Organophosphorus insecticides

The toxicities of organophosphate insecticides vary a great deal. For example, as little as 120 mg of parathion has been known to kill an adult human, and a dose of only 2 mg has killed a child. Most accidental poisonings have occurred by absorption through the skin. Since its use began, several hundred people have been killed by parathion.

In contrast, **Malathion** shows how differences in structural formula can cause pronounced differences in the properties of organophosphate pesticides. Malathion has two carboxyester linkages that are hydrolysable by carboxylase enzymes to relatively nontoxic products, as shown by the following reaction.



The enzymes that accomplish Malathion hydrolysis are possessed by mammals, but not by insects, so mammals can detoxify Malathion and insects cannot. The result is that Malathion has selective insecticidal activity. For example, although Malathion is a very effective insecticide, its LD_{50} (dose required to kill 50% of test subjects) for adult male rats is about 100 times that of parathion, reflecting the much lower mammalian toxicity of malathion compared with some of the more toxic organophosphate insecticides, such as parathion.

Unlike the organohalide compounds they largely displaced, the organophosphates readily undergo biodegradation and do not bioaccumulate. Because of their high biodegradability and restricted use, organophosphates are of comparatively little significance as water pollutants.

5.4.4 Carbamates

Dear student, what are Carbamates?

Pesticidal organic derivatives of carbamic acid are known collectively as **carbamates**. Carbamate pesticides have been widely used because some are more biodegradable than the formerly popular organochlorine insecticides, and have lower dermal toxicities than most common organophosphate pesticides.

Carbaryl has been widely used as an insecticide on lawns or gardens. It has a low toxicity to mammals. **Carbofuran** has high water solubility and acts as a plant systemic insecticide. As such, it is taken up by the roots and leaves of plants so that insects are poisoned by the plant material on which they feed. **Pirimicarb** has been widely used in agriculture as a systemic aphicide. Unlike many carbamates, it is rather persistent, with a strong tendency to bind to soil. The toxic effects of carbamates to animals are due to the fact that these compounds inhibit acetylcholinesterase. Unlike some of the organophosphate insectcides, they do so without the need for undergoing a prior biotransformation and are therefore classified as direct inhibitors. Their inhibition of acetylcholinesterase is relatively reversible. Loss of acetylcholinesterase inhibition activity may result from hydrolysis of the carbamate ester, which can occur metabolically.

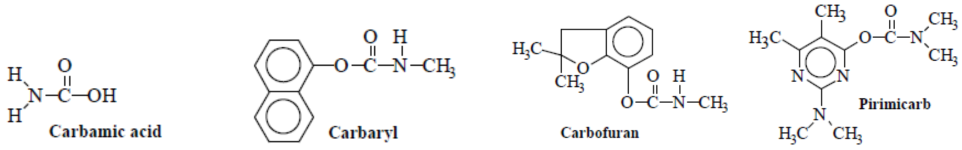

Carbamic acid
Carbaryl
Carbofuran
Pirimicarb

Figure 5.4.4 Carbamic acid and three insecticidal carbamates

5.4.5 Herbicides

Dear student, what are Herbicides? Can you mention different types of Herbicides?

Herbicides are substances that are used to control weeds. The herbicides named were atrazine, simazine, cyanazine, metolachlor, and alachlor, of which the first three are the most widely used. Herbicides are applied over millions of acres of farmland worldwide and are widespread water pollutants as a result of this intensive use.

Bipyridilium Compounds

A bipyridilium compound contains 2 pyridine rings per molecule. The two important pesticidal compounds of this type are the herbicides **diquat** and **paraquat**, the structural formulas of which are illustrated below:

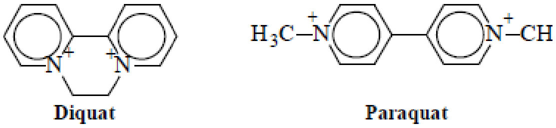


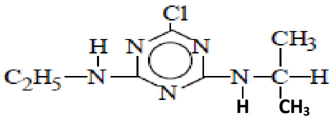
Figure 5.4.5 Two major bipyridilium herbicides (cation forms)

Other members of this class of herbicides include chlormequat, morfamquat, and difenzoquat. Applied directly to plant tissue, these compounds rapidly destroy plant cells and give the plant a frostbitten appearance. However, they bind tenaciously to soil, especially the clay mineral fraction, which results in rapid loss of herbicidal activity so that sprayed fields can be planted within a day or two of herbicide application.

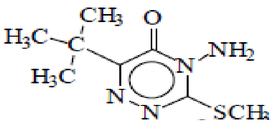
Paraquat, which was registered for use in 1965, has been one of the most used of the bipyridilium herbicides. Highly toxic, it is reputed to have "been responsible for hundreds of human deaths. Exposure to fatal or dangerous levels of paraquat can occur by all pathways, including inhalation of spray, skin contact, ingestion, and even suicidal hypodermic injections. Despite these possibilities and it's widespread application, paraquat is used safely without ill effects when proper procedures are followed. Because of its widespread use as a herbicide, the possibility exists of substantial paraquat contamination of food. Drinking water contamination by paraquat has also been observed.

Heterocyclic Nitrogen Compounds

A number of important herbicides contain three heterocyclic nitrogen atoms in ring structures and are therefore called **triazines**. Triazine herbicides inhibit photosynthesis. Selectivity is gained by the inability of target plants to metabolize and detoxify the herbicide. The longest established and common example of this class is atrazine, widely used on corn, and a widespread water pollutant in corn- growing regions. Another member of this class is metribuzin, which is widely used on soybeans, sugarcane, and wheat.



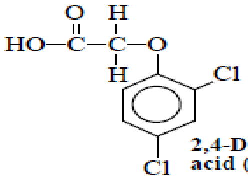
Atrazine



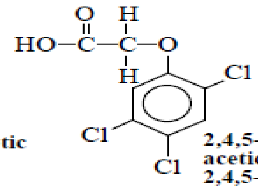
Metribuzin (Sencor®)

Cylclophenoxy herbicides

The chlorophenoxy herbicides, including 2, 4-D and 2, 4, 5-trichlorophenoxyacetic acid (2,4,5-T) shown below, were manufactured on a large scale for weed and brush control and as military defoliants. At one time, the latter was of particular concern because of contaminant that present as a manufacturing byproduct.



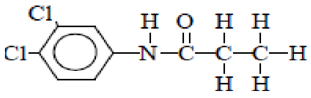
2,4-Dichlorophenoxyacetic acid (and esters), 2,4-D



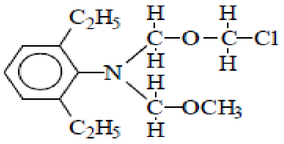
2,4,5-Trichlorophenoxy-acetic acid (and esters), 2,4,5-T

Substituted Amides

A diverse group of herbicides consists of substituted amides. Prominent among these are propanil, applied to control weeds in rice fields, and alachlor, marketed as Lasso and widely applied to fields to kill germinating grass and broad-leaved weed seedlings:



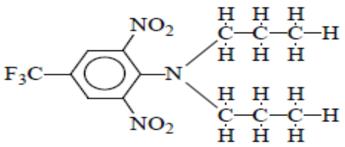
Propanil



Alachlor

Nitroaniline

Nitroaniline herbicides are characterized by the presence of $NO_2$and a substituted – This class of herbicides is widely represented in agricultural applications and includes benefin (Balan), oryzalin (Surflan), pendimethalin (Prowl), and fluchoralin (Basalin). NH_2 group on a benzene ring as shown for trifluralin:



Trifluralin
(Treflan®)

5.5. Poly Chlorinated Biphenyl (PCB’s)

Dear student, in the previous content, you have introduced about pesticides. Now you learn about PCB’s (Poly Chlorinated Biphenyl). Let warm up yourself with the following activities.

Learning task 5.5

a) What do you know about PCB’s?
b) Explain the source of PCB’s
c) Explain the effect of PCB’s in the Environment
d) Describe how the effects of PCB’s on the Environment can be minimized

They are made by substituting from 1 to 10 Cl atoms onto the biphenyl aryl structure as shown on the left below. This substitution can produce 209 different compounds (congeners), of which one example is shown on the right in formula below.

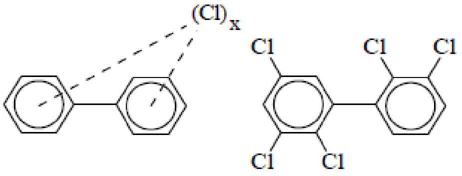


Figure 5.5 General formula of polychlorinated biphenyls (left, where X can range from 1 to 10) and a specific 5-chlorine congener (right).

Polychlorinated biphenyls have very high chemical, thermal, and biological stability; low vapor pressure; and high dielectric constants. These properties have led to the use of PCBs as coolant-insulation fluids in transformers and capacitors; for the impregnation of cotton and asbestos; as plasticizers; and as additives to some epoxy paints. The same properties that made extraordinarily stable PCBs so useful also contributed to their widespread dispersion and accumulation in the environment.

PCB's was first discovered as environmental pollutants in 1966, **polychlorinated biphenyls (PCB** compounds) have been found throughout the world in water, sediments, bird tissue, and fish tissue. These compounds constitute an important class of special wastes.

The manufacture of PCBs was discontinued and their uses and disposal were strictly controlled. Several chemical formulations have been developed to substitute for PCBs in electrical applications. Disposal of PCBs from discarded electrical equipment and other sources have caused problems, particularly since PCBs can survive ordinary incineration by escaping as vapors through the smokestack. However, they can be destroyed by special incineration processes.

5.5.1 Biodegradation of PCBs

Although it was well known that aerobic bacteria could degrade PCBs with only one or two Cl atom constituents, most of the PCB congeners discharged to the sediments had multiple chlorine atom constituents, specifically an average of 3.5 Cl atoms per PCB molecule at the time the PCBs were discharged. However, investigations during the late 1980s revealed that the PCBs in the sediments had been largely converted to mono- and dichlorosubstituted forms.

Ideally, in the case of PCBs in sediments, about half of the work of remediation by biodegradation-conversion of highly substituted PCBs to molecules with one or two chlorines-is done by the slow, steady action of anaerobic bacteria without human intervention. Since the PCB products tend to stay in anaerobic surroundings, some assistance is required to provide oxygen to finish the biodegradation aerobically by introducing aerobic bacteria acclimated to PCB biodegradation, along with the oxygen and nutrients required for their growth.

5.6 Chlorofluorocarbon compounds and Stratospheric Ozone Depletion

Dear student, in the previous content, you have introduced about PCB's (Poly Chlorinated Biphenyl). Now you learn about chlorofluorocarbon compounds. Let warm up yourself with the following activities.

Learning task 5.6

a) Explain what Chlorofluorocarbon compounds are?
b) Describe the source of Chlorofluorocarbon compounds
c) Explain the effect of Chlorofluorocarbon compounds in the Environment

Dear student, as you have learnt in chapter 3, Chlorofluorocarbon compounds are compounds that are responsible for the destruction of ozone in Stratosphere layer of the atmosphere

Chlorofluorocarbons (**CFC**s), such as dichlorodifluoromethane, commonly called **Freons**, are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon. These compounds are notably stable and nontoxic. They were widely used in recent decades in the fabrication of flexible and rigid foams and as fluids for refrigeration and air conditioning. A related class of compounds, the **halons**, such as $CBrClF_2$ (Halon-1211), are used in fire extinguisher systems particularly on aircraft.

The nonreactivity of CFC compounds, combined with worldwide production of approximately one-half million metric tons per year and deliberate or accidental release to the atmosphere, has resulted in CFCs becoming homogeneous components of the global atmosphere. In 1974 it was convincingly suggested, in a classic work that earned the authors a Nobel Prize that chlorofluoromethanes could catalyze the destruction of **stratospheric ozone** that filters out cancer-causing ultraviolet radiation from the sun. More-recent data on ozone levels in the stratosphere and on increased ultraviolet radiation at Earth's surface have shown that the threat to stratospheric ozone posed by chlorofluorocarbons is real. Although quite inert in the lower atmosphere, CFCs undergo photodecomposition by the action of high-energy ultraviolet radiation in the stratosphere, which is energetic enough to break their very strong C-Cl bonds through reactions such as

$$Cl_2CF_2 + h\nu \rightarrow Cl\cdot + ClCF_2\cdot$$

thereby releasing Cl atoms. The Cl atoms are very reactive species. Under the rarefied conditions of the stratosphere, one of the most abundant reactive species available for them to react with is ozone, which they destroy through a process that generates ClO:

$$Cl + O_3 \rightarrow ClO + O_2$$

In the stratosphere, there is an appreciable concentration of atomic oxygen by virtue of the reaction

$$O_3 + h\nu \rightarrow O_2 + O$$

Nitric oxide, NO, is also present. The ClO species may react with either O or NO, regenerating Cl atoms and resulting in chain reactions that cause the net destruction of ozone:

$$\begin{array}{l} ClO + O \rightarrow Cl + O_2 \\ Cl + O_3 \rightarrow ClO + O_2 \\ \hline O_3 + O \rightarrow 2O_2 \end{array}$$

$$\begin{array}{l} ClO + NO \rightarrow Cl + NO_2 \\ O_3 + Cl \rightarrow ClO + O_2 \\ \hline O_3 + NO \rightarrow NO_2 + O_2 \end{array}$$

Both ClO and Cl involved in the above chain reactions have been detected in the 25 to 45 km altitude region. Also involved as an intermediate in the stratospheric ozone destruction caused by chlorofluorocarbons is the $(ClO)_2$ dimer. The effects of CFCs on the ozone layer may be the single greatest threat to the global atmosphere.

5.7. Nitrogen and phosphorous Compounds

Dear student, in the previous content, you have introduced about chlorofluorocarbon compounds. Now you learn about Nitrogen and phosphorous Compounds. Let warm up yourself with the following activities.

Learning task 5.7

a) Mention the common nitrogen and phosphorous compounds
b) Describe the source of nitrogen and phosphorous compounds
c) Explain the effect of nitrogen and phosphorous compounds the environment

Dear student, as you have learnt in the preceding chapters, nitrogen compounds are compounds that are responsible acid rain and phosphorous compounds are responsible for eutrophication in water bodies.

5.7.1 Nitrogen and its compounds

Nitrogen has a high spreading potential. A number of plants are relatively susceptible to NO_2. Nitric acid is an important constituent of precipitation. Together with H_2SO_4 it causes acid rain, which negatively affects crops and soils. At increasing nitrogen concentrations in surface layers, plankton production increases, leading to algal blooms. This may occur in any type of surface water. Large amounts of nitrate may cause eutrophication, which means an excess of nutrients resulting in oxygen deprivation and fish deaths. Nitrogen does not limit algal growth, because phosphorus is generally a limiting factor in water bodies. This means that phosphorus is the determining factor of algal spreading through surface waters.

Oxygen deficits in surface water generally result in nitrate reduction to elementary nitrogen or nitrous oxide. NO_x compounds react with water to soluble nitric acid. This means that oceans can reduce atmospheric nitrogen oxide concentrations. PAN compounds (Peroxy Acetyl Nitrate) are derived from terrestrial environmental pollution, but may also be transported in the troposphere and in oceans. Eventually, these compounds are decomposed to NO_x. There are some examples of toxic nitrogen compounds for nitro aniline the LD_{50} for rodents is 1-3.6 mg/kg. For example, the non-toxic concentration for fish is approximately 10 mg/L (in 48 hour).

Nitrites and amines from protein-rich food form so-called nitrosamines, which are carcinogenic substances. This reaction may be prevented by the reducing and anti-oxidant properties of vitamin C. Examples of toxic nitrogen compounds are PAN-compounds, which are fifty times more toxic than the nitrogen compounds these are converted from (nitriles and nitrilo compounds).

5.7.2 Phosphorus and its compounds

Biological use of Phosphorus and its compounds

Phosphorus is a key element in all known forms of life. Inorganic phosphorus in the form of the phosphate PO_4^{3-} plays a major role in biological molecules such as DNA and RNA where it forms part of the structural framework of these molecules. Living cells also use phosphate to transport cellular energy in the form of adenosine triphosphate (ATP).Nearly every cellular process that uses energy obtains it in the form of ATP. ATP is also important for phosphorylation, a key regulatory event in cells. Phospholipids are the main structural components of all cellular membranes. Calcium phosphate salts assist in stiffening bones.

Toxic nature of Phosphorus and its compounds

Organic compounds of phosphorus form a wide class of materials, some of which are extremely toxic. Fluorophosphate esters are among the most potent neurotoxins known. A wide range of organophosphorus compounds are used for their toxicity to certain organisms as pesticides (herbicides, insecticides, fungicides, etc.) and weaponised as nerve agents. Most inorganic phosphates are relatively nontoxic and essential nutrients. Some of environmentally adverse effects of phosphates are eutrophication and algal blooms in surface waters and lakes.

5.8. Toxic Heavy Metals and Organo-Metallic Compounds

Dear student, in the previous content, you have introduced about nitrogen and phosphorous compounds. Now you learn about Toxic Heavy Metals and Organo-Metallic Compounds. Let warm up yourself with the following activities.

Learning task 5.8

a) Classify organometallic compounds for the purpose of discussing their toxicology
b) Mention the common toxic heavy metals.
c) Explain the source of heavy metals in the environment
d) Explain the source of organo-metallic compounds in the environment
e) Explain the effect of toxic heavy metals and organo-metallic Compounds in the Environment.

Organo-Metallic Compounds and their toxic effects

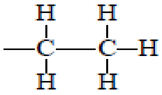
The interaction of metals with organic compounds is of utmost importance in determining the role played by the metal in an aquatic system. There are two major types of metal-organic interactions to be considered in an aquatic system. The first of these is complexation, usually chelation when organic ligands are involved.

$$ML + 2H^{+} \leftarrow\!\rightarrow M^{2+} + H_2I$$

Organometallic compounds, on the other hand, contain metals bound to organic entities by way of a carbon atom and do not dissociate reversibly at lower pH or greater dilution. Furthermore, the organic component, and sometimes the particular oxidation state of the metal involved, may not be stable apart from the organometallic compound.

A simple way to classify organometallic compounds for the purpose of discussing their toxicology is the following:

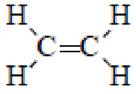
1. Those in which the organic group is an alkyl group such as ethyl in tetra ethyl lead, Pb $(C_2H_5)_4$:



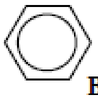
2. **Carbonyls**, some of which are quite volatile and toxic, having carbon monoxide bonded to metals:

$$:C\equiv O:$$

3. Those in which the organic group is a electron donor, such as ethylene or benzene



Ethylene



Benzene

Combinations exist of the three general types of compounds outlined above, the most prominent of which are arene carbonyl species in which a metal atom is bonded to both an aryl entity such as benzene and to several carbon monoxide molecules.

A large number of compounds exist that have at least one bond between the metal and a C atom on an organic group, as well as other covalent or ionic bonds between the metal and atoms other than carbon. Because they have at least one metal-carbon bond, as well as properties, uses, and toxicological effects typical of organometallic compounds, it is useful to consider such compounds along with organometallic compounds. Examples are monomethylmercury chloride, CH_3HgCl, in which the organometallic CH_3Hg^+ ion is ionically bonded to the chloride anion. Another example is phenyldichloroarsine, $C_6H_5AsCl_2$, in which a phenyl group is covalently bonded to arsenic through an As-C bond, and two Cl atoms are also covalently bonded to arsenic.

The interaction of trace metals with organic compounds in natural waters is too vast an area to cover in detail in this chapter; however, it can be noted that metal- organic interactions may involve organic species of both pollutant (such as EDTA) and natural (such as fulvic acids) origin. These interactions are influenced by, and sometimes play a role in, redox equilibria; formation and dissolution of precipitates; colloid formation and stability; acid-base reactions; and microorganism-mediated reactions in water.

Toxicity of Organometallic Compounds

Organometallic compounds have a variety of toxic effects. They often behave in the body in ways totally unlike the inorganic forms of the metals that they contain, due in large part to the fact that compared with inorganic forms; organometallic compounds have an organic nature, higher lipid solubility, and greater ability to penetrate cell membranes.

Perhaps the most notable toxic organometallic compound is **tetraethyl lead**, Pb $(C_2H_5)_4$, a colorless, oily liquid that was widely used as a gasoline additive to boost octane rating. Tetraethyl lead has a strong affinity for lipids and can enter the body by all three common routes of inhalation, ingestion, and absorption through the skin. Acting differently from inorganic compounds in the body, it affects the central nervous system with symptoms such as fatigue, weakness, restlessness, ataxia, psychosis, and convulsions.

Methylated mercury species, CH_3Hg^+ and $(CH_3)_2Hg$, are produced by anaerobic bacteria. They are extremely toxic. Anaerobic bacteria also produce methylated forms of arsenic. Metal carbonyls, regarded as extremely hazardous because of their toxicities, include nickel tetra carbonyl (Ni $(CO)_4$), cobalt carbonyl, and iron pentacarbonyl. Some of the hazardous carbonyls are volatile and readily taken into the body through the respiratory tract or through the skin. The carbonyls affect tissue directly and they break down to toxic carbon monoxide and products of the metal, which have additional toxic effects.

Toxic Heavy metals

Dear student, a heavy metal is a member of a loosely-defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed; some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity.

Heavy metal pollution

Motivations for controlling heavy metal concentrations in gas streams are diverse. Some of them are dangerous to health or to the environment (e.g. mercury, cadmium, lead, chromium), some may cause corrosion (e.g. zinc, lead), some are harmful in other ways (e.g. arsenic may pollute catalysts).

One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnification causing heavier exposure for some organisms than is present in the environment alone.

5.8.1 Mercury

Dear student, can you explain why mercury is classified as heavy metal?

Mercury is found in batteries, thermometers and barometers. It can also be found in fungicides used in the agricultural industry. In medicine, mercury is used in dental amalgams and various antiseptic substances. It can also be found in deep sea water fish. Mercury is toxic in any form.

Mercury poisoning can result from vapor inhalation, ingestion, injection, or absorption through the skin. Nervous, digestive and renal systems are most commonly affected in mercury exposure. Long-term effects on the nervous system are most worrying. Children and pregnant women are especially vulnerable to mercury exposure.

Dear student, there are three forms of Mercury:

i) Elemental mercury in its pure liquid form elemental mercury, when vaporized, has the ability to penetrate the Central Nervous System, where it is ionized and trapped, attributing to its significant toxic effects. It is not well absorbed by the digestive system and, for this reason, is only mildly toxic when ingested. So the most toxic effect of elemental mercury happens through its inhalation.

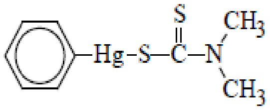
ii) Inorganic mercury in the form of salts is highly toxic. “It gains access to the body orally or dermally and is absorbed at a rate of 10% of that ingested. Although poor lipid solubility characteristics limit CNS penetration, slow elimination and chronic exposure allow for significant CNS accumulation of mercuric ions and subsequent toxicity. Long-term dermal exposure to inorganic mercury may also lead to toxicity”.

iii) Organic mercury can be found in 3 forms, aryl and short and long chain alkyl compounds. Organic mercurials are absorbed more completely from the GI tract than inorganic salts are; this is because of intrinsic properties, such as lipid solubility and mild corrosiveness (although much less corrosive than inorganic mercury). Once absorbed, the aryl and long chain alkyl compounds are converted to their inorganic forms and possess similar toxic properties to inorganic mercury.

The short chain alkyl mercurials are readily absorbed in the gastro intestinal tract (90-95%) and remain stable in their initial forms. Alkyl organic mercury has high lipid solubility and is distributed uniformly throughout the body, accumulating in the brain, kidney, liver, hair, and skin. Organic mercurials also cross the blood brain barrier and placenta and penetrate erythrocytes, attributing to neurological symptoms, teratogenic effects and high blood to plasma ratio respectively.

Because of its toxicity, mobilization as methylated forms by anaerobic bacteria, and other pollution factors, **mercury** generates a great deal of concern as a heavy- metal pollutant. Mercury is found as a trace component of many minerals, with continental rocks containing an average of around 80 parts per billion, or slightly less, of this element. Cinnabar, red mercuric sulfide, is the chief commercial mercury ore. Fossil fuel coal and lignite contain mercury, often at levels of 100 parts per billion or even higher, a matter of some concern with increased use of these fuels for energy resources.

Metallic mercury is used as an electrode in the electrolytic generation of chlorine gas, in laboratory vacuum apparatus, and in other applications. Significant quantities of inorganic mercury (I) and mercury (II) compounds are used annually. Organic mercury compounds used to be widely applied as pesticides, particularly fungicides. These mercury compounds include aryl mercurials such as phenyl mercuric dimethyldithiocarbamate formerly used in paper mills as a slimicide and as a mold retardant for paper), and alkyl mercurials such as ethylmercuric chloride, C_2H_5HgCl, which was used as a seed fungicide. Because of their resistance to degradation and their mobility, the alkyl mercury compounds are generally considered to be more of an environmental threat than either the aryl or inorganic compounds.



Mercury enters the environment from a large number of miscellaneous sources related to human use of the element. These include discarded laboratory chemicals, batteries, broken thermometers, amalgam tooth fillings, and formerly lawn fungicides and pharmaceutical products. Taken individually, each of these sources may not contribute much of the toxic metal, but the total effect can be substantial. Sewage effluent sometimes contains up to 10 times the level of mercury found in typical natural waters.

The toxicity of mercury was tragically illustrated in the Minamata Bay area of Japan during the period 1953–1960. A total of 111 cases of mercury poisoning and 43 deaths were reported among people who had consumed seafood from the bay that had been contaminated with mercury waste from a chemical plant that drained into Minamata Bay. Congenital defects were observed in 19 babies whose mothers had consumed seafood contaminated with mercury. The level of metal in the contaminated seafood was 5–20 parts per million.

Among the toxicological effects of mercury are neurological damage, including irritability, paralysis, blindness, or insanity; chromosome breakage; and birth defects. The milder symptoms of mercury poisoning such as depression and irritability have a psychopathological character. Because of the resemblance of these symptoms to common human behavior, mild mercury poisoning may escape detection. Some forms of mercury are relatively nontoxic and were formerly used as medicines, for example, in the treatment of syphilis. Other forms of mercury, such as soluble Hg (II) salts and methyl mercury compounds, are highly toxic.

Because there are few major natural sources of mercury, and since most inorganic compounds of this element are relatively insoluble, it was assumed for some time that mercury was not a serious water pollutant. It was found that several chemical plants, particularly caustic chemical manufacturing operations, were each releasing up to 14 or more kilograms of mercury in wastewaters each day.

The unexpectedly high concentrations of mercury found in water and in fish tissues result from the formation of soluble monomethylmercury ion, CH_3Hg^+, and volatile dimethylmercury, $(CH_3)_2Hg$, by anaerobic bacteria in sediments. Mercury from these compounds becomes concentrated in fish lipid (fat) tissue and the concentration factor from water to fish may exceed 10^3. The methylating agent by which inorganic mercury is converted to methylmercury compounds is methylcobalamin, a vitamin B_{12} analog:

$$HgCl_2 \xrightarrow{\text{Methylcobalamin}} CH_3HgCl + Cl^-$$

It is believed that the bacteria that synthesize methane produce methylcobalamin as an intermediate in the synthesis. Thus, waters and sediments in which anaerobic decay is occurring provide the conditions under which methylmercury production occurs. In neutral or alkaline waters, the formation of dimethylmercury, $(CH_3)_2Hg$, is favored. This volatile compound can escape to the atmosphere.

5.8.2 Lead

Dear student, can you explain why Lead is classified as heavy metal?

Inorganic **lead** arising from a number of industrial and mining sources occurs in water in the +2 oxidation state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually entered natural water systems. In addition to pollutant sources, lead-bearing limestone and galena (PbS) contribute lead to natural waters in some locations.

Despite greatly increased total use of lead by industry, evidence from hair samples and other sources indicates that body burdens of this toxic metal have decreased during recent decades. This may be in part the result of less lead used in plumbing and other products that come in contact with food or drink.

Acute lead poisoning in humans may cause severe dysfunction of the kidney, reproductive system, liver, brain, and central nervous system leading to sickness or death. Lead poisoning from environmental exposure is thought to have caused mental retardation in many children. Mild lead poisoning causes anemia. The victim may have headaches and sore muscles, and may feel generally fatigued and irritable.

Except in isolated cases, lead is probably not a major problem in drinking water, although the potential exists in cases where old lead pipe is still in use. Lead used to be a constituent of solder and some pipe-joint formulations, so that household water does have some contact with lead. Water that has stood in household plumbing for some time may accumulate significant levels of lead (along with zinc, cadmium, and copper) and should be drained for a while before use.

5.8.3. Arsenic

Dear student, can you explain why Arsenic is classified as heavy metal?

Inorganic and organic **arsenic** occur naturally in the environment, with inorganic forms being most abundant. Inorganic arsenic is associated with other metals in igneous and sedimentary rocks, and it also occurs in combination with many other elements, especially oxygen, chlorine, and sulfur. Organic arsenic contains carbon and hydrogen.

Both inorganic and organic forms exist naturally in soils, plants, animals, and humans. Most pure, inorganic arsenic compounds are white or colorless powders with no specific smell or taste. Because it is an element, arsenic does not degrade nor can it be destroyed.

Arsenic has been recognized as a poison since ancient times. In past centuries it was used to treat syphilis, and decades ago it was a common active ingredient in pesticides and was also a common wood preservative. Today, about 90% of arsenic produced is used as a wood preservative (chromated copper arsenate). Although organic arsenicals continue to be used as pesticides, primarily on cotton, inorganic compounds can no longer be used. Arsenic is also used as a feed additive for poultry and swine and in cattle and sheep dips to control lice and ticks. In addition, arsenic is used in alloys (primarily in lead-acid batteries for automobiles) and in semiconductors and light-emitting diodes.

Arsenic occurs everywhere in the environment. Weathering of rock is the major natural source of inorganic arsenic, and it is also released by human activities. For example, arsenic is emitted as a fine dust when arsenic-containing ores are heated at smelters to process copper or lead. The concentration of arsenic in the earth's crust ranges from 2 to 5 milligrams per kilogram (mg/kg), or parts per million (ppm).

The mean natural soil concentration is 5 mg/kg, and it ranges from about 1 to 40 mg/kg. Water-soluble arsenites (the trivalent form, As III) and arsenates (the pentavalent form, As V) are the most common forms. Arsenites especially can be relatively mobile, with a typical concentration associated with soil particles estimated to be 10 to 200 times higher than in the interstitial water (water in the pore spaces between the soil particles). Levels in drinking water are commonly 2 to 20 parts per billion (ppb). Bacteria, fungi, and some plants methylate inorganic arsenic, converting it to organic compounds.

Many methylated forms are volatile, such as dimethylarsine. Some organisms (notably in aquatic systems) can accumulate nontoxic, organic forms of arsenic; for example, levels of arsenobetaine in shrimp are often high. However, the typical ratio of the arsenic concentration in plants to that in soil is low, estimated at 0.006 (or 0.6%).

Arsenic can be taken in by eating food, drinking water, or breathing air, and to a limited degree via skin contact. Children, and to a lesser extent adults, can also be exposed by ingesting soil. When ingested, dissolved arsenic compounds are readily absorbed (80-90%) through the gastrointestinal tract and distributed in the blood to the liver, kidney, lung, spleen, aorta, and skin.

Two processes are involved in arsenic metabolism:

- Oxidation/reduction reactions that interconvert arsenate and arsenite, and
- Methylation of arsenite to form monomethyl arsenic acid and dimethyl arsenic acid.

The methylated forms are less toxic and more easily excreted in the urine.

Most arsenic is eliminated in the urine within a week (75-90%, depending on the compound), especially from the liver, kidney, and spleen, while that in the skin, brain, skeleton, and especially hair and nails, remains somewhat longer. When arsenic is inhaled and deposited in the lungs, about 80% is absorbed into the bloodstream and distributes throughout the body as above. Arsenic in soil or dissolved in water does not readily penetrate the skin (only 3% is estimated to be absorbed), so dermal exposures are not typically a concern.

Depending on the amount ingested, arsenic can be beneficial (animal studies suggest that low levels of arsenic in the diet are essential) or adverse (high levels can be toxic). The acute lethal dose to humans can be about 2 to 20 mg/kg body weight per day (mg/kg-day). Ingesting high doses of arsenic irritates the stomach and intestines, with symptoms including nausea, vomiting, diarrhea and liver swelling. However, wide recognition of its toxicity makes arsenic poisoning today very rare.

Ingesting small amounts over time produces chronic effects such as skin darkening and formation of corns, damage to peripheral nerves, cardiovascular system effects, hair and appetite loss, and mental disorders. Effects from inhaling arsenic dust include respiratory irritation, rhinitis, pharyngitis, laryngitis, and sometimes nasal perforation. Skin contact with inorganic arsenic dusts can cause dermatitis, allergic hypersensitivity, and conjunctivitis. Occupational exposure studies show a correlation between chronic arsenic exposure and lung cancer.

Arsenic can also cause reproductive/developmental effects, including spontaneous abortions and reduced birth weights. Epidemiological studies indicate an association between arsenic concentrations in drinking water and increased incidences of skin, liver, kidney, lung, and bladder cancers. Studies also show an association between inhaling arsenic and lung cancer. From these sets of data, the U.S. Environmental Protection Agency (EPA) has classified inorganic arsenic as a known human carcinogen. Limited information is available on the joint toxicity of arsenic with other chemicals.

The EPA has developed toxicity values to estimate the risk of getting cancer or other adverse health effects as a result of inhaling or ingesting inorganic arsenic. These toxicity values have been developed based on studies of workers exposed to arsenic in occupational settings, workers applying arsenical pesticides, and populations consuming drinking water containing high concentrations of arsenic.

5.8.4. Chromium

Dear student, can you explain why Chromium is classified as heavy metal?

Chromium is of crucial importance because of its use in stainless steel and super alloys. These materials are vitally important to industrialized societies because of their applications in jet engines, nuclear power plants, chemical-resistant valves, and other applications in which a material that resists heat and chemical attack. Chromium is almost impossible to recover from chrome-plated objects, and this use should be eliminated insofar as possible, as has been done with much of the decorative chrome-plated adornments formerly put on automobiles.

Chromium (VI) (chromate) is a toxic form of the metal and its uses should be eliminated wherever possible. The use of chromium in leather tanning and miscellaneous chemical applications should be curtailed. One important use of chromium is in the preparation of treated CCA lumber, which resists fungal decay and termites.

Health Effects of Hexavalent Chromium

Hexavalent chromium is a toxic form of the element chromium. Hexavalent chromium compounds are man-made and widely used in many different industries. Some major industrial sources of hexavalent chromium are:

- chromate pigments in dyes, paints, inks, and plastics
- chromates added as anti-corrosive agents to paints, primers and other surface coatings
- chrome plating by depositing chromium metal onto an item’s surface using a solution of chromic acid
- particles released during smelting of ferrochromium ore
- fume from welding stainless steel or nonferrous chromium alloys
- impurity present in Portland cement

Chapter Summary

- **Toxicity** is of the utmost concern in dealing with hazardous substances. **Toxicology** is the science of poisons.
- **A poison**, **or toxicant**, is a substance that is harmful to living organisms because of its detrimental effects on tissues, organs, or biological processes.
- **Acute local exposure** occurs at a specific location over a time period of a few seconds to a few hours and may affect the exposure site, particularly the skin, eyes, or mucous membranes.
- **Chronic systemic exposure** differs in that the exposure occurs over a prolonged time period.
- **Biomonitors** are organisms that can serve as indicators of various kinds of pollutants.
- **Additive** effect of pollutants is substances that have the same physiologic function.
- **Synergistic effect** is the total effect is greater than the sum of the effects of each separately.
- **Potentiation** occurs when an inactive substance enhances the action of an active one.
- **Antagonism is** the effect when an active substance decreases of another active one.
- **Dose** is the amount, usually per unit body mass, of a toxicant to which an organism is exposed.
- **Response** is the effect upon an organism resulting from exposure to a toxicant.
- **Organic pollutants** are sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants, including organic pollutants.

Inorganic pollutants are trace elements and contribute to acidity, alkalinity, or salinity to water. Other important inorganic pollutant species are cyanide ion, CN^-, is probably the most important. Others include ammonia, carbon dioxide, hydrogen sulfide, nitrite, and sulfite.

- **Pesticides** are Chemicals used in the control of invertebrates include i**nsecticides**, **molluscicides** for the control of snails and slugs, and **nematicides** for the control of microscopic roundworms.
- **Polychlorinated biphenyls (PCB's)** are benzene ring containing compounds that have very high chemical, thermal, and biological stability; low vapor pressure; and high dielectric constants.
- **Chlorofluorocarbons** (**CFC**s), such as dichlorodifluoromethane, commonly called **Freons**, are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon.
- The chemistry of P-N compounds is characterized by the existence of polymeric compounds. Many derivatives of the six membered ring systems (NPCl) and of the eight membered systems (NPCl) are known
- Toxic metals are elements that can cause detrimental effect on the environment
- **Organo-Metallic Compounds** are organic compounds that interact with trace metals or organometallic compounds are those in which metals are bound to carbon atoms in hydrocarbon groups or, in the case of carbonyls, to CO molecules.

Self test exercises

1. Define Environmental Toxicity and Toxicology.
2. Compare and contrast Synergism, Potentiation and Antagonism
3. Explain Dose-Response relationships of pollutants?
4. Compare and contrast organic and inorganic pollutants.
5. Explain the source and effects of Agricultural and pharmaceutical contaminants on the environment.
6. Explain the effect of pesticides upon the Environment?
7. Discuss the effect of pesticides, PCB's and Chlorofluro compounds upon the Environment.
8. Explain the source of toxic heavy metals and organo-metallic compounds in the environment
9. Discuss why Mercury, Lead, Arsenic and Chromium are regarded as toxic heavy metals
10. Explain the effect of toxic heavy metals and organo-metallic Compounds in the Environment.

Chapter 6

Introduction to Green Chemistry

Unit introduction

Dear student, this chapter deals with Introduction to Green Chemistry. This unit tried to introduce the concepts of Green Chemistry and to give students a chance to think about the field of Chemistry from a different perspective.

Learning objective of the unit

Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:-

- Describe concepts of Green Chemistry
- Discuss the 12 Principles of Green Chemistry
- Explain the difference among Environmental Science, Environmental Chemistry and Green Chemistry
- Explain whether Green Chemistry is more expensive than traditional Chemistry
- Explain the concept of atom economy

6.1 Introduction to Green Chemistry

Dear student, under this main content you learn about Introduction to Green Chemistry**.** Do you know some of the concepts of Green Chemistry, Let warm up yourself with the following activities

Learning task 6.1

1. What is Green Chemistry?
2. Explain what a chemist does and their role in solving global environmental problems
3. Explain how Green chemistry goes to the root of the problem and aims to eliminate the hazard itself.
4. Describe how Green chemistry minimizes the hazards of some chemical products?

Green chemistry is a pro-active approach to pollution prevention. It targets pollution at the design stage, before it even begins. If chemists are taught to develop products and materials in a manner that does not use hazardous substances, then much waste, hazards and cost can be avoided. Green Chemistry is designing chemical products and processes that reduce or eliminate the use and/or the generation of hazardous substances.

Think about the simple equation of risk: **Risk = Hazard x Exposure**. Traditional approaches to pollution prevention focus on mitigating the hazard or end-of-pipe pollution prevention controls. These traditional technologies focus on limiting the *exposure* of a hazardous material. Unfortunately, exposure precautions can and will fail (i.e., gloves can tear, goggles can break, chemical releases can occur). Green chemistry goes to the root of the problem and aims to eliminate the hazard itself.

Green Chemistry is the ***only*** science that focuses on the intrinsic *hazard* of a chemical or chemical process. It seeks to minimize or eliminate that hazard so that we do not have to worry about exposure.

6.1.1 What is the relation between Environmental Science, Environmental Science and Green Chemistry?

***Dear student, all these areas of study seek to make the world a better place*.**

They are complimentary to each other. Environmental Science identifies sources, elucidates mechanisms and quantifies problems in the earth's environment. Green Chemistry seeks to solve these problems by creating alternative, safe technologies. Green Chemistry is *not* Environmental Chemistry. Green Chemistry targets pollution prevention at the source, during the design stage of a chemical product or process, and thus prevents pollution before it begins.

6.1.2 Is Green Chemistry more expensive that traditional Chemistry?

***Dear student the answer is No*.**

A simplified analysis of the cost structure associated with any chemical process takes into account the cost of materials, equipment and the human resources necessary. But, in reality, disposal, treatment and regulatory costs associated with the buying, using and generating hazardous materials involves numerous hidden costs. When you buy and use a hazardous material you are paying for it twice, once when you use it and once when you get rid of it. It makes sense that if you use materials that are non-hazardous and thus have minimal regulatory or disposal costs associated with them, the benefit to the economic bottom line is obvious.

The Presidential Green Chemistry Challenge Award has provided illustrations of several examples where industry has not only accomplished goals of pollution prevention, but has achieved significant economic benefits simultaneously.

How Chemists are taught Green Chemistry?

One way that chemists are learning how to do Green Chemistry is by following the 12 principles of Green Chemistry. They are a set of guidelines that chemists use in order to perform chemistry in a better way. As you take a closer look at them, you will find they are very intuitive and simply good practice. Each is briefly described below.

6.2 The twelve Principles of Green Chemistry

Dear student, under this main content you learn the 12 Principles of Green Chemistry**.** Can you mention some of the 12 Principles of Green Chemistry, Let warm up yourself with the following activities.

Learning task 6.2

a) Mention some of the Principles of Green Chemistry
b) Re-write the 12 principles of Green Chemistry in your own words so that you are understandable
c) Explain what meant by atom economy
d) Interpret the 12 Principles of Green Chemistry

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Dear student the Twelve Principles of Green Chemistry are summarized as below. Therefore, try to think about what it means to you.

1. Prevention

This principle is the most obvious and over-arches the other principles. It goes back to the old proverb ***"an ounce of prevention is worth a pound of cure"***. It is better to prevent waste than clean it up after-the-fact. Throughout history there have been many cases of environmental disasters that demonstrated this (**For example**; Bopal, India; Love Canal; Times Beach; Cuyahoga River).

2. Atom Economy

This principle gets into the actual chemistry of how products are made. As chemists, atoms are assembled to make molecules. The molecules are assembled together to make materials. This principle states that it is best to use all the atoms in a process. And, those atoms that are not used end up as waste. The atom economy is a simple calculation that can be used when teaching stoichiometry and chemical reactions. The calculation is: A.E. = Formula Weight (FW) of Product divided by the FW of all of the reactants. It is a simple measure of the amount of waste in a process.

3. Less Hazardous Chemical Synthesis

This principle is focused on *how* we make molecules and materials. The goal is to reduce the hazard of the chemicals that are used to make a product (the reagents). Throughout the history of how we have invented products and developed the process for making them, chemists have traditionally not thought about what reagents they are using and the hazards that are associated with them. Chemists have traditionally used whatever means necessary. Today we are finding that less hazardous reagents and chemicals can be used in a process to make products… and, many times they are made in a more efficient manner!

4. Designing Safer Chemicals

The previous principle was focused on the *process*. This principle focuses on the *product* that is made. Everyone wants safe products. Everyone also wants products that do what they are supposed to do (they have to work!). This principle is aimed at designing products that are safe, non-toxic and efficient. A good example of this is pesticides; which are products that are designed to be toxic. Many researchers are focused on created pesticides that are highly specific to the pest organism, but non-toxic to the surrounding wildlife and ecosystems.

5. Safer Solvents and Auxiliaries

Many chemical reactions are done in a solvent. Traditionally organic solvents have been used that pose hazards and many are highly toxic. They also create volatile organic compounds (VOC's) which add to pollution and can be highly hazardous to humans. This principle focuses on creating products in such a way so that they use less hazardous solvents (such as water). We use solvents regularly in our daily lives (cleaning products, nail polish, cosmetics, etc.) and in the chemistry laboratory. An example that many can relate to is that of nail polish products. Have you walked by a nail salon and caught a smell of the solvents that are used? The solvents traditionally used have potential toxicity and are certainly not pleasant to smell. A water-based alternative polish would avoid the exposure that goes along with the nail products and reduce the hazards associated with traditional products.

6. Design for Energy Efficiency

Today there is a focus on renewable energy and energy conservation. We use energy for transportation purposes and to provide electricity to our homes and businesses. Traditional methods for generating energy have been found to contribute to global environmental problems such as Global Warming and the energy used can also be a significant cost. This principle focuses on creating products and materials in a highly efficient manner and reducing the energy associated with creating the products, therefore reducing associated pollution and cost.

7. Use of Renewable Feedstocks

90-95% of the products we use in our everyday lives are made from petroleum. Our society not only depends on petroleum for transportation and energy, but also for making products. This principle seeks to shift our dependence on petroleum and to make products from renewable materials that can be gathered or harvested locally. *Biodiesel* is one example of this where researchers are trying to find alternative fuels that can be used for transportation. Another example is alternative, bio-based plastics. PLA (polylactic acid) is one plastic that is being made from renewable feedstocks such as corn and potato waste.

8. Reduce Derivatives

This principle is perhaps the most abstract principle for a non-chemist. The methods that chemists use to make products are sometimes highly sophisticated. And, many involve the manipulation of molecules in order to shape the molecules into what we want them to look like. This principle aims to simplify that process and to look at natural systems in order to design products in a simplified manner.

9. Catalysis

In a chemical process catalysts are used in order to reduce energy requirements and to make reactions happen more efficiently (and many times quicker). Another benefit of using a catalyst is that generally small amounts (catalytic amount versus a stoichiometric amount) are required to have an effect. And, if ***the catalyst is truly a "green" catalyst*** it will have little to no toxicity and it will be able to be used over-and-over again in the process. Enzymes are wonderful examples of catalysts that have been proven to perform amazing chemistry – our bodies are wonderful examples! Green chemists are investigating using enzymes to perform chemistry in the laboratory in order to obtain the desired product. Many times enzymes will have reduced toxicity, increased specificity and efficiency.

10. Design for Degradation

Not only do we want materials and products to come from renewable resources, but we would also like them to not persist in the environment. There is no question that many products we use in our daily lives are far too persistent. Plastics do not degrade in our landfills and pharmaceutical drugs such as antibiotics build up in our water streams. This principle seeks to design products in such a way so that they perform their intended function and then, when appropriate, will degrade into safe, harmless by-products when they are disposed of.

11. Real-time Analysis for Pollution Prevention

Imagine if you have never baked a cake before in your life and you did not have a cookbook to refer to. You mix the ingredients that you believe you need and you place the cake in the oven. But, for how long do you cook it and at what temperature? How will you know when the cake is done? What happens if you cook it too long or for not enough time? This process is similar to what chemists have to do when they make products. How long do they allow the reaction to run for? When do they know it will be "done"? If there was a way to see inside the reaction and to know exactly when it would be done, then this would reduce waste in the process and ensure that your product is "done" and is the right product that you intended to make.

12. Inherently Safer Chemistry for Accident Prevention

This principle focuses on safety for the worker and the surrounding community where an industry resides. It is better to use materials and chemicals that will not explode, light on fire, ignite in air, etc. when making a product. There are many examples where safe chemicals were not used and the result was disaster. The most widely known and perhaps one of the most devastating disaster was that of Bhopal, India in 1984 where a chemical plant had an accidental release that resulted in thousands of lives lost and many more injuries.

The chemical reaction that occurred was an exothermic reaction that went astray and toxic fumes were released to the surrounding community. When creating products, it is best to avoid highly reactive chemicals that have potential to result in accidents. When explosions and fires happen in industry, the result is often devastating.

Chapter Summary

- The concepts of Green Chemistry and the 12 principles of Green Chemistry are summarized as follows:
  - ***Green chemistry*** is a pro-active approach to pollution prevention. It targets pollution at the design stage, before it even begins.
  - **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
  - **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
  - **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
  - **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
  - **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
  - **Design for Energy Efficiency.** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
  - **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

- **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible.
- **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- **Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
- **Real-time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
- **Inherently Safer Chemistry for Accident Prevention.** Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions.

Self test exercises

1. Describe the concept of Green Chemistry
2. Explain the difference among Environmental Science, Environmental Chemistry and Green Chemistry
3. Explain whether Green Chemistry is more expensive than traditional Chemistry?
4. Explain the concept of atom economy
5. Explain what a chemist does and their role in solving global environmental problems
6. Explain how Green chemistry goes to the root of the problem and aims to eliminate the hazard itself.
7. Describe how Green chemistry minimizes the hazards of some chemical products?
8. Briefly discuss the 12 Principles of Green Chemistry

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