

GEOCHEMISTRY OF ORGANIC MATTER IN RIVER-SEA SYSTEMS

Geochemistry of Organic Matter in River-Sea Systems

by

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INTRODUCTION

One of the basic concepts of ocean biogeochemistry is that of an ocean with extremely active boundary zones and separation boundaries of extensive biochemical interactions. The areas of these zones are characterized by a sharp decrease of element migration intensity and consequently the decrease in their concentrations gave the boundaries for the naming of the geochemical barriers (Perelman, 1972). For the purposes of biogeochemistry the most important ones are the boundaries of separation between river–sea, ocean–atmosphere, and water–ground (Lisitzin, 1983). The most complicated of them is the river–sea boundary, where the biogeochemical processes are the most active and complicated (Monin and Romankevich, 1979, 1984).

The necessity of studying organic matter in rivers, mouth regions and adjoining sea aquatories has been repeatedly pointed out by V.I. Vernadsky (1934, 1960) who noted both the importance of registration of solid and liquid run-off of rivers, coming into the sea, and “the quality and the character of those elements, which are washed-down into the sea”, emphasizing that “wash-down of organic substances into the sea is of great value”.

The interest in studying organic matter in natural waters, including river and sea waters, has grown considerably over the last 30 years. During this period essential material was collected on the content and composition of organic matter in various types of river waters of the USSR, and this was published in papers by B.A. Scopintzev, A.D. Semenov, M.V. Tarasov, M.P. Smirnov, A.V. Maltzeva (see References), as well as on the largest rivers of foreign countries (Degens *et al.*, *Transport of Carbon and Minerals in Major World Rivers* 1982, 1983, 1985, 1987, 1988). However, the majority of publications dedicated to studying organic matter in natural water of the USSR contain information about the C_{org} content in non-filtered water, where C_{org} is in both dissolved form and in the composition of suspension particles (Maltzeva, 1980, 1984; Maksimova and Metreveli, 1984; Maltzeva *et al.*, 1984, 1987).

Information about spatial distribution of organic matter in river mouths is extremely limited (Scopintzev and Krylova, 1955; Scopintzev and Tzurikova, 1957). There is practically no data about C_{org} content in bottom river sediments of mouth regions, bordering with sea.

Organic matter plays a fundamental role in all biogeochemical processes in the World Ocean. The theoretical and practical value of organic matter study for revealing common

factors of forming commercial minerals in the ocean is universally recognized, primarily in oil formation (Vassoevich *et al.*, 1970, 1972, 1976; Geodekyan *et al.*, 1980, 1985; Trotsuk, 1979). The oceanic organic matter and its geochemical role is the subject of detailed studies by E.A. Romankevich (1977, 1984), Yu.A. Bogdanov (Bogdanov *et al.*, 1970), O.K. Bordovsky (1974), D.E. Gershanovich (Gershanovich *et al.*, 1974), A.I. Danyushevskaya (1984), and I.I. Volkov (1984). As for the organic matter geochemistry in the field of river run-off influence on the sea medium in the river–sea systems, there are no generalizing papers on this theme. From our point of view the study of the river-region system of the mixing of river and sea waters allows the possibility of revealing the basic properties of the mechanism for transportation and transformation of organic matter on its way from rivers into seas and oceans. The fact that a river and a sea form a system in their contact region was pointed out by A.M. Almazov (1962): “. . . In spite of the differences, existing both between various types of reservoirs, incoming in the mouth region, and between various representatives of the same type of reservoirs, they form the united system “river–liman–sea”, the typical peculiarity of which is the permanent transfer from the river mode to the sea one”.

The problems of organic matter behaviour in the regions of river and sea water mixing (or estuaries, see Chapter 3) were separately studied by many researchers both in our country and abroad. Among the most essential generalizations devoted to the consideration of problems of organic matter biogeochemistry in estuaries are the following: Barnes and Green, *Estuarine Environment*, 1972; Gronin, *Estuarine Research*, 1975; Burton and Liss, *Estuarine Chemistry*, 1976; Wiley, *Estuarine Processes*, 1976; Bockris, *Environmental Chemistry*, 1977; Olausson and Cato, *Chemistry and Biogeochemistry of Estuaries*, 1980; Hallberg, *Environmental Biogeochemistry*, 1983; Degens *et al.*, *Transport of Carbon and Minerals in Major World Rivers*, 1982–1988.

The study of organic matter and biogeochemical processes in the river–sea system is important for the following reasons:

1. Information about organic matter transport by rivers is required for estimating total run-off of dissolved and suspended substances from the earth's surface into seas and oceans. They give a possibility to judge the quantity and the quality of organic matter in various climatic zones of the Earth, sources of organic matter, peculiarities of its transformation and migration in various sections of the rivers, from the head to the mouth.

2. The majority of river suspensions (70–95%) are deposited on the geochemical river–sea barrier, huge sedimentary bodies being formed here, catching elements contained in river suspensions.

3. The cardinal change of sedimentation material takes place on the geochemical river–sea barrier: from the prevalence of suspended forms of elements, typical for river waters, to the domination of dissolved forms, typical for bio-inert ocean systems, which predetermine the motion of geochemical processes in open ocean. Thus the river–sea barrier determines the ocean pelagic zone biogeochemistry (Lisitzin, 1983).

4. The study of ocean peripheries and river mouth regions is also of interest for studying the perspectives of oil-and-gas bearing aquatories, since it is a zone of higher concentrations of C_{org} both in waters and in bottom sediments (Romankevich, 1977; Geodekyan *et al.*, 1980, 1985).

5. Estuaries represent an important stage of transportation of the solid products of erosion of the Earth's crust. It is difficult to determine the total quantity of solid material, brought into oceans by various agents, but the calculations (Goldberg, 1971) showed that 1.8×10^{16} g/year of suspended particles is transported by rivers through estuaries, while the contribution of particles, transported by atmospheric processes amounts to $1-5 \times 10^{14}$ g/year.

6. Estuaries are an important economical zone, concentrating not only large mineral but also biological resources. 60–80% of sea fish reserves are either partially or fully bound up with estuaries (Woodwell *et al.*, 1973). Estuaries also concentrate activities of human beings. They often are the sites of industry waste discharge including toxic substances, transported into them by river run-off. Nowadays the study of biogeochemical processes in estuaries is of important ecological value due to pollution effect on the natural medium. Physical, chemical, biogeochemical processes effecting mixing and distribution of materials in the regions of mixing river and sea waters determine which of the natural and anthropogenous materials, transported with river run-off are arrested in them and which penetrate into the open ocean.

All the factors mentioned above emphasise the importance of the detailed study of regions of river and sea water mixing, including the necessity of detailed investigation of geochemical and biogeochemical processes occurring in them.

The purpose of this work is the study of generalities of transformation and transportation of organic matter in the river–sea system. To achieve the specified goal we collected and analyzed the material from river mouths and from river and sea water mixing regions, located in various climatic zones of the Earth, and formulated the following main problems:

- to study peculiarities of quantitative distribution, correlation of forms and organic matter composition in river mouths in various climatic zones;
- to determine the mechanism of transportation and transformation of dissolved and suspended organic matter and organic matter of bottom sediments in the regions of river and sea water mixing;
- to study the character of interconnection of organic substances with inorganic material (micro-elements) and bioproducts, seasonal peculiarities of transportation of dissolved and suspended organic matter in the river–sea system.

The author revealed for the first time the peculiarities of behaviour and the mechanism of transformation and transportation of organic matter forms (dissolved, suspended, organic matter of bottom sediments) from the river into the sea at various stages of river and sea water mixing, and determined the generalities of the transformation of organic matter composition in suspension and bottom sediments in the river–sea system.

The practical value of these studies consists in the fact that the determined regulations of organic matter behaviour (fluctuation, transportation, transformation) in water suspension, and bottom sediments at various stages of its transportation from a river into a sea or an ocean may be used for determining ways of migration and the distance of chemical pollution spread, places of anomalous concentrations of organic matter on the bottom of the seas and oceans adjacent to river mouths. The biogeochemical studies in the river–sea system expand our ideas about oil formation processes in river mouths in the

geological past, contributing to more reliable estimations of the prospectives of oil content of near-shore water areas.

The results of these studies were presented by the author at the All-Union seminars on "Organic Substance of Modern and Fossil Sediments" (1970, 1976, 1979, 1982), All-Union Schools of Sea Geology (1978, 1980, 1982, 1984, 1986, 1990), VIIIth International Congress on "Organic Geochemistry" (Moscow, 1977), Ist-IIIrd All-Union Conference of Oceanologists (1977, 1982, 1987), at the International Conference on "Biogeochemical Cycles of Carbon and Sulphur" (Settlement Listvianka, 1988), 9th International Symposium on "The Environmental Biogeochemistry" (Moscow, 1989), as well as at colloquiums of the ocean chemistry laboratory and meetings of the Working Group "Ocean Chemistry", etc.

Personnel of the laboratories of the ocean chemistry and physico-geological researches, the analytic laboratory of the Institute of Biochemistry and Physiology of Micro-Organisms of the Academy of Sciences of Russia, central analytical laboratory of the V.I. Vernadsky Institute of Geochemistry and Analytic Chemistry of the Academy of Sciences of Russia, laboratory of soil chemistry of the Soil Faculty of the Moscow State University, laboratory of organic geochemistry of the Scientific and Research Institute of Oceanology (St. Petersburg), as well as the personnel of the Centre for Control of Environmental Pollution of the Northern Department of the State Committee for Hydrometeorology, North Dvina and Pechora river mouth stations, Riga hydrometeo-observatory, Danube hydrometeo-observatory, Dnieper-Bug, Don and Kuban mouth stations assisted in obtaining the material under expedition conditions, performance of chemical analyses, and advised on some sections of the paper; the author is sincerely thankful to all.

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ABBREVIATIONS

OM	– organic matter
DOM	– dissolved organic matter
POM	– particulate organic matter
ROM	– residual organic matter
C _{org}	– organic carbon
C ^d	– dissolved organic carbon
C ^p	– particulate organic carbon
N _{org}	– organic nitrogen
N ^d _{org}	– dissolved organic nitrogen
N ^p _{org}	– particulate organic nitrogen
DC	– dissolved carbohydrates
PC	– particulate carbohydrates
AA	– amino acids
HA	– humic acids
FA	– fulvic acids
HS	– humic substances
HC	– hydrocarbons
C ^d _c	– dissolved carbohydrate carbon
C ^p _c	– particulate carbohydrate carbon
A _{cl}	– chloroform bitumoid 'A'
A _{a–b}	– alcohol-benzol bitumoid 'A'
VA	– vanillin aldehyde
PA	– p-oxybenzaldehyde
SA	– syringyl aldehyde

Chapter 1

MATERIALS AND METHODS OF STUDY

1.1. Regions and Objects of Studies

Proceeding from the problems raised when choosing the region of work we were guided by the following basic criteria: climatic zonality, river run-off value, type of rivers (plain, mountain) and estuaries (see Chapter 3). The important role of climatic zonality and formation of river organic matter composition was pointed out by V.I. Vernadsky: "Already it is possible to determine two separate types of fresh river waters, tightly bound up with the certain climatic zones . . . These are near-pole rivers with light brown water and black rivers of tropical and subtropical regions. The chemical studying of the waters of these rivers is urgently required" (Vernadsky, 1960). To compare the trends of organic matter transformation processes in the line suspension-bottom sediments in estuaries of northern and tropical rivers the following studies were performed in the southern part of Dvinsky Bay on the section North Dvina–sea and the Amazon estuary.

To clarify the mechanism of transportation and the peculiarities of transformation of dissolved and particulate organic matter of bottom sediments in the widest range of salinity from 0.0 to 36.0‰ in tropical oceanic estuary at various stages of mixing river and ocean water, estimation of distances of spread and scales of river organic matter effect on the ocean medium we chose the estuary of the largest river of the world – the Amazon.

To determine the character of interconnection of dissolved and particulate organic matter with primary products and micro-elements in sea estuaries of the moderate climatic zone, the effect of water stratification on the organic matter behaviour in estuaries and comparative analysis of this data with the behaviour of the same parameters in oceanic tropical estuary, research was undertaken in Temryuk, Riga, Taganrog and Dvina bays. The study of seasonal variations of organic matter behaviour in the river–sea system would be useful in the estuary of northern latitudes with contrasting distributions of meteorological, hydrochemical and geochemical indexes and liquid and solid run-off and organic matter run-off values. Therefore, such research was performed in the White Sea, on the section of "mouth of North Dvina–Mudiyug Island". To estimate organic matter behaviour in the area of mixing in mountain rivers waters and sea waters, investigations were performed on the section "mouth of Mzymta River–Black Sea".

The basic areas of our investigations were river and sea water, suspension and bottom sediments. Plankton, bacterial micro-flora and soils were studied to a comparatively lesser degree.

1.2. Organizing of Water and Bottom Sediments Sampling

The material for the study was taken during expeditions, organized by both the Institute of Oceanology of the Academy of Sciences of Russia, together with other organizations. To study the peculiarities of organic matter transportation by time in the river–sea system and some mouths of rivers and estuaries, samples were taken during different seasons and hydrological phases (flood, low water, tide, ebb tide) and at various times of day (at daily and half-daily stations).

Sampling in mouths of rivers and the regions of mixing of sea and river waters can be performed from various boats, from the research ships of ocean class (“Academik Kurchatov”, Professor Shtokman”) to ships of such class as medium fishing trawlers, small fishing trawlers, as well as from cutters, boats, and motor boats. In winter, samples of water (in the mouth of North Dvina river) are taken from ice through a hole drilled with an auger.

Samples of river water (salinity less than 1‰) are taken in mouths of rivers in front of the conditional border with the region of mixing of river and sea waters, the salinity of which is within the limits from 1‰ to the maximum salinity for this reservoir (sea, ocean).

Depending upon the width and the depth of the river, samples are taken either in one point (on race) or in three points – near the right and left shores and at the middle of the river from the surface (0–0.5 m),¹ bottom (1 m from the bottom)² and, sometimes, intermediate horizons. The principles of sampling and the number of water samples taken vertically are predetermined by the supposed character of water stratification, expected thickness of river and sea water layers and the bottom depth. Water and bottom sediment sampling in the regions of river and sea water mixing is performed on river–sea sections, the number of sections being determined by the size of the studied water area. Initial point (points) of section (sections) is located in the river water, the final one is located in the sea water. The length of river–sea section depends upon several factors: thickness and direction of river run-off velocity and direction of wind (piling down, piling up, calm), tides and up-tides. Therefore, these circumstances shall be taken into primary consideration when planning and performing works in the river–sea system. To specify correctly the places (points) of locations of stations for sampling on “river–sea” section and the distance between them it is necessary to have the data on the horizontal and vertical distribution of salinity in this region. This will give the possibility for uniform sampling of water on the section by the change of salinity in the process of mixing of river and sea water. If the data on salinity distribution is absent or doubtful it is necessary to measure the salinity of the water before

¹Thickness of taken “surface” layer of water depends upon the height of bathometer, used for sampling.

²It is not recommended to lower the bathometer closer to bottom to avoid rolling on the surface layer of bottom sediments

sampling for analysis of organic matter. During our expeditions, samples of water were taken on the "river-sea" cross-section in waters with salinity 0–10‰ through 1‰, in the more saline waters (from 10 to 20‰) through 2–3‰, in waters with salinity more than 20‰ through 5‰.

To obtain more reliable results on the organic matter geochemistry in the studied area of the river-sea system it is necessary to have the data not only of organic matter analysis results but also the velocity and direction of wind and streams, bioproducts, optical characteristics of water, biogenous elements, etc.

1.3. Methods for Sampling and Sample Analyses

Water samples were taken by sterilized bathometers with capacities of 1, 5, 10 and 20 litres. Suspension was obtained by means of water filtering through fibre glass filters GF/F and GF/C. Bottom sediments were taken by means of a dredge.

During our explorations the water salinity was determined by the method of argentometric titration, as well as by means of salt meter GM-65, oxygen – by Vinkler method, phosphates phosphorous – by Strickland and Parsons (1968), nitrogen of nitrates – by Wood *et al.* (1967).

Dissolved and suspended organic carbon was determined by the method of sulphur-chromium oxidation with subsequent coulometric determination of formed carbon dioxide (Lyutsarev and Smetankin, 1980a, 1980b). Organic carbon in bottom sediments was determined by the Knopp method (Uspensky *et al.*, 1966). Organic carbon in soils was determined by the method offered by Tyurin (Orlov and Grishina, 1981). Organic nitrogen in suspension was determined by means of the persulphate method (Konnov and Konnova, 1985), nitrogen in bottom sediments was determined by the method suggested by Kjeldal. The total sum of carbohydrates was determined by the phenol method (Artemyev *et al.*, 1971). Lignin in suspension and bottom sediments was determined by the means of nitrobenzol oxidation in an alkaline medium with subsequent determination of oxidation products by gas-liquid chromatography (Bobileva, 1982; Peresyupkin *et al.*, 1989).

Bituminological analyses of suspension and bottom sediments were performed by the scheme published in the paper by Danyushevskaya (1985). The molecular composition of *n*-alkanes of methano-naphthene fractions of bottom sediments bitumoids outlined by uprising chromatography on silica gel (Silina, 1973) was analyzed by gas-liquid chromatography (Belyaeva, 1987).

Humic acids (HA) in bottom sediments were analyzed by the methods assumed in bituminological researches (Uspensky *et al.*, 1966). HA in soils were determined by the pyrophosphate scheme suggested by Kononova–Bechikova (Orlov and Grishina, 1981).

The content and the composition of amino acids (AA) was determined by quantitative chromatography on paper: "free": directly from suspensions, "bound": from the hydrolysate of the bottom sediments amino acids (Danyushevskaya, 1985).

Dissolved and suspended forms of micro-elements were determined by the methods described by Demina (1982).

Chapter 2

ORGANIC SUBSTANCE OF RIVER RUN-OFF

2.1. Peculiarities of River Water Chemical Composition

River and sea waters differ sharply in their chemical composition. Average concentrations of some elements in river and sea waters are given in Tables 1 and 2 for comparative purposes. Without any doubt the chemical compositions of some rivers, i.e. those rivers of different water collecting basins (Table 3) may differ from the data given in Tables 1 and 2. It should be noted that our knowledge about chemical composition of water is far from complete even for the large rivers of the world.

As it is seen from Table 4, river and sea waters and estuaries also differ sharply by the content of C_{org} . The quantity of dissolved organic matter (DOM) of the majority of natural waters is many times greater than the quantity of particulate organic matter (POM); also, these forms of organic matter are often present in rivers and estuaries in equal quantities. The majority of river waters are acidic or neutral solutions of low ionic force.

Supply of dissolved substances to a territory of a river basin is provided by the following sources: soils, sedimentary and volcanic rocks, atmospherical precipitations, ash suspension, products of mineralization or humification of organism remains. In this case as V.I. Vernadsky noted (1960) "soil solutions of a river basin predetermine the main part of the salt composition for river water".

Waters of the majority of the world rivers belong to the hydrocarbonatic class and by composition of cations they are almost exclusively referred to the calcium group (Alekin, 1948, 1979).

Waters of sulphate and chloride class rivers are comparatively infrequent. Mineralization of river waters differs during the period of summer low water and spring flood. The water composition during low water time is essentially different from waters during flood due to their supply from deeper horizons and artesian waters. The river water composition depends upon the supply source: rain, snow, mountain snows, glaciers. The variety of climatic conditions, predetermining different quantity of precipitation, their character, conditions of accumulation, as well as combinations of other physico-geographical conditions create differences in the water and consequently in the hydrochemical regime of rivers.

Table 1. Average concentrations of some dissolved components in global river run-off and sea waters (Livingstone, 1963).

Component	River water		Sea water	
	concentration mg/l	% of sum of dis- solved components	concentration mg/l	% from content of salts
Na	6.3	5.0	10770	31.0
K	2.3	2.0	399	1.0
Mg	4.1	3.5	1294	4.0
Ca	15.0	12.5	412	1.0
Cl	7.3	6.5	19340	55.0
SO ₄	11.2	9.0	2712	8.0
HCO ₃	58.4	49.0	140	0.4

Table 2. Average concentrations of some dissolved micro-elements in river and ocean waters (Gordeev and Lisitzin, 1979).

Element	Concentration, mg/l		Element	Concentration, mg/l	
	River water	Sea water		River water	Sea water
Li	2.58	180.00	Co	0.3	0.003
Ba	20.00	18.00	Cu	7.0	1.400
U	0.50	3.00	Ni	2.5	0.500
Mo	1.00	10.00	Zn	20.0	5.000
Cr	1.00	0.25	Sb	1.0	0.300
Fe	410.00	0.50	Pb	1.0	0.030
Mn	10.00	0.40			

Table 3. Elements of basic salt composition of rivers falling into ocean, mg/l (Martin and Gordeev, 1985).

Ocean	SiO ₂	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	Sum	
Atlantic	9.9	10.5	2.5	4.2	1.4	5.7	7.7	37.0	69.0	78.9
Indian	14.7	21.6	5.4	8.5	2.5	6.8	7.9	94.9	140.2	154.9
Arctic	5.1	16.1	1.3	8.8	1.2	11.8	15.9	63.5	118.6	123.7
Pacific	11.7	13.9	3.6	5.2	1.2	5.1	9.2	55.4	93.6	105.3

Table 4. C_{org} concentration in natural waters, mg/l.

C _{org}	Rivers	Estuaries	Inshore sea waters	Open sea	
				Surface waters	Deep waters
C ^d	2–30	1–8	1–5	1.0–1.7	0.5–0.8
C ^p	1–10	0.1–5.0	0.1–1.0	0.005–1.000	0.001–0.010

Therefore, the hydrochemical regimes of rivers, located in different physico-geographical regions, are not similar.

Non-uniformity of the chemical composition of river waters is most clearly expressed along the river bed (falling of inflows, supply of ground waters, etc.) and to a lesser degree by width and depth.

Fluctuations of river water organic matter composition may be most clearly traced in various climatic zones depending upon the type of soil. Therefore, the maximum quantity of organic matter, as it will be shown further on, is revealed in northern rivers, followed by rivers of mid and tropical latitudes.

2.2. Soils As the Basic Source of Organic Substance in Rivers

2.2.1. THE BIOGEOCHEMICAL ROLE OF SOILS

The greatest part of river organic matter is of allochthonous genesis, coming from soils. Emphasizing the important role of soils as the source of organic matter, supplied to rivers and further on to sea, V.I. Vernadsky noted (1960): “We usually don’t take into account and understand the great value of soil mantle of our land for life and chemical reactions of the ocean . . . Soil and sea water are bound up chemically and genetically”. It was shown (Hedges *et al.*, 1986) that soils may be a potential source of both dissolved and particulate organic matter in rivers. The second terrigenous source of river organic matter may be products of agricultural activities and finally comparatively small autochthonous fraction of river organic matter is formed by products of *in situ* river plankton, consisting basically of labile components (Ittekkot *et al.*, 1986), as well as leaves, waste wood, grass, etc. (Hedges *et al.*, 1986).

It is known that mineralization and chemical composition of surfacial waters depend on processes of destruction of mountain rocks, minerals and organic residues in the soil layer. The basic source of organic matter washed out by atmospheric precipitations are residues of annually dying plants, and to a lesser degree the residues of animals, insects and micro-organisms. Water-soluble organic matter run-out from drainage systems into fluvial systems of rivers are formed in the thickness of soils by chemical decomposition of vegetable residues as a result of microbial activities.

Formation and accumulations of organic substances of soils (humus) is carried out mainly in the upper horizons of the soil mantle due to slow physico-chemical processes of organic matter oxidation. Organic matter of humus origin, washed out from the soil mantle of water collectors and some products of decomposition of vegetable residues (tannins) taint surfacial waters into yellow-brown colours of various intensity (Voronov *et al.*, 1966).

Since dead organic matter are preferably accumulated on the soil surface in a comparatively thin layer, dissolving of certain parts is carried out mainly in this layer during spring flood. Further infiltration of waters, transformation of organic matter takes place mainly due to their oxidation and partial deposition of colloids from solution.

It was shown convincingly by V.I. Vernadsky that living and dead substances are in close interaction in nature, which bio-inert systems or bodies arising (the natural structures, consisting of inert and living bodies, for example soils). V.I. Vernadsky described bottom sediments of lakes, seas and oceans as stagnant systems: "Mud . . . is a natural body, essentially similar to soil, where hydrosphere replaces atmosphere" (Vernadsky, 1960). Bottom sediments are referred to as bio-inert systems since they contain both inert (mineral) and living (micro-organisms, benthos, plankton residues, etc.) parts.

B.B. Polynov noted (1956): "Geological activity of living substance is concentrated in soils, soils are that material of continental and sea deposits, from which new rocks are formed in future". Thus, the bio-inert system of soils gives the beginning for the bio-inert system of river waters and further on bio-inert system of ocean waters and through it to the bio-inert systems of oceanic sediments. Therefore, humus of reservoirs does not actually differ from humus of soils. The nature of water humus is, of course, somewhat different than humus of soils, since decomposition of vegetable and animal residues in reservoirs of land and sea differ from the analogous decomposition in soil (different chemical nature of decomposing residues, micro-organisms, predetermining decomposition processes, etc.). In general genesis of soil humus and humus of reservoirs is similar. As in soil reservoir humus consists of two parts: the major one being lignin-proteinous and the minor one, consisting of carbohydrates, fats and waxes (Muraveisky, 1960).

Humus, fertilizing salts (nitrogen, phosphorous, potassium, etc.), mineral combinations determining the basic salt composition of water, as well as dissolved gases create a complex of properties, coinciding with the complex properties determining the qualitative specificity of soils. Consequently, by its properties, water of reservoirs belong to natural bodies of soil type but not that of mineral. Water is soil in the broad sense of this word (Muraveisky, 1960).

This point of view completely corresponds to Williams' views on the existence of unified soil forming processes, covering both land and ocean (Williams, 1936). This complicated process of interaction, expressed in exchange of water masses of the ocean and the land, covers both ocean waters and land waters. Knowledge of this process is possible only on the basis of qualitatively different processes, arising as a result of the exchange of water masses of the ocean and the land (Muraveisky, 1960). V.I. Vernadsky (1960) noted that soil solution plays a "great role in the water mechanism of the planet, determining existence of the living substance, composition of its rivers and (through them) the salt composition of sea water".

Table 5. Basic reservoirs of C_{org} on the Earth (Kobak and Kondrashova, 1986).

Reservoir	C_{org} content, 10^{12} kg
Ocean	2000
Soil	2100
Terrestrial biosphere (except soil)	700
Fossil fuel:	4130
coal	3510
oil	230
gas	140
other	250

2.2.2. FORMATION OF SOIL ORGANIC MATTER. CONTENT OF C_{org} IN SOILS AND CLIMATIC ZONALITY

Organic matter created by living organisms of land, and first of all by plants during their life activities, are finally supplied to the soil, forming its organic part or humus. Organic residues (plants, micro-organisms, soil fauna) are subjected to various transformations in the soil, as a result of which a part of the organic matter is broken down to simple combinations (CO_2 , H_2O , NH_3 , etc.). Another part of the organic matter is transformed into more stable forms: peat, saporpels, etc.

Humus is formed from the layer of dead parts of trees, bushes, grass, soil fauna and micro-organisms.

The character and the rate of transformation of organic residues during humus formation are predetermined by the composition of these residues, chemical composition of soil, moistening degree, etc.

The total content of C_{org} in the Earth soils is equal (Kobak and Kondrashova, 1986) to 2100×10^{15} g, i.e. soils are the largest reservoir of C_{org} of our planet. The quantity of C_{org} contained in them is considerably larger than that in the biomass of ground ecosystems and has a value in the same order with reserves of C_{org} in the ocean and fossil fuel (Table 5).

The zonality of nature, and that of climate was initially noted even in the ancient times. The first scientific generalization in the field of geographical zonality (horizontal and altitudinal) belongs to Gumboldt (beginning of 19th century). Division of earth surface into geographical zones was first suggested by V.V. Dokuchaev in 1898. Dokuchaev was the first one to determine zonality of climate, flora and fauna (Tziganenko, 1972) and suggested the division of the northern hemisphere into seven zones: boreal (tundra), taiga, forest-steppe, desert-steppe, areal (desert), subtropical and tropical forests.

Latitudinal variation of C_{org} in soils is expressed in its growth from equator to poles, the maximum being in the boreal zone (Figure 1). It was determined that boreal belt soils accumulated the maximum quantity of C_{org} – 35% of total reserves; soils of tropical

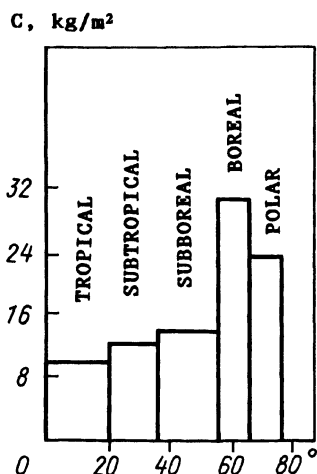


Fig. 1. The content of C_{org} in soils of different climatic zones (Tziganenko, 1972).

belts – 27%; and so on. The lowest concentration of C_{org} was revealed in desert belt soils (Table 6).

2.2.3. COMPOSITION OF SOIL ORGANIC MATTER

The organic part of soil is a complex system of various substances. The dynamics of it are determined by the supply of residue of animal and vegetable origin to the soil and their change under action of various groups of micro-organisms, as well as fauna representatives. Some changes of organic residues and their components may take place under direct action of precipitations, acid or alkaline reaction of soil, wind, and variation of temperature (Kononova, 1963).

All the varieties of soil organic matter may be classified into two basic groups. The first group of substances includes matter composed of organic residues: it is the product of their decomposition or life activity of living organisms. These are proteins, amino acids, hydrocarbons, organic acids, fats, resins, lignin, pigments, etc. In total this organic matter amounts to 10–15% of the total reserve of organic matter in mineral soils.

However, the majority of the organic content of the soil is represented by humus substances: humic acids, fulvic acids and humates (Tables 7 and 8), the formation of which is effected in the process of complex transformations of initial vegetable and animal residues. This group of substances represents up to 85–90% of the total reserve of humus in mineral soils. They may remain in soils for a long time and determine stable, typical signs of soils. According to radiocarbon dating the average interval of humic acids presence in the soil profile amounts to hundreds and even thousands of years (Orlov, 1985).

Table 6. Distribution of C_{org} in soils by belts (Tziganenko, 1972).

Belt (zone), regions	Area		C_{org}		
	10^4 km^2	%	10^{12} kg	kg/m^2	%
Tropical	5634.1	42.1	579.14	10.28	27.5
humid	2590.7	19.4	349.52	13.49	16.6
dry	3043.4	22.7	229.62	14.60	10.9
Subtropical	2571.9	19.3	330.52	12.85	15.7
humid	655.4	4.9	133.33	20.34	6.4
dry	1916.5	14.4	197.19	21.64	9.3
Subboreal	2188.7	16.5	319.80	14.61	15.2
forest	601.0	4.5	108.65	18.08	5.2
steppe	793.0	6.0	168.96	21.31	8.0
desert	794.7	6.0	42.19	5.31	2.0
Boreal	2373.7	17.8	738.63	31.12	35.1
taiga-forest	1536.2	11.5	549.33	35.76	26.1
frozen ground- taiga	837.5	6.3	189.30	22.60	9.0
Polar	570.7	4.3	136.38	23.90	6.5
Total	13339.1	100.0	2104.47	15.78	100.0

Fulvic acids (FA) differ essentially from humic acids by their elementary composition. They contain considerably lower quantities of carbon and more oxygen (Table 8).

The richest of the humus are thick chernozems (Table 9), where a one metre layer contains more than 700 t/ha of humus and about 40 t/ha of nitrogen. Reserves of humus and nitrogen in soils are decreased both in regions characterized by increasing quantity of precipitation and decrease of temperatures (leachable chernozems, grey forest and podzol soils) and in the regions, being in arid conditions (southern chernozems, chestnut, brown, desert-steppe soils).

2.2.4. ORGANIC MATTER OF RIVER FLOOD PLAIN SOILS

From the standpoint of problems raised in this work, river flood plain soils are of the most interest among soils as the source of organic matter in river waters. River flood plains are parts of the river bottom covered with plants and submerged during flood (Tziganenko, 1972).

The climate, the relief and extent of mastering the territory in the river basin have a great effect on the properties and the quantity of alluvial deposits. In the basins completely covered with forest, for example in those of some northern rivers of the USSR, where snow melts slowly under the forest cover, aqueous erosion is absent and does not supply mud for flood plains. But, in such rivers as the Don, the basin of which is fully free

Table 7. Average element composition of humic acids of soils (Orlov, 1985).

Source of humic acid	Content, at. %				Atomic ratio		
	C	H	O	N	H/C	O/C	C/N
Peaty-marshy soils, peat bogs	40.2	41.0	16.8	2.0	1.0	0.4	20.1
Flood plain, meadow soils	41.1	36.4	20.2	2.3	0.9	0.5	17.9
Dark colour soils	37.4	41.5	19.8	2.2	1.1	0.5	17.0
Dern-podsolic soils, podsols	37.5	39.8	20.3	2.4	1.1	0.5	15.6
Brown, wood soils, brown soils	37.4	42.2	17.9	2.5	1.1	0.5	14.9
Grey wood soils	38.1	40.3	19.2	2.4	1.1	0.5	15.9
Chernozems	42.5	35.2	19.9	2.4	0.8	0.5	17.7
Chestnut soils	37.7	42.1	17.4	2.8	1.1	0.5	13.5
Solonetz (salt garden)	40.5	36.4	19.9	3.2	0.9	0.5	12.7
Grey soils	39.0	40.1	18.1	2.8	1.0	0.5	13.9
Terra rossa	42.1	33.4	21.8	2.7	0.8	0.5	15.6
Mountain meadow soils	42.7	32.0	22.3	3.0	0.7	0.5	14.2
Limits	37.4–42.7	32.0–42.2	16.8–22.3	2.0–3.2	0.7–1.1	0.4–0.5	12.7–17.9
Average	39.7	38.4	19.5	2.6	1.0	0.5	15.7

of forest, floods are usually very intensive, relatively short and bring a large quantity of suspended deposits to river valleys.

Occupying the lowest areas of land, river plains accumulate various nutrient substances and chemical elements for plants brought with river run-off from interfluves. The flood plains are supplied with the most biologically active and most productive soils, washed off with rain and melt waters. As for their potential productivity of the soils, which are mostly spread in flood plains, exceed podsolic and chestnut soils but are second to chernozems enriched with humus. A metre thick layer of grainy flood plain soils contains up to 350–550 t and more humus per hectare, which exceeds that in podsolic soils by 5–7 times and that in chestnut ones by 3–4 times.

Genesis and properties of flood plain soils are different from those of watershed soils which are bound with a great variety of natural factors effecting their formation. More than 60% of the total area of flood plain soils of Russia are located within the boundaries of the taiga-forest zone. Soils of river flood plains are marked by their productivity on the background of turf-podsolic zone soils (Sokolov *et al.*, 1974). In central chernozem areas and southern regions of the steppe zone (flood plains of the Don and the Kuban) flood plain soils are very productive and are used intensively (Gorokhov, 1960). Their humus content varies from 1 to 6%, averaging 3.2%.

Table 8. Average element composition of fulvic acids of soils (Orlov, 1985).

Soil	Content, at. %			N	Atomic ratio		
	C	H	O		H/C	O/C	C/N
Podsollic, dem-podsolic soils	33.4	39.8	25.3	2.0	1.2	0.8	16.6
Brown, wood soils	30.8	40.9	26.1	2.2	1.3	0.8	13.9
Grey wood soils	31.9	40.9	25.3	1.9	1.3	0.8	17.0
Chernozem, chestnut soils	30.9	40.6	26.3	2.2	1.3	0.8	14.3
Grey soils	29.4	41.7	26.7	2.2	1.4	0.9	13.3
Brown soils	32.2	34.9	30.9	2.0	1.1	1.0	16.3
Terra rossa	36.6	33.4	27.9	2.1	0.9	0.8	17.6
Mountain-meadow soils	30.2	42.1	25.4	2.3	1.4	0.8	13.2
Meadow soils	31.9	41.2	24.4	2.5	1.3	0.8	12.8
Dark colour soils	32.9	39.4	26.0	1.7	1.2	0.8	18.8
Limits	29.4–36.6	33.4–42.1	25.3–30.9	1.7–2.5	0.9–1.4	0.8–1.0	12.8–18.8
Average	32.0	39.4	26.4	2.1	1.2	0.8	15.4

Table 9. Composition of humus of the USSR soils (Kononova, 1963).

Soil	Humus %	Carbon of some groups, % of its total content in soil				Carbon of remainder
		Substance obtained during decalcination		HA	FA	
Tundra soil	about 1	20–30	10	30	0.3	30–40
Strongly podsollic	2.5–3.0	10–20	12–15	25–28	0.6	30–45
Dem-podsolic	3.0–4.0	up to 10	20	25	0.8	30–35
Grey, wood	4.0–6.0	5–10	25–30	25–27	1.0	30–35
Chernozem:						
thick	9.0–10.0	5–10	35	20	1.7	30–35
ordinary	7.0–8.0	2–5	40	16–20	2.0–2.5	30–35
southern	5.5–6.0	3–5	30–35	20	1.5–1.7	30–35
Dark chestnut	3.0–4.0	2–5	30–35	20	1.5–1.7	up to 40
Light chestnut	1.5–2.0	8–10	25–29	20–25	1.2–1.5	30–38
Brown desert-steppe	1.0–1.2	3–5	15–18	20–23	0.5–0.7	–
Grey soil	1.5–2.0	up to 10	20–30	25–30	0.8–1.0	25–35
Terra rossa	4.0–6.0	10–20	15–20	22–28	0.6–0.8	35–38

Unfortunately, the data on content of humus (or C_{org}) in flood plain soils of other large rivers of the European part of Russia are absent at present. During the 9th expedition of research vessel "Professor Shtokman" we sampled and later on studied, in the stationary laboratory,¹ soils from the shores of the Amazon tributaries (Tables 10 and 11). Soils of the Amazon basin are the source or river dissolved organic matter which is borne out by the similarity of the composition of humic substances, found in the Amazon waters and humic substances of podsollic and latosolic soils of the Amazon region (Leenheer, 1980). Humic substances get into river waters of the Amazon river either as a result of drainage by underground waters of podsollic soils (Negru river) covered with a thick layer of organic residues, or latosolic soils (for example, Topazhos river) which do not have, like podsol, a layer enriched with organic matter (Table 5). At the same time, passing latosolic soils, coloured solutions of humic substances are to a considerable extent adsorbed at clay minerals, contained in latosols.

Content of C_{org} in the soils of the Amazon river varied from 0.63 to 3.30%, and equals an average to 1.83%, which when converted to humus is equal to 1.1–5.7% or 3.2% as an average. The maximum content of C_{org} was found in Negru river soils. In latosolic soils taken from the shores of other investigated tributaries of the Amazon, the content of C_{org} humic and fulvic acids is essentially lower.

As it is seen from Table 5 the basic part of the organic matter of soils consists of "non-hydrolysed" or "residual" organic matter. Bitumoids in the composition of soils organic matter play secondary roles, being equal to about 45% of the total content of organic matter. In this case, there are no essential differences in content of bitumoid "A" in various types of soils. More detailed studies of chlorophormic bitumoid "A" (bit. A_{cl}) and hydrocarbons (HC) in soils of the Amazon (Table 11) gave a possibility to reveal differences in the studied soils. Bitumoid A_{cl} of Negru podsol is more "carbonic" than in other soils. Resin components prevail in it. But latosolic soils are characterized by a higher content of asphaltenes and asphaltenic acids. The main component of the hydrocarbons of Negru river podsollic soil oils (more than 90%) consists of methano-naphthene and their proportion amounts to 0.33% of organic matter (in latosolic soils 0.05%).

2.3. Role of River Run-Off for Organic Matter Delivery to Sea Medium

As it is known, continents are the area of preferable denudation, and oceans are the area of preferable accumulation of substances, washed off the land. Dissolved and suspended substances are delivered with river run-off from water collecting basins into oceans.

Even if the biogenic material, playing an important role in the sedimentation, originates in ocean, organisms of plankton and benthos use mainly elements and compounds supplied to ocean from river run-off (Table 12).

¹Analyses of organic matter of soils were performed in the laboratory of soil chemistry of the Soil Faculty of the Moscow State University and in the laboratory of organic geochemistry of the "Ocean-Geology" Research Institute (St. Petersburg).

Table 10. Composition of organic substances in Amazon Basin soils.

Place of sampling	Content in soils, %						Content in OM of soils, %											
	C _{org}			Humus			Bitumoid "A"			Bitumoid "A"			Chlor.* Eth.benz.**					
	C	H	O+N+S	C/H	H _{ar} /C	C/H	CH _A	C _{FA}	Chlor.*	Eth.benz.**	CH _A	C _{FA}	Chlor.*	Eth.benz.**	HA	FA	HA/FA	ROM
Negru river	3.30	5.7	0.03	0.03	0.03	0.60	0.37	1.4	1.4	1.4	18.2	11.2	1.6	1.6	67.8			
Topazhos river	1.60	2.8	0.03	0.03	0.13	0.13	0.13	1.4	1.4	1.4	8.1	8.1	1.0	1.0	80.9			
Shingu river	2.69	4.6	0.09	0.10	0.43	0.26	1.9	2.1	2.1	15.9	9.6	1.7	70.3					
Limits	1.60-3.30	2.8-5.7	0.03-0.09	0.03-0.10	0.13-0.60	0.13-0.37	1.4-1.9	1.4-2.1	1.4-2.1	8.1-18.2	8.1-18.2	1.0-1.7	67.8-80.9					
Average	2.53	4.4	0.05	0.05	0.39	0.25	1.6	1.6	1.6	14.1	9.6	1.4	73.0					

* Chloroform

** Ethanol-benzol

Table 11. Physicochemical characteristics of OM for the Amazon basin.

River, station no.	Composition of bitumoid A _{el}										Composition of bitumoid A _{sl}									
	Elementary, %					Group, %					Group, %					Group, %				
	C	H	O+N+S	C/H	H _{ar} /C	resins	oils	A+A* acids	Me-NF	AR	HC of oils, %	Me-NF	AR	Me-NF/AR	HC, %	Me-NF, %	in OM			
Shingu, 1006	72.4	10.6	17.0	6.8	1.76	5.6	41.1	51.7	50.0	50.0	50.0	50.0	1.0	0.005	0.11	0.05				
Negru, 1030	76.6	11.1	12.3	6.9	1.74	25.5	60.9	5.4	90.4	9.6	9.4	9.6	9.4	0.008	0.36	0.33				
Negru, 1031	75.1	11.6	13.3	6.5	1.85	9.4	76.0	14.5	90.4	9.6	9.4	9.6	9.4	0.002	0.12	-				
Topazhos, 1039	73.5	11.4	15.1	6.4	1.86	9.7	63.2	26.9	90.4	9.6	9.4	9.6	9.4	0.003	0.14	-				
Limits	72.4-76.6	10.6-11.6	12.3-17.0	6.4-6.9	1.74-1.86	5.6-25.5	41.1-76.0	5.2-51.7	50.0-90.4	9.6-50.0	1.0-9.4	0.002-0.008	0.11-0.36	0.05-0.33						
Average	74.4	11.2	14.4	6.6	1.81	12.5	60.3	27.2	70.9	30.0	5.2	0.004	0.17	0.12						

* Asphaltenes + Asphaltogenic

Table 12. Entrance of sedimentary material to the ocean (Lisitzin, 1974).

Type of sedimentary material	Quantity, mlrd t/year	%
Terrigenous fragmentary and shaly	22.6	77.2
Volcanic	2-3	8.8-10.3
Biogenic, plankton (dry)	110	-
including:		
carbonaceous	1.36	4.7
siliceous	0.46	1.6
Cosmic	0.01-0.08	0.03
Total (without dry substance of plankton)	26.43-27.50	100.03

From the data presented by Lisitzin (1974) it is clear that the main role in delivery of material from the continent to the ocean is played by rivers, suspended and dissolved run-off of which totals respectively 18.53 mlrd t/year and 3.2 mlrd t/year. An exclusive role of rivers as a binding link between land and ocean was noted by V.I. Vernadsky (1960), who emphasized "what a great work is performed by river's water, washing off continents and transporting huge quantities of substances to the sea".

The majority of high-water rivers of the Earth are rivers of tropical regions and the greatest of them is the Amazon (Table 13).

The main part (more than 50%) of all suspended material is delivered into seas and oceans by rivers of the equatorial humid zone. Even if river run-off in the northern moderate zone is sufficiently great, the content of suspension in it is significantly lower than in the equatorial zone (Table 13).

Holeman (1968) and later Milliman and Meade (1983) showed that about 70% of suspension, delivered by rivers into oceans comes from 21 large rivers of the Earth. However, only 5-10% of it reaches ocean depth (Postma, 1980; Eisma, 1981a; Milliman and Meade, 1983). More than 90% of suspension remains on the shelf (including that in estuaries, limans, deltas) and the continental slope.

The main part of dissolved and particulate organic matter, washed out from continents to ocean is also delivered to ocean waters with river run-off, causing a noticeable effect on the surrounding medium. Organic matter is the main regulator of all chemical, geochemical and biogeochemical processes, going on in the volume of ocean waters and in the bottom sediments. Run-off of dissolved and particulate organic matter is an important geochemical factor, reflecting multiform processes of organic matter migration and transformation in the studied region. In spite of the fact that river waters total only a small part of surficial waters on the planet (0.006% of world reserves of fresh water),

Table 13. Entrance of organic matter to seas and oceans with river run-off (from the data presented by Lisitzin, 1974; Kemple, 1985; Spitzky *et al.*, 1991 and the author).

Latitude	River	Liquid run-off km ³ /y	Solid run-off mlrd t/year	C ^d mg/l	C ^p mg/l	POM, % from sus- pension	C ^{d+p} mg/l	OM flows, 10 ⁶ t/year		Oil reserves in delta sedi- ments mlrd t*	
								C ^d /C ^p	C ^d		C ^p
60°–75°N	Lena	533.0	0.015				9.5				
	Ob	419.0	0.016			8.8			1.85		
	Yenisey	562.0	0.013				7.4				
	Pechora	129.0	0.007	12.7	0.3	32.1	13.0	42.3	1.64	0.04	
	North Dvina	110.0	0.005	20.1	3.2	46.6	23.4	6.3	2.22	0.35	
	Yukon	210.0	0.088	8.8	1.2		11.0	7.3	2.40	0.34	
	Mackenzey	248.0	0.015	4.5	3.2		7.7	1.4	1.30	0.93	
	Sum total	2211.0	0.159						7.56	3.51	0.6 (North seas, Beaufort Sea)
30°–60°N	Rona	68.0	0.031	3.5	1.4		4.9	2.5			
	Garonna	19.2	0.006	3.1	2.5		5.6	1.2			
	Kuban	11.3	0.008	1.9	2.8	3.6	4.7	0.7	0.03	0.04	
	Don	22.8	0.006	4.2	1.7	5.6	5.9	2.5	0.41	0.05	
	Daugava	21.0	0.0004	13.2	–	7.3	13.3	–	0.27	–	2.4 (Gulf of Mexico, Shelf of Argentina and West Australia)
	St. Lawrence	413.0	0.004	4.9	0.5		5.4	9.8	0.71	0.17	
	Mississippi	398.0	0.500	6.0	1.4		7.4	4.3	3.48	0.85	
Colombia	135.0		2.7	0.6		3.3	4.5	0.45	0.11		
40°–30°S	Parana	480.0	0.13	6.1	1.3		7.4	4.7	3.20	0.70	
	Uruguay	158.0		3.2	–	–	–	–	0.50	–	
30°–60°N	Hwang Ho	44.0	1.9	16.5	–	–	–	–	0.54	0.36	
	Danube	203.0	0.067	4.7	4.1	2.4	8.8	1.1	0.95	0.83	
	Dnieper	54.0	0.001	4.9	0.9	29.2	5.8	5.4	0.26	0.05	
	Visla	30.0	0.002	8.2							
	Sum total	2057.3	2.65						10.80	3.16	
30°N–30°S	Orinoko	1135.0	0.086	2.9	–	–	–	–	3.20	4.80	
	Yangtze	883.0	0.5	12.4	–	–	–	–	11.80	4.40	
	Ganges	366.0		4.6					1.70	9.20	
	Brahmaputra	609.0		3.2					1.90	30.00	
	Congo	1237.0	0.065	8.5	1.2		9.7	7.1	10.50	1.50	
	Indus	211.0	0.4	16.1	–		–	–	0.80	–	
	Niger	192.0	0.067	2.9	3.4		6.3	0.8	0.60	0.70	
	Amazon	5780.0	0.50	5.0	2.0	3.0	7.0	2.5	26.90	11.00	
	Sum total	10413.0	3.80						57.40	61.60	
		13878.0						76.76	68.27		

* Geodekyan *et al.*, 1988.

their role in geochemical processes is great. V.I. Vernadsky wrote about the important role of particulate organic matter (1960): "... Mud of rivers is most closely bound up with living substance, with geochemical energy of life. It is washed off into rivers in a form of thinnest dust by winds and meteoric waters. Its quantity is most closely bound up with the laminating work in soil, performed first of all by animals and mostly by human beings".

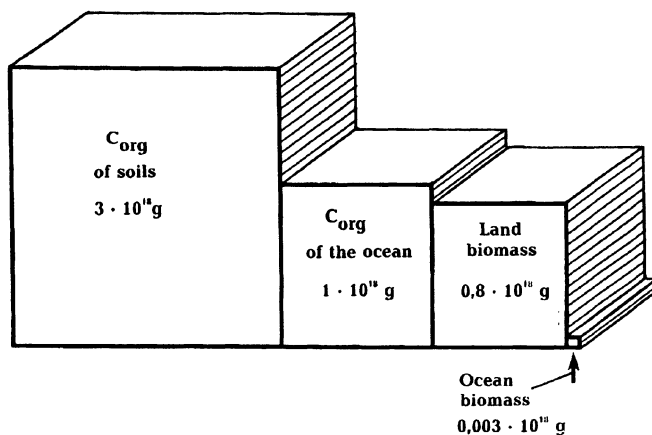


Fig. 2. Organic carbon at continents and in the ocean (Degens *et al.*, 1984; Romankevich, 1990).

At present the ionic run-off of rivers as the main component of the general run-off of dissolved substances is studied in the best way. Information about run-off of basic ions from the Russian territory to seas and oceans, formation of ionic run-off, its connection with geographical and geochemical factors is most detailedly considered in works of Alekin (1951, 1970) and Alekin and Brazhnikova (1961, 1984). Compared with ionic run-off the run-off of organic matter is sparsely studied. The most complete information about continental organic matter run-off from the Russian territory (without distinction between dissolved and particulate organic matter) was published by Mateva *et al.* (1987). The data from dissolved and particulate organic matter transfer with rivers of the world are given in the collected articles *Transport of Carbon and Minerals in Major World Rivers*, by Degens *et al.* (1982–1991), review articles by Degens and Ittekkot (1983, 1985); Duce and Duursma (1977); Schleisinger and Melack (1981), and in the present work (Tables 13–15).

The main reserves of C_{org} on land and in sea are shown in Figure 2. As it is seen here, the basic mass of C_{org} on the Earth is accumulated in soils. Dissolved forms of C_{org} (C^d) plays the main role in the ocean. The maximum quantity of C_{org} in ocean was found in comparatively small volumes of water over shelves (Figures 3 and 4) which is first of all bound up with the supply of C_{org} with river run-off, as well as with the production of C_{org} *in situ*, due to the high content of nutritional salts in river run-off.

The biggest flows of both C^d and C^p are delivered by rivers to seas and oceans in the equatorial humid zone – 75.8 and 90.2% respectively from global run-off. On the whole, rivers deliver approximately equal quantities of C^d and C^p to waters of seas and oceans: 0.204×10^9 t/year and 0.184×10^9 t/year respectively.

The main flow of river waters (liquid run-off) and C^d to ocean is from the territory of South America and the maximum quantity of suspended material, and C^p is supplied by rivers of Asia (Figures 5–7, Table 13).

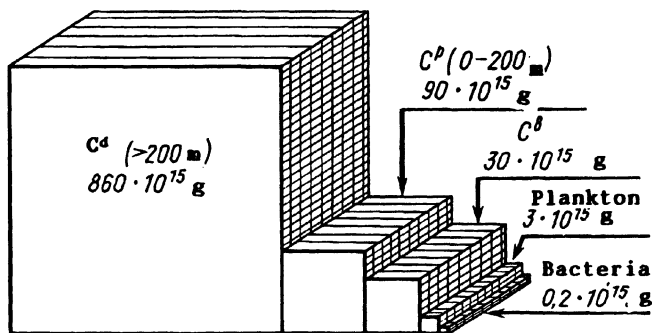


Fig. 3. The distribution of C_{org} in ocean waters (Degens *et al.*, 1984).

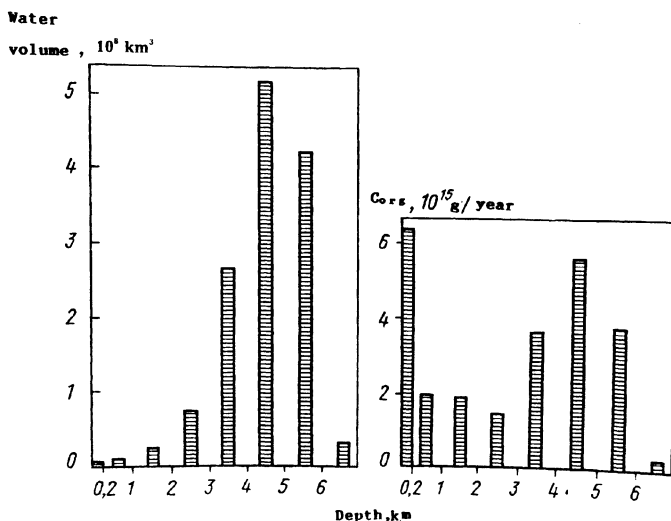


Fig. 4. Water volumes and the amount of C_{org} in waters above different depths of the ocean bottom (Degens and Ittekkot, 1984).

The run-off of Russian rivers amounts to 10% of the global river run-off. The river run-off of the European part of Russia amounts to about 39% of the European total, and the river run-off of the Asian part of Russia totals 42% of the Asian one.

Rivers, specified in Table 13 cover 37.1% of the global river run-off, which amounts to $37\,400 \text{ km}^3/\text{year}$ (Spitzky *et al.*, 1991). Extrapolating to 100% gives $204 \times 10^6 \text{ t/year}$ (52.6%) for C^d , and $184 \times 10^6 \text{ t/year}$ (47.4%) for C^p , C^{d+p} totals to $388 \times 10^6 \text{ t/year}$. If it is accepted that 25% of river dissolved organic matter and 80% of particulate organic

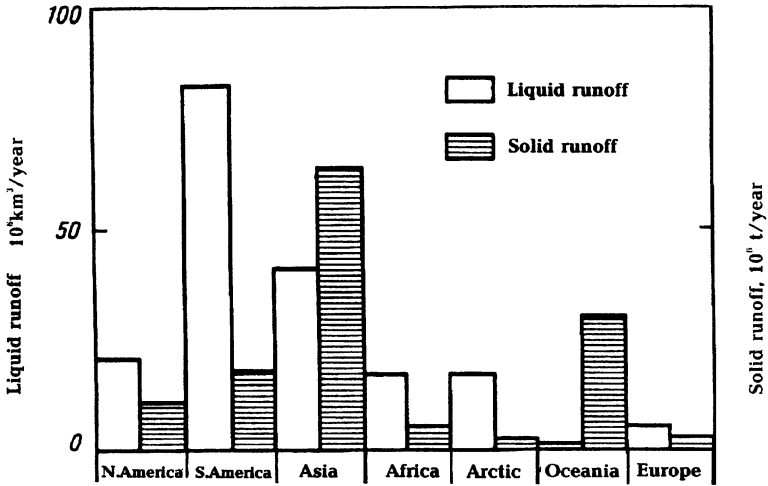


Fig. 5. Solid and liquid run-off from continents (Degens and Ittekkot, 1985).

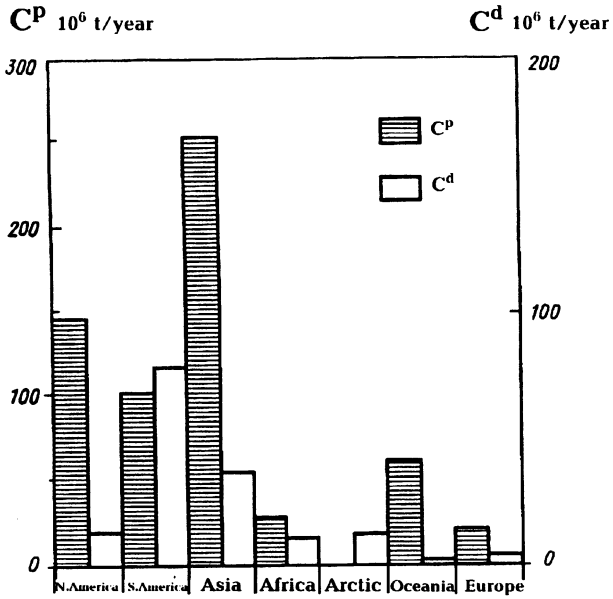


Fig. 6. Annual input of the river C_{org} from continents to the ocean (Degens *et al.*, 1984; Degens and Ittekkot, 1985).

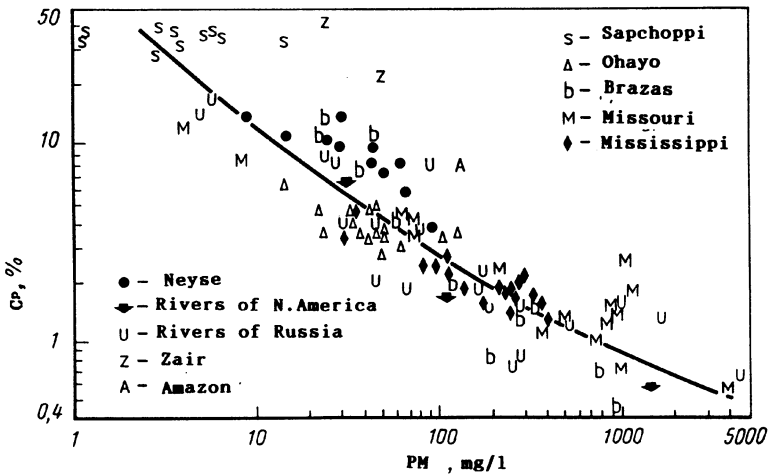


Fig. 7. Dependence of C^p content in rivers from the particulate matter content (Meybeck, 1981 and the author).

Table 14. C_{org} entrance to the Russian marginal seas with river run-off (Maltseva *et al.*, 1987).

Sea	Run-off km ³ /year	C_{org} 10 ³ t/year	Average concentration of C_{org} , mg/l	Area 10 ³ km ²
Barents Sea,				
White Sea	417.7	5516.5	13.21	1250.0
Kara Sea	1337.2	12522.5	9.36	6200.0
Laptev Sea	789.6	8519.5	10.79	3670.0
East Siberian Sea	238.0	1696.5	7.13	1390.0
Chuckchee Sea	.28.6	101.5	3.55	102.0
Bering Sea	220.4	1020.5	4.63	575.1
Okhotsk Sea	674.4	5388.5	7.99	2500.0
Japan Sea	43.5	226.5	5.21	135.0
Baltic Sea	168.3	1988.5	10.65	640.0
Black Sea, Azov Sea	146.3	937.0	6.40	1329.0

matter remains in river mouths during the mixing of river and sea water (see Chapter 3), this will total 51×10^6 t/year and 147×10^6 t/year for C^d and C^p , respectively.

The highest values of C_{org} run-off in Russia are typical for rivers of Asian North, falling into the Kara Sea and the Laptev Sea (Table 14). In accordance with the data (Maltseva

Table 15. Discharge of C_{org} ($C^d + C^p$) from the Russian territory to ocean basins (Romankevich and Artemyev, 1985).

Ocean	Run-off km ³ /year (%)	C_{org} 10 ⁶ t (%)	C_{org} mg/l	Drainage area 10 ⁶ km ² (%)
Arctic Ocean	2811.3 (69.2)	28.36 (75.2)	10.10	12.6 (69.7)
Pacific Ocean	938.3 (23.1)	6.64 (17.6)	7.07	3.51 (19.4)
Atlantic Ocean	314.3 (7.7)	2.73 (7.2)	8.67	1.97 (10.9)
Sum total	4063.9 (100)	37.72 (100)	9.28 (average)	18.09 (100)

et al., 1987) the total run-off of C_{org} from the Russian territory amounts approximately to 41×10^6 t/year, but the run-off to ocean amounts to 38×10^6 t/year or 92%. The main mass of C_{org} , 28.3×10^6 t or 75% of summary run-off to the ocean, is delivered to the Arctic Ocean (Table 15). The Pacific receives 6.6×10^6 t/year of C_{org} or 17.0%, and the Atlantic 2.7×10^6 t/year or 7.2% of summary run-off from the Russian territory to the ocean.

2.4. Organic Carbon in Rivers of Various Climatic Zones

According to our data (Table 13) and the data of Meybeck (1982) the content of C^d in world rivers averages 7 mg/l, and C^p 2 mg/l. Concentrations of C^p in the suspension composition varies from 0.5 to 40% (see Figure 7). Content of C_{org} in river waters and the proportion of dissolved and suspended forms of organic matter depend upon many factors: type of drained soils, products *in situ*, presence of anthropogenous pollutions, etc., which on the whole is bound up with climatic and ecological peculiarities of the water catchment basin. It was found, for example, that organic matter and some of its components in mouths of plain rivers are mainly (60–70%) in the dissolved form, and particulate organic matter prevails in mountain rivers (Artemyev, 1981). It was also shown that suspension of mountain rivers contains 4–5 times fewer organic particles (converting into dry substance of suspension) than plain one, which is bound up with relative enrichment of mountain river suspension with terrigenous inorganic material.

Content of dissolved nitrogen and phosphorus in river waters is 1–2 orders lower than the content of C_{org} and amounts, respectively, to 100–600 mg/l and 1–35 mg/l (Meybeck, 1982).

Suspended nitrogen of river waters amounts to 0.1–1.3% of dry suspension. Ratio C^p/N^p varies from 7 to 54 and average is equal to 25 (Artemyev, 1988; Subramanian and Richey, 1985).

Table 16. C^d and C^p (mg/l) in the North Dvina mouth.

Station No.	Horizon	C ^d		C ^p		C ^d + C ^p	
		May 1985 Spring	Febr. 1987 Winter	May 1985 Spring	Febr. 1987 Winter	May 1985 Spring	Febr. 1987 Winter
	0.0	33.7	28.2	6.1	1.5	39.8	29.7
	7.5	14.7	11.2	2.1	0.7	16.8	11.9
	0.0	16.5	22.4	3.1	–	19.6	–
	5.0	20.5	17.4	4.1	0.4	24.6	17.8
	0.0	20.4	27.5	2.8	1.0	23.2	28.5
	7.0	21.8	20.5	3.7	1.8	25.5	22.3
	0.0	20.1	21.1	1.6	0.6	21.7	21.7
	6.0	16.7	16.5	1.8	0.8	18.5	17.3
	0.0	17.0	24.7	3.8	1.6	20.8	26.3
	6.0	–	15.2	–	0.8	–	16.0
Limits		14.7–33.7	11.2–28.2	1.6–6.1	0.4–1.8	16.8–39.8	11.9–29.7
Average		20.1	20.5	3.2	1.0	23.4	21.3

2.4.1. RIVERS OF NORTHERN LATITUDES

Our investigations showed that the highest concentrations of C^d (11.2–33.7 mg/l, 20 mg/l on average) of all the studied rivers were found in the mouth of the North Dvina river (Tables 13 and 16). It is bound up with the fact that rivers of the Arctic Ocean basin cross excessively moist taiga-forest, forest-tundra and tundra zones with podsollic, paludal soils. Combination of natural conditions in these zones favours the formation of river waters with high concentrations of organic matter of humus origin (Maltseva *et al.*, 1987). Largest rivers of the White Sea and the Barents Sea such as Pechora and North Dvina deliver about 8×10^6 t of organic matter (Table 13) per year or 73% of the total quantity of organic matter, run-off by rivers into these seas. It should be noted that concentrations of C^d and C^p in river waters change essentially in time and space depending upon the season, time of day, place of sampling and depth of river. The detailed results of studying the seasonal changes of C^d and C^p concentrations in river waters are considered below. Since, as a rule, the basic part of organic matter (up to 90%) is run-off by rivers into the final reservoir of run-off during flood, calculation of dissolved and particulate organic matter flows was performed on the basis of data, typical for this hydrological phase. Location of sampling stations and the results of analyses of C^d and C^p in the mouths of the North Dvina and the Pechora are shown on Figures 8 and 9 and in Tables 16 and 17.

One of the typical peculiarities of the suspension of the studied northern rivers is the higher content of organic substances they contain, which are bound up with climatic peculiarities of the drained territory, when compared with rivers of other climatic zones.

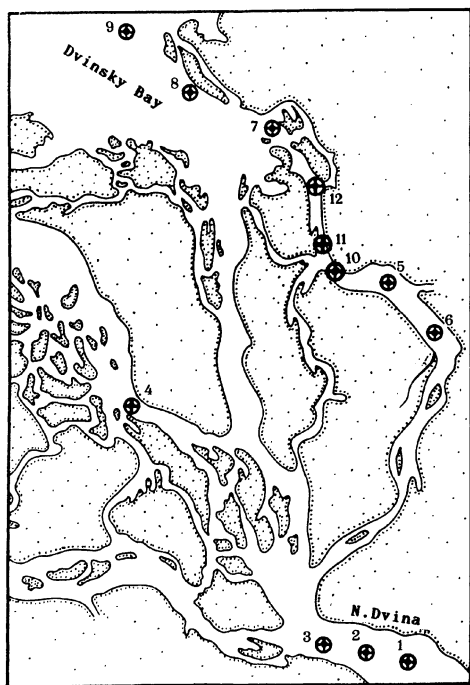


Fig. 8. Sampling stations in the North Dvina mouth and southern part of Dvina Bay (1980–1987).

The maximum content of C^p in the North Dvina mouth was observed within the period of flood: more than 3 mg/l (Table 16). During the rest of the year C^p in the Pechora and the North Dvina is equal to 0.3–1.0 mg/l.

The prevalence of the dissolved form of organic matter over the suspended form in the northern rivers is testified by high ratios of C^d/C^p in the mouth of the North Dvina.

In the mouth of the North Dvina and in the Dvina Bay we have also studied organic matter of bottom sediments, mainly sands, taken on the river–sea section (Figure 8, Table 18). Content of C_{org} in bottom sediments of the North Dvina mouth varies from 0.07 to 1.41% and on average is equal to 0.5%. Higher content of C_{org} was found in aleurites (1.18 and 1.41%), in sands content of C_{org} is considerably less (0.07–0.14%) and is close to average values for bottom sediments of this type in the White Sea (Nevesky *et al.*, 1977). Low contents of C_{org} in sands is bound up with the presence of quartz, which in contrast to other minerals of crystalline rocks does not contain metal ions in grid and is characterized by low sorptional capacity.

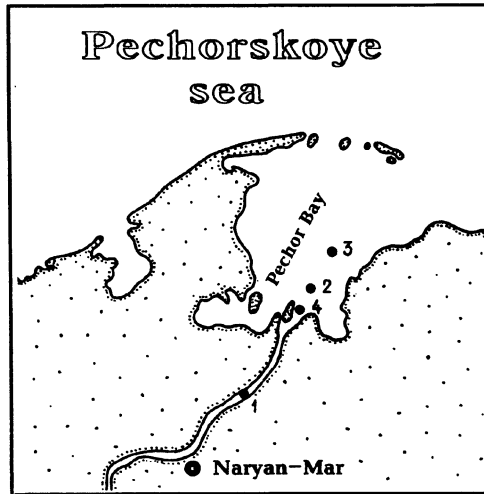


Fig. 9. Sampling stations in the Pechora river (July 1980).

Content of nitrogen in sands and aleurites of the North Dvina mouth is extremely low, 0.004–0.066%, 0.03% on average, and the ratio C/N amounts to 17.5–24.0, 21.3 on average.

2.4.2. RIVERS OF MODERATE LATITUDES

Rivers of moderate climatic zones are characterized by lower concentrations of C^d , than that of rivers of northern latitudes (Table 13). Organic carbon is represented mainly by the dissolved form, the quantity of which is however somewhat less than that of northern rivers. Therefore, an increase of the relative content of particulate organic matter is typically observed not only during flood but during other seasons in European rivers of moderate climatic zones (Artemyev, 1981; Artemyev *et al.*, 1982). This is also testified by lower values of the C^d/C^p ratio when compared with northern rivers.

It was determined, using the example of rivers of the Black Sea and the Azov Sea basin, that the vertical and horizontal distribution of organic matter in river mouths is quite a complicated one (Table 19) specific for each river and therefore free of common regularities. It is seen from Table 19 that concentrations of C^p , even within the limits of water layer of several metres, may change by 2–4 times with the maximum content either in surfacial waters (S. Bug river) or in the bottom layer of water (Danube, Don). It is possible to see in the example of vertical distribution of C^p in the Don mouth how sharply concentrations of C^p may change at the same section of river channel (for example, near left hand shore) over a distance of several kilometres.

Table 17. C^p in the Pechora mouth (July23–25, 1980).

Sampling place	Horizon, m	Sampling time	Water		Suspension mg/l	C^p mg/l	% C^p of suspension	
			T°	S, ‰				
"Kuiskey shar" buoy	0	14.00	13.5	0.04	1.40	0.26	18.8	
	12		12.5	0.44	2.33	0.46	19.7	
Pechora Gulf, 10 km	0	17.00	10.0	0.06	1.41	0.27	19.1	
from Bolvansky Cape	4		10.0	0.05	1.27	0.39	30.7	
Pechora Gulf, 10 km from mouth	0	13.45	10.5	0.06	2.43	0.41	16.9	
	4		10.5	0.09	3.60	0.33	10.5	
Green Island	0	04.30 (tide)	12.5	0.04	–	0.31	–	
	7		12.0	0.05	1.33	0.29	21.8	
tide- ebb tide	0	0.630	12.5	0.10	1.90	0.33	17.4	
	7		–	0.05	1.72	0.26	15.1	
cycle	0	08.30	13.0	0.04	1.46	0.28	19.2	
	7		12.5	0.04	1.23	0.37	30.1	
	0		10.30 (ebb tide)	13.0	0.09	0.54	0.32	59.2
	7				0.04	–	0.35	
Limits			10.0–13.5	0.04–0.10	0.54–3.60	0.26–0.46	10.5–59.2	
Average			12.6	0.06	1.70	0.34	19.9	

The same inhomogeneity is also typical for horizontal distribution of C^p on the river surface (Table 19). As it is seen, the content of organic matter on the cross-sections of river beds may change by a factor of 1.5–1.6. In this case no regular connections of extreme values to that or another section of river bed are noted.

Thus, to obtain accurate data on the concentrations of C^d and C^p in the river mouth, taking into account the inhomogeneity of the spatial distribution of C_{org} in river mouths, it is necessary to take water samples for analyses in three points of cross-section of the river bed: near the right and left shores and in the middle of the river from surfacial, intermediate (when depth is more than 3 m) and bottom horizons. The average value of all the obtained data will be the real value of C^d and C^p concentration in the river mouth.

Mountain rivers of the Caucasian coast of the Black Sea are first of all characterized by an abundance of suspension, exceeding its content in all other studied rivers by many times (Artemyev, 1981). The absolute content of C_{org} both C^d and C^p is comparable to that for plain rivers of the basin of the Black Sea and the Azov Sea. But, relative content of C^p in mountain river suspension is equal to only 2%.

Table 18. Geochemical characteristics of bottom sediments

Region of works	Station No.	Depth	Type of sediment	Content in sediment, %				
				SiO ₂ amorph.	C _{carb}	CaCO ₃	C _{org}	OM
River	1	8.0	Sand, fine-grained, grey-brown	0.26	n.f.	n.f.	0.07	0.13
	2	7.0	Sand, fine-grained, grey-brown	0.25	0.04	0.33	0.14	0.25
	3	14.0	Sand, fine-grained, grey-brown	0.25	0.04	0.33	0.12	0.22
	4	6.5	Sand, fine-grained, grey-brown	–	n.f.	n.f.	0.08	0.15
	5	2.1	Aleurite with interbeds of shaly muds, dark brown	0.44	0.20	1.67	1.18 2.15	
	6	2.5	Aleurite with interbeds of shaly muds, dark brown	0.42	0.24	2.00	1.41	2.57
			Sands {					
			Limits	0.25–0.26	0.04	0.33	0.07–0.14	0.013–0.25
			Average	0.25	0.04	0.33	0.10	0.19
			Aleurites {					
		Limits	0.42–0.44	0.20–0.24	1.67–2.00	1.18–1.41	2.15–2.57	
		Average	0.43	0.22	1.83	1.30	2.36	
Estuary	7	10.0	Sand, fine-grained with interbeds of shaly muds	0.24	0.08	0.67	0.48	0.87
	8	12.0	Sand, medium-grained with gravel	0.14	0.10	0.83	0.32	0.58
	9	14.0	Gravel with aleurite interbeds	–	0.48	4.00	0.96	1.75
			Limits	0.14–0.24	0.08–0.48	0.67–4.00	0.32–0.96	0.58–1.75
		Average	0.19	0.22	1.80	0.59	1.07	

n.f. = not found.

in the section "mouth of the North Dvina-sea" (May 1985).

N	Content in sediment, %				Group content of OM, %			
	C/N	bitumoid "A"		HA	bitumoid "A"			ROM
		Chloroform	Alc.ben.		Chloroform	Alc.ben.	HA	
0.004	17.5	0.01	0.01	n.f.	7.7	7.7	n.f.	84.6
0.006	23.3	0.01	0.01	n.f.	4.0	4.0	n.f.	92.0
0.005	24.0	0.01	0.01	n.f.	4.5	4.5	n.f.	91.0
-	-	0.01	0.01	n.f.	6.7	6.7	n.f.	86.6
0.066	17.8	0.04	0.04	0.46	1.9	1.9	21.4	74.8
0.059	23.9	0.07	0.05	0.52	2.7	1.9	20.2	75.2
0.004-0.006	17.5-24.0	0.01	0.01	n.f.	4.0-7.7	4.0-7.7	n.f.	84.6-92.0
0.005	21.2	0.01	0.01	n.f.	5.7	5.7	n.f.	88.5
0.059-0.066	17.8-23.9	0.04-0.07	0.04-0.05	0.46-0.52	1.9-2.7	1.9	20.2-21.4	74.8-75.2
0.062	20.8	0.05	0.04	0.48	2.3	1.9	20.8	75.0
0.029	16.5	0.02	0.02	0.13	2.3	2.3	14.9	80.5
0.006	53.3	0.02	0.01	n.f.	3.4	1.7	n.f.	94.9
0.029	33.1	0.04	0.02	0.23	2.3	1.1	13.1	83.5
0.006-0.029	16.5-53.3	0.02-0.04	0.01-0.02	n.f.-0.23	2.3-3.4	1.1-2.3	0.0-14.9	80.5-94.9
0.02	34.3	0.03	0.01	-	2.7	1.7	9.3	86.3

Table 19. Distribution of organic matter on water surface in river mouths (Artemyev, 1981).

River	Horizon	C ^p			C _c ^p mg/l		
		Left shore	River middle	Right shore	Left shore	River middle	Right shore
Danube	surficial	<u>1.10</u> 0.33	<u>2.19</u> 0.81	<u>6.99</u> 2.09	<u>1.13</u>	<u>1.71</u>	<u>1.77</u>
	bottom	–	<u>6.0</u> –	–	–	–	–
South Bug, below Nikolaev city	surficial	<u>2.54</u> 9.20	<u>2.15</u> 8.11	<u>1.05</u> 3.17	–	–	0.26
	bottom	–	<u>1.86</u> 6.16	–	–	–	–
Kuban, Petrushevsky Creek	surficial	<u>2.59</u> 2.33	<u>3.55</u> 2.98	<u>2.19</u> 1.38	0.27	0.60	0.73
	Don, Old Don Creek, above Azov	surficial	<u>1.58</u> 5.23	<u>1.33</u> 5.43	<u>1.76</u> 6.22	–	–
Don, Sandy Creek, below Azov	bottom	<u>1.54</u> 1.74	<u>1.26</u> 4.77	<u>1.30</u> 3.87	–	–	–
	surficial	<u>0.45</u> 8.65	<u>1.22</u> 4.03	<u>1.82</u> 1.30	–	–	–
	bottom	<u>2.84</u> 4.20	<u>2.16</u> 5.12	<u>1.81</u> 4.68	–	–	–

Note: Numerator contains contents of organic matter in mg/l, denominator the same in %.

2.4.3. RIVERS OF TROPICAL LATITUDES (THE AMAZON BASIN)

To clarify the nature of river organic compounds it is important to study their spacial distribution in various sections of the river basin both in the main channel and in the main tributaries. Especially important are such studies in the largest rivers of the Earth, the waters of which have the greatest effect on wide water areas of the ocean. So the Amazon river flow, coming into the Guiana stream is spread in northerly and easterly directions and has an effect on the waters of the equatorial tropical Atlantic covering 10^7 km² during the maximum run-off.

One of the first summaries of hydro- and geochemical data of the Amazon was prepared by Clarke (1924) and later on published by Livingstone (1963). Studies of the geochemistry of organic substance in the Amazon basin were started in the seventies and eighties, mainly as a result of studies on the research ship "Alfa Helix" and other research ships (Wissmar *et al.*, 1981; Richey, 1981, 1982; Richey *et al.*, 1980, 1985; Furch and Junk, 1985). However, this data was insufficient for revealing the main regularities of spacial distribution of dissolved and particulate organic matter in the river basin, since samples were taken at a small number of stations and only from the river surface. Therefore, dur-

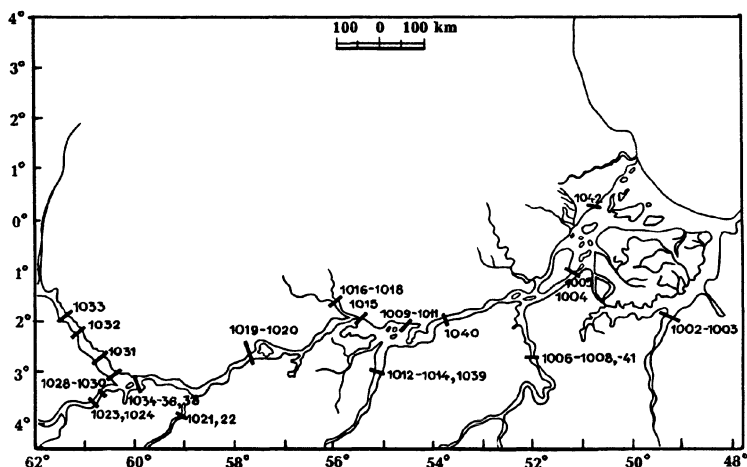


Fig. 10. Sampling stations in the Amazon River Basin (March–April 1983).

ing the 9th cruise of research vessel “Professor Shtokman” to the Amazon (March–April, 1983), we carried out more detailed studies of peculiarities of C^d and C^p distribution both vertically and horizontally, C_{org} in bottom sediments, composition of organic matter in the Amazon river from interflow of the Solimoins and the Negru rivers to the mouth and in its main tributaries: Solimoins, Negru, Madeira, Topazhos, Trombetas, Shingu and Tokatins (Artemyev, 1988), Figure 10 and Table 20.

2.4.3.1. General Information about the Amazon River

The Amazon occupies first place among the world rivers by the value of river run-off, 5780 km³/year on average (Meade *et al.*, 1979).

This huge run-off is explained by the size of the draining surface – 7 050 000 km² – and by the quantity of precipitations – 2500 mm/year. The water velocity in the Amazon varies from 0.5 to 1 m/s during the dry season (June–December) and 1.0–2.0 m/s during the rainy season (January–June). Near Obidus (800 km from the river mouth) where standard hydrological tests are carried out and in some parts of the Solimoins river the velocity may be equal to 3–4 m/s. The water temperature in the Amazon is relatively stable (+29° throughout the year). The highest water (flood) is in the lower Amazon, in May, the lowest is in November.

The Amazon is the final collector of a uniquely complicated draining system, with numerous branches, tributaries, channels, flooded values, lakes, lagoons, etc. As a result of geological development the Amazon draining surface is now limited at the west by the Andes, at the north by Guiana and at the south by the Central Brazil massifs. The Amazon draining waters are subdivided into three main categories: black, white and pure (Sioli,

Table 20. Bioproduction, organic carbon and nitrogen in the waters of the Amazon and its main tributaries (according to data, presented by Artemyev, 1988).

Sampling places (river)	Number of samples	pH	PP* mgC/m ³ /h	Breathing* mgC/m ³ /h	Volume of phy- toplankton* 10 ⁴ m ³ /m ³	Density of bacteria 10 ¹² cl/m ² *	Suspension mg/l	CP, % of suspension	NP, mg/l	C ^d /NP	C ^d , mg/l	C ^d /C ^p	N ^d **	C ^d /N ^d **
Negru (above Manaus)	13	5.1	5.1	-	-	-	5.0	1.1	0.09	15	8.1	7.0	0.20	31
Negru (below Manaus)	7	5.4	20.1	0.48	20381	2.81	5.8	0.5	0.04	14	7.2	14.7	0.14	42
Solimoiis	6	7.1	-	-	-	-	124.0	1.8	1.3	0.09	17	5.2	3.3	0.13
Madeira	3	6.9	-	0.85	-	2.09	272.0	2.3	0.8	0.14	14	4.5	2.2	-
Trombetas	4	7.2	22.5	0.72	335575	3.16	10.1	1.1	10.8	0.05	22	-	-	-
Topazhos	6	6.7	14.4	1.30	564137	1.73	5.4	0.8	16.7	0.08	22	4.5	7.0	-
Shingu	7	6.9	31.0	0.95	129670	2.43	8.4	0.8	15.5	0.04	17	5.3	11.2	-
Tokantins	4	7.4	48.0	8.30	24176280	3.19	26.5	2.5	9.2	0.09	39	5.8	2.5	-
Amazon	28	7.1	1.7	0.53	9000	1.58	121.0	2.0	1.7	0.10	20	5.1	2.5	0.14

*Wissmar *et al.*, 1981.

**Williams, 1968.

1975). “Black” waters (Negru and Branku rivers) have their origin in the central part of the Amazon river and are acidic (pH = 5) waters, which are exclusively poor in nutrients and are of a reddish-black colour. The colour is caused, as it will be considered below, by humic acids, produced in podsollic soils. The colour of solutions is explained by presence of many chromophore groups, which may be aromatic nucleuses of free radical groups. In spite of the low concentration of inorganic feeding salts black waters are characterized by high concentrations of C^d (see below).

“White” waters (the Amazon river, Madeira river) are characterized by the presence of large quantities of sedimentary material (suspensions) and contain more nutrients than “black” waters. “Pure” waters (Shingu, Topazhos and Tokantins rivers) are typical for northern and periphery zones and are predetermined by sedimentation of suspension in large mouth bays of these rivers.

2.4.3.2. Sources and Forms of Organic Matter

On the whole the Amazon waters are not rich in organic matter and may be compared with distilled water, slightly polluted (Richey, 1982). Dissolved organic matter are supplied to the Amazon waters mainly from underground and ground flows. The primary production (PP) of macrophytes and phytoplankton in the Amazon water is very low, due to the high content of suspended material, supplied to river waters as a result of erosive processes in the river head and insignificant concentrations of nutrients. The lowest values of primary production were observed in the waters of the Amazon river (1.7 mgC/m³/hour), the highest – in the mouths of the Tokantins and the Shingu rivers – more than 30 mgC/m³/hour (Table 20). The intermediate values of primary production are typical for the black waters of Negru river – about 20 mgC/m³/hour. Similar types of distribution are observed on the Amazon basin in such biological parameters as breathing, volume of phytoplankton organisms and density of bacteria (Wissmar *et al.*, 1981).

The year-round observations of primary production value in the Negru river (15 km above Manaus port) showed that primary production varies from 0.27 to 0.02 gC/m³/day (Shmidt, 1976). As it was already noted, conditions for primary producing are not favourable in “black” waters due to low pH, as well as extremely low concentration and the non-balanced composition of biogenic elements and insufficient illumination (as a result of selective absorption of light by dissolved humic substances (HS) and the influence of water muddiness).

The basic volume of river dissolved organic matter is represented by humic substances originating from the organic matter of soils, formed in their turn from organic matter of plants, animals and micro-organisms. Humic substances are represented by polymers – humic acids (HA) and fulvic acids (FA) – products of reactions of extracellular condensation of organic matter, released as a result of micro-biological degradation of ground plants. Composition of dissolved organic matter may vary from river head to the lower part of river due to differences in chemical composition of tributary waters, the sources and the value of dissolved fractions. Dissolved organic matter, produced as a result of humus destruction is supplied to the river water with underground waters.

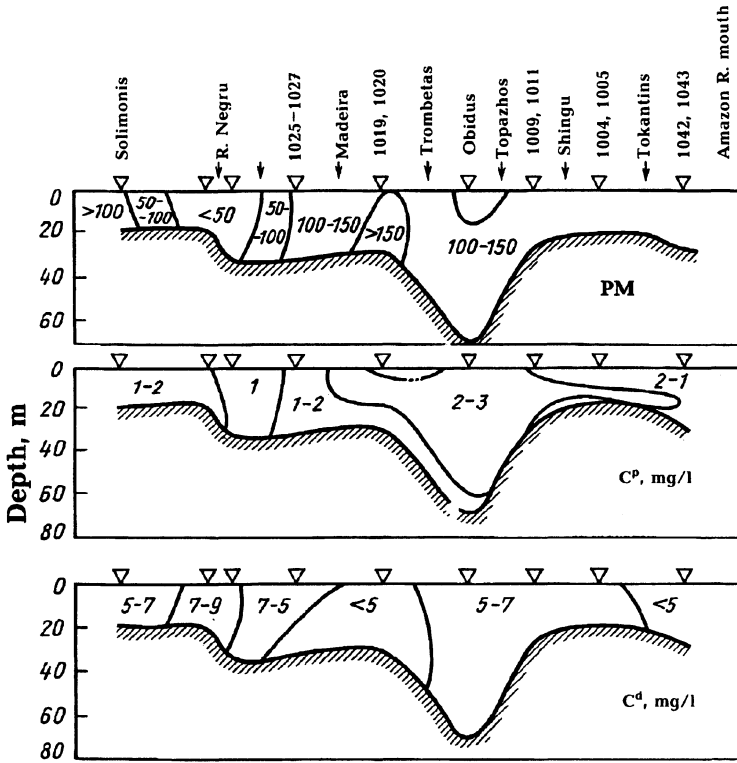


Fig. 11. The distribution of particulate matter, C^d and C^p in the Amazon river basin from Solimons river mouth to Amazon river mouth (March–April 1983).

The sources of particulate organic matter in the Amazon waters are phytoplankton, periphyton, bacteria, moss, non-wood vegetable tissues and their residues, grass, macrophytes and timber. The Amazon basin is considered as a region which is not particularly polluted with products of agricultural activities (Stallard and Edmond, 1983). Therefore, it is possible to ignore anthropogenous sources of particulate organic matter (as well as dissolved organic matter). Besides the enumerated sources the source of particulate and dissolved organic matter in the Amazon basin water may be wood, floating on the main surface.

According to existing estimates (Richey, 1982) the land surface products, drained by the Amazon waters totals to 470×10^{13} gC/year, $8\text{--}16 \times 10^{13}$ gC/year being supplied to river waters from the drained land. Considerable quantities of C_{org} in the Amazon basin are accumulated in so-called “Varsea”, where the sources of carbon are macrophytes

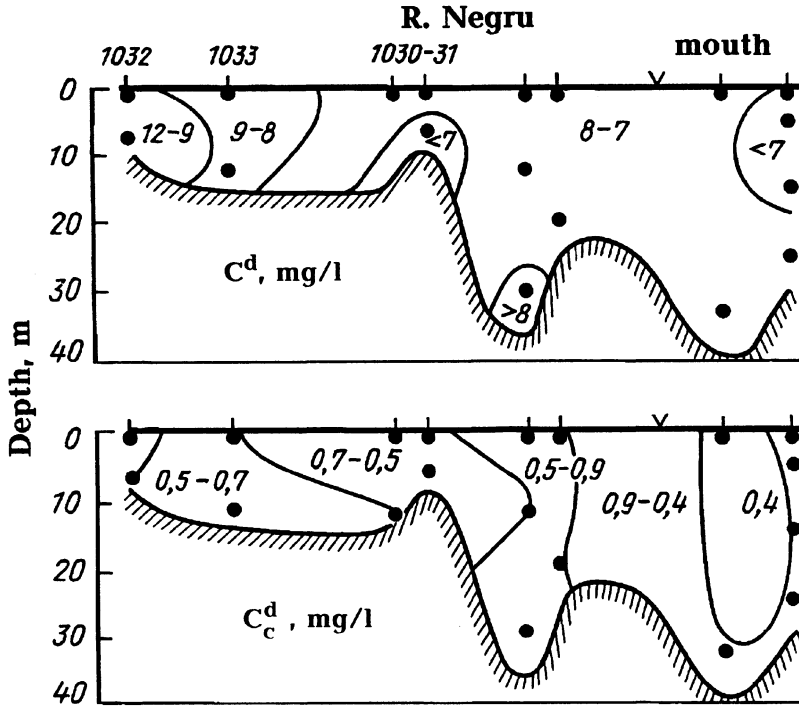


Fig. 12. C^d and C_c^d in the Negru river (March 1983).

(about 5×10^{13} gC/year). In this case about 1×10^{13} gC/year of products of macrophytes may be exported to river waters. As the studies show a considerable part of plankton carbon is oxidized *in situ* (Richey, 1982).

2.4.3.3. Dissolved and Particulate Organic Carbon

Content of C^d in the Amazon basin water varies from 2.0 to 11.5 mg/l and average is equal to 5.7 mg/l for surfacial and bottom waters (Table 20 and Figure 11). The maximum content of C^d is in waters of the Negru river (below Manaus), about 8 mg/l, the lowest one is in the Trombetas river (4.3 mg/l).

Concentrations of C^d vary little with depth. Relatively high concentrations of C^d in the Negru waters are predominated primarily by the delivery of organic matter from soil humic acids, as well as by activity of primary products (Figure 12).

In the waters of the Amazon river, from the place of interflow of the Solimoiins and Negru rivers to the mouth, C^d concentration is within the limits of 5–7 mg/l and the spacial

distribution of dissolved organic matter is rather homogenous in both surfacial waters and depth (Figure 11). In the Amazon mouth C^d content is approximately 5 mg/l.

Content of C^p in the studied waters varies from 0.3 to 4.3 mg/l and on average is 1.6 mg/l for surfacial waters and 1.2 mg/l for bottom waters (Artemyev, 1988). The highest content of C^p in both surfacial and bottom waters was found in the suspension of the Tokantins river: 2.8 and 2.3 mg/l respectively, the lower is the surfacial waters of the Topazhos river and in the Negru river below Manaus: 0.6 mg/l.

In spite of close values of the average concentrations of C^p in surfacial and bottom waters of rivers of the Amazon basin, contents of C^p in waters of surfacial and bottom horizons at the separate stations differ by 1.5–4 times in the majority of studied rivers (Negru, Solimoins, Shingu, Tokantins, Topazhos) (Artemyev, 1988). In this case there is no regular connection of higher (or lower) concentrations of C^p with the surfacial or bottom horizons. This testifies that the basic factor, determining behaviour of suspension and particulate organic matter in the Amazon basin waters is a windous or turbulent mix of waters.

The highest content of C^p in studied waters of the Tokantins river is bound up with the activity of phytoplankton organisms. The highest (compared with other Amazon waters) values of primary production and biomass of phytoplankton (Table 20) are obtained there too.

The share of river C^p in suspension varies from 0.5 to 31.5%, the average share in surfacial waters amounts to 8.6%, in depth waters it is equal to 11.0% (Figure 13). The richest suspension (by organic matter) is that in the Negru river above the port of Manaus, where the content of C^p in surfacial and bottom waters amounts to 23.9 and 30.7% respectively. The lowest content of C^p is in the suspension of the Madeira river (0.8%). As a rule, C^p equals to 10–20% of the Amazon suspension.

According to our investigations organic matter in the waters of the Amazon is mainly in the dissolved form, which is illustrated, in particular, by the C^d/C^p ratio (Table 20). This value varies from 1.2 to 18.5 and amounts to 5.9 and 6.7 on average for surfacial and bottom waters respectively.

Assuming (by our data) that the average contents of C^d and C^p in the Amazon water is equal to 5 and 2 mg/l respectively (Artemyev, 1988, Table 20) and that the annual water consumption is 183 000 m³/sec (Meade *et al.*, 1979a) we find that the river discharges 1.17×10^{13} g of C^p and 2.7×10^{13} g of C^d a year.

As it was shown as a result of investigations (Meybeck, 1981) nitrogen is available in river waters mainly in the suspended form. This is nitrogen of protein-like material, as well as that adsorbed in clays and other mineral particles. It was determined that nitrogen of protein-like material is equal to 85–90% of the total N_{org}^p .

Content of N_{org}^p in the Amazon waters varies from 0.03 to 0.19 mg/l and averages 0.06 mg/l in surfacial waters and 0.08 mg/l in bottom ones. As it follows from the data given in Table 20, the results of determination of N_{org}^p in the Amazon waters, is obtained by various authors with use of various methods and in different seasons, are as a rule, of one order. And there are no essential differences in contents of surfacial and bottom waters.

Annual flux of N_{org}^p of the Amazon amounts to 5.57×10^{11} g (Ittekkot *et al.*, 1983).

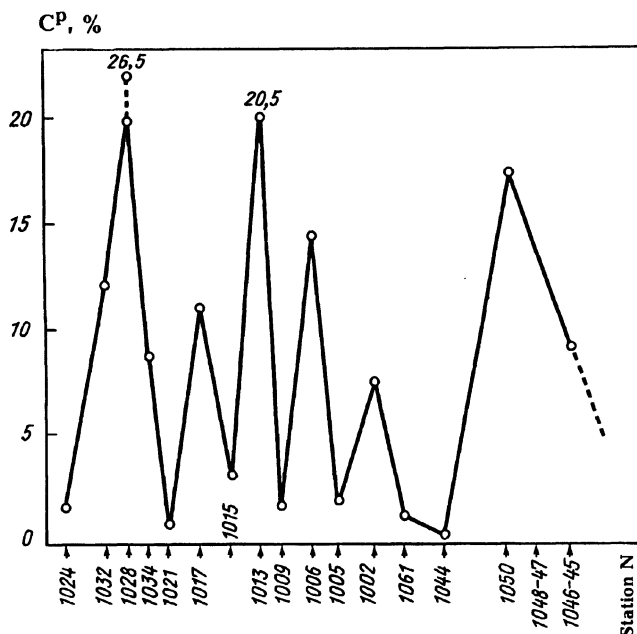


Fig. 13. The distribution of C^P in the Amazon basin and estuary (March–April 1983).

The C^P/N^P ratio in the studied waters varies from 7 to 80 and is equal on average to 27 for surficial waters and to 16 in bottom waters. The highest value of C^P/N^P are typical for the Tokantins river, where organic matter-containing compounds are represented in minimum quantities. The highest quantity of nitrogen-containing compounds is in the organic matter of the Negro rivers, where one of the lowest C^P/N^P (13–16) was found. An increase of the relative content of nitrogenous organic matter in the Negro river waters was caused by the fact that one of the main sources of organic matter in these waters are soils – the main suppliers of nitrogen-containing organic matter in river waters (amino acids, amino sugars). In the Tokantins river, where activity of primary producers is most intensive (Table 20), delivery of organic matter from soils is of minor value.

2.4.3.4. Organic Carbon of Bottom Sediments

In the Amazon river basin sediments are represented by terrigenous sands and muds and differs essentially by content of C_{org} (Table 21). So in sands C_{org} amounts to 0.06–0.30% (0.14% on average) and to 1.81–3.55% in muds (2.9% on average). The lowest concentrations of C_{org} are in the bottom sediments of the Solimoiis river (0.06%) and

Table 21. Organic matter of bottom sediments of basin

Ord. No.	Station No., river	Depth m	Sampling interval	Type of sediment	Content on sediment, %			
					SiO ₂ amorph.	C _{carb}	CaCO ₃	C _{org}
1	2	3	4	5	6	7	8	9
1	1002, Tokantins	30	0-5	sand, terrigenous, grey	0.52	0.01	0.08	0.09
2	1005, Amazon	13	0-5	sand, terrigenous, dark grey	0.46	0.03	0.25	0.19
3	1006, Shingu	16	0-10	mud, pelite, terrigenous dark grey	10.02	0.01	0.08	2.94
4	1009, Amazon	11	0-10	sand, terrigenous, grey	0.32	0.01	0.33	0.30
5	1013, Topazhos	25	0-5	mud, pelite, terrigenous, grey	4.96	0.03	0.25	2.76
6	1015, Amazon near Obidos	68	0-5	sand, polymictic, grey	0.45	0.02	0.17	0.11
7	1017, Trombetas	7	0-5	mud, aleurite-pelite terrigenous, grey with remains of plants	0.38	0.03	0.25	3.41
8	1021, Madeira	17	0-5	sand, terrigenous dark grey	0.42	0.01	0.08	0.17
9	1024, Solimoiins	23	0-5	sand, terrigenous yellowish-grey	0.40	0.01	0.08	0.06
10	1028, Negru, above Manaus	23	0-5	mud, pelite, terrigenous, dark grey	0.77	0.03	0.25	1.81
11	1032, Negru, above Manaus	9	0-5	sand, quartz, greyish-yellow	0.42	0.03	0.25	0.09
12	1034, Negru, below Manaus	30	0-5	mud, pelite, terrigenous	0.43	0.03	0.25	3.55
13	Sands			Limits	0.32-0.52	0.01-0.04	0.08-0.33	0.06-0.30
14				Average	0.43	0.02	0.18	0.14
15	Muds			Limits	0.38-10.0	0.01-0.03	0.08-0.25	1.81-3.55
16				Average	3.31	0.03	0.22	2.90
ESTUARY								
17	1044, estuary, section "Amazon mouth-ocean"	13	0-5	mud, pelite, terrigenous, with interbeds of sand	0.54	0.05	0.42	0.47
18	1050, section "Amazon mouth-ocean"	14	0-5	mud, aleurite, pelite, terrigenous, grey	0.44	0.03	0.25	0.29
19	1055, norther section "continent-ocean"	11	0-5	mud, pelite, terrigenous	0.80	0.03	0.25	0.67
20	1061, estuary	13	0-5	mud, pelite, terrigenous	0.33	0.01	0.08	0.46
				Limits	0.33-0.80	0.01-0.05	0.08-0.42	0.29-0.67
				Average	0.53	0.03	0.25	0.47

and estuary of the Amazon (March–April 1983).

Content in sediment, %						Group content of OM, %			
N	C/N	OM	Bitumoid "A"		HA	Bitumoid "A"			ROM
			Chloroform	Alc.ben.		Chloroform	Alc.ben.	HA	
10	11	12	13	14	15	16	17	18	19
–	–	0.16	0.01	0.01	–	6.2	6.2	–	87.6
–	–	0.35	0.01	–	–	2.9	2.9	–	94.2
0.30	10.0	5.35	0.09	0.20	2.25	1.7	3.7	42.1	52.5
–	–	0.55	0.01	0.02	–	1.8	3.6	–	94.6
0.30	9.2	5.02	0.10	0.10	1.97	2.0	2.0	39.2	56.8
–	–	0.20	0.03	0.003	–	15.0	1.5	–	83.5
0.20	17.0	6.21	0.08	0.15	1.71	1.3	2.4	27.5	68.8
–	–	0.31	0.01	0.01	–	3.2	3.2	–	93.6
–	–	0.11	0.02	0.02	–	18.2	18.2	–	63.6
0.14	12.9	3.29	0.01	0.03	2.47	0.3	0.9	75.1	23.7
–	–	0.16	0.01	0.01	–	6.2	6.2	–	87.6
0.30	11.8	6.46	0.07	0.18	3.54	1.1	2.8	54.8	41.3
–	–	0.11–0.55	0.01–0.03	0.003–0.02	–	1.8–18.2	1.5–18.2	–	63.6–94.6
–	–	0.26	0.01	0.01	–	7.6	6.0	–	86.4
0.14–0.3	9.2–17.0	3.29–6.46	0.01–0.10	0.03–0.20	1.71–3.54	0.3–2.0	0.9–3.7	27.5–75.1	23.7–68.8
0.25	12.2	5.27	0.07	0.13	2.39	1.3	2.4	47.7	48.6
ESTUARY									
–	0.85	0.02	0.02	0.19	2.3	2.3	22.3	73.1	–
0.02	14.5	0.53	0.01	0.01	–	1.9	1.9	–	96.2
–	1.22	0.02	0.02	0.05	1.6	1.6	4.1	92.7	–
0.05	9.2	0.84	0.01	0.02	0.06	1.1	2.4	7.1	89.3
0.02–0.05	9.2–14.5	0.53–1.22	0.01–0.02	0.01–0.02	??–0.06	1.3–2.3	1.6–2.4	4.1–22.3	73.1–96.2
0.035	11.85	0.86	0.02	0.02	0.04	1.75	2.05	8.37	87.8

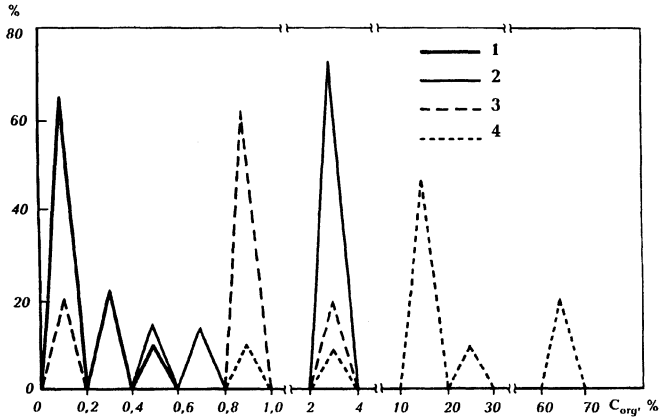


Fig. 14. C_{org} content in soils, particulate matter and bottom sediments of the Amazon river basin (March–April 1983). 1. Sands, 2. muds, 3. soils, 4. suspension.

the highest ones in muds of the Negro river (3.55%). Figure 14 illustrates that the most frequent concentrations of C_{org} in sands and muds amount to 0.1 and 3%, respectively.

Content of nitrogen in the Amazon muds varies from 0.14 to 0.30%, average 0.25%. The C/N ratio values (9.2–17.0, 12.2 average) give a possibility to suppose the combined, mainly humus-like genesis of organic matter of studied river sediments. The role of highest plants residues is, probably, the greatest one for sediments of the Negro and the Trombetas rivers.

The content of amorphous silica and calcium carbonate in sediments of the Amazon basin is, as a rule, a very low one (less than 1%), which testifies to the low propagation of silica-containing and carbonate-containing organisms, and the presence of mineral and inorganic particles in sediments.

Comparative analysis of organic matter concentration variation in the Amazon basin in the case of passage from suspensions to bottom sediments signifies the character of organic matter bottom sediments inherited from organic matter suspension. This is expressed in connection with absolute contents of C_{org} of bottom sediments with C_{org} content in the suspension (Figure 13). Lower contents of C^p and C_{org} in bottom sediments, taken at the same stations on the rivers Solimoiis, Madeira and Amazon are determined by the low bioproductivity, active hydrodynamics, as well as by the granulometric composition of bottom sediments (medium-grained sands) which are not able to accumulate organic matter supplied from the water mass.

Higher content of organic matter (Figure 13) (mainly humus genesis) was found in suspension and bottom sediments of the rivers Negro, Topazhos, Trombetas and Shingu. Influence of economic activities of human society (sewage discharge, etc.) on the concentration of organic matter is not excluded.

Concentration of organic matter in bottom sediments is decreased on the way to the ocean: clay sediments in the Amazon estuary contain the lowest quantity of organic matter for muds of this type.

2.4.4. VARIATION OF ORGANIC MATTER CONTENT IN RIVER MOUTHS IN TIME

V.I. Vernadsky noted such variation of organic matter content of river waters as “variation of chemical composition of dissolved and micro-dispersive substance, borne by rivers . . . These variations are sharply expressed for each individual river. The rivers are extremely sensitive, balanced systems, which vary permanently . . . It [the river] changes perpetually, and this variation is different for each place of its course, varies every day and night, by the seasons of the year and during long-term periods” (1960).

2.4.4.1. Factors, Determining Seasonal Variation of Drainage and Concentration of Organic Matter

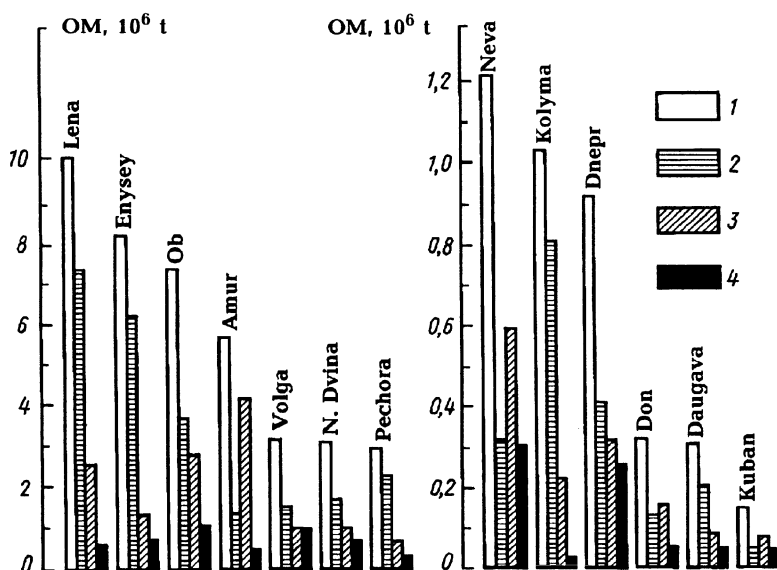
Seasonal variations of organic matter drainage depend, first of all, upon the climate and ground plant development stages. During warm periods, activity of plants for extraction of micro-elements from water is intensified, as is the decomposition of organic matter in soil. All three main phases of drainage usually exist during this period of the year: underground, river bed and slope-type drainage. During the period of maximum precipitations (spring, autumn) the intensity of substance transfer is increased, as is their content in river waters. In spring, when wash-off and transportation are performed mainly by the surfacial drainage – slope and bed-type – the maximum drainage of colloidal, suspended particles is observed. Most often the maximum quantity of mineral and organic substances is transported to reservoirs in spring. In winter activity of plants connected with extraction of chemical elements from river water is reduced to the minimum or stopped entirely. At this time evacuation of mineral and organic substances to reservoirs with river drainage is decreased owing to the decrease of temperature, slowing the rate of chemical reactions, decrease of the absolute quantity of water in drainage, decrease of ground flow supply, almost complete halting of slope drainage and considerable decrease of river-bed drainage (Muraveisky, 1960).

The maximum drainage of water over most of the Russian territory is noted during the spring flood period. The highest concentrations of organic matter in river waters are observed during the same period (Table 16). Distribution of organic matter drainage within the year depends, in particular, upon the type of water regime of the rivers. So the rivers of the Barents, White and Kara Sea basins are related to the type of water regime, with the prevalence of snow supply and spring drainage; therefore, the maximum drainage of organic matter into these areas is typically during the spring flood (Table 22).

Different quantities of organic matter migrate in various seasons from water collecting areas, their qualitative composition is also different (Voronkov, 1970). Various waters ended their formation on the surface or in the thickness of soils-grounds prevalence in the river bed network in various hydrological periods. The upper layer of forest zone soils is enriched with movable forms of organic matter, entering the river bed during the flood

Table 22. Organic matter run-off (in %) into the Russian seas by seasons (Smirnov, 1974).

Sea	Spring	Summer-Autumn	Winter
Barents Sea and White Sea	58	34	8
Kara Sea	63	26	11
Baltic Sea	35	43	22
Black Sea and Azov Sea	48	36	16

Fig. 15. The seasonal distribution of organic matter run-off of some large U.S.S.R. rivers: 1. year; 2. spring; 3. summer-autumn; 4. winter (Maltseva *et al.*, 1987).

period. Supply of rivers with ground waters containing considerably less organic matter than surfacial-slope water is intensified in summer.

Variation of organic matter content in steppe waters in various seasons are usually expressed less clearly (Figure 15). For the majority of northern and moderate humid zone rivers, except for the rivers of the western European part of Russia, the Azov region and Caucasus, with uniform distribution of organic matter drainage for the whole year, the drainage of organic matter is typically prevalent during spring flood (Figure 15). Drainage of organic matter during the spring flood in the basis of the North Dvina and the Pechora rivers is equal to as much as 65% of the annual one (Maltseva *et al.*, 1987).

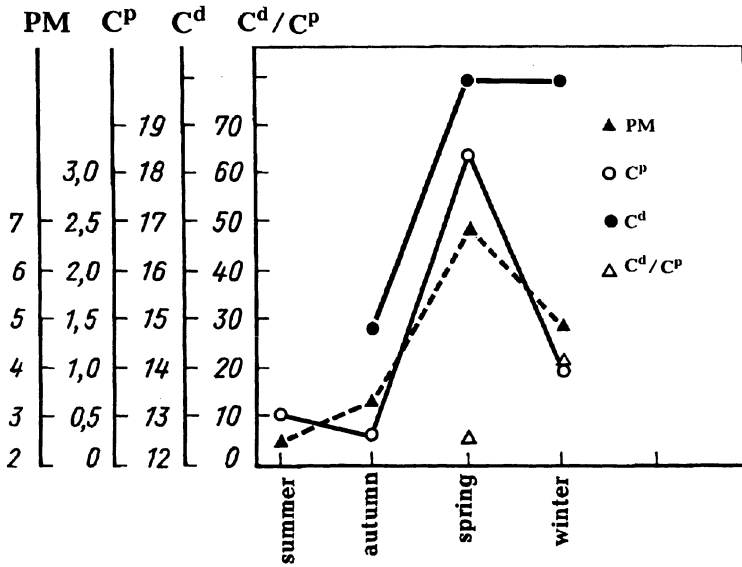


Fig. 16. The seasonal distribution of particulate matter, C^d and C^P (mg/l) in the North Dvina river mouth (Artemyev *et al.*, 1984; Artemyev and Romankevich, 1988).

The results of determining C^d and C^P content in the North Dvina mouth during various seasons (Table 16, Figure 16) demonstrate essential differences of concentrations of both C^d and C^P in river waters. The highest content of C^d is typical in winter, which is bound up with low rates of dissolved organic matter destruction under the conditions of low water temperature. Higher concentrations of C^P were noted during the spring flood period in connection with the general increase of suspension content. Similar results were obtained when studying seasonal peculiarities of distribution of C^d and C^P, as well as that of nitrogen in the mouth of the Mackenzie river (Telang, 1985), flowing like the North Dvina river in the northern humid zone. Higher concentrations of C^d in the mouth of the Mackenzie river (as well as in the mouth of the North Dvina river) were observed in the winter months and the lower values in summer, when the higher concentrations of C^P and N^P were noted within the period of flood and lower concentrations when the rivers were frozen.

It may be considered that the essential seasonal variations of C^d and C^P concentrations in the mouths of rivers were observed everywhere, where we observe seasonal variations of climate, determining both quantity and composition of river organic substance.

The cyclical character of organic matter distribution during the year is observed in the mouths of some rivers; it is determined first of all by local climatic conditions (Figure 17).



Fig. 17. The seasonal distribution of C^d and C^p in the St. Lawrence river mouth (Pocklington, 1985).

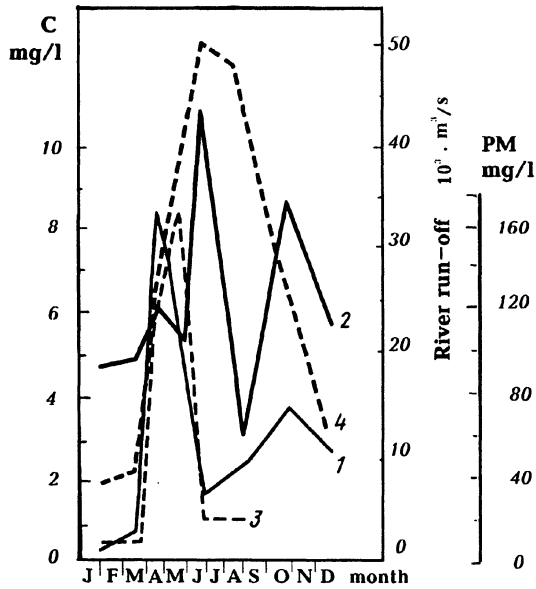


Fig. 18. The seasonal change of particulate matter content (1), C^d (2) and C^p (3) in the Orinoko river (Nemeth *et al*, 1982).

Seasonal fluctuations of organic matter concentrations were observed in many large rivers of the world, studied in accordance with the programmes SCOPE-UNEP² in the seventies and eighties (Figures 18 and 19). In 1975 year round monthly measurements

²SCOPE – Scientific Committee on Problems of Environment; UNEP – United Nations Environment Programme

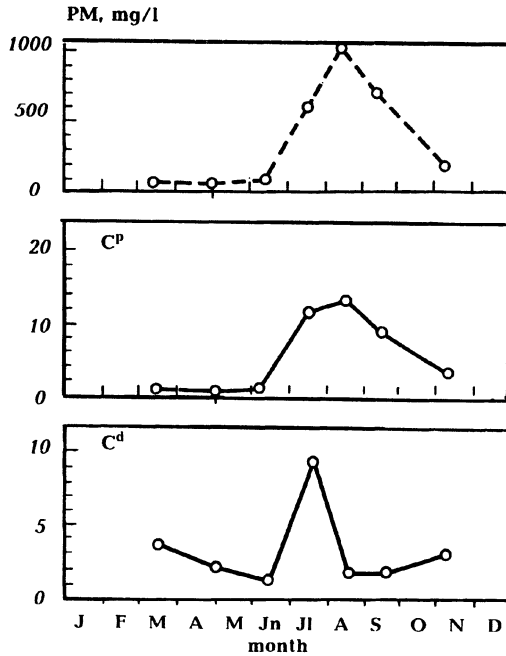


Fig. 19. The seasonal change of particulate matter, C^d and C^p concentrations in the Ganges river (Ittekkot *et al.*, 1985).

were performed for the first time in the Amazon in the region of port Obidus (Kempe, 1982).

The study of seasonal distribution of C^d and C^p in the Amazon itself was not carried out. However, the studies carried out in the Solimoiis river (Furch and Junk, 1985) showed that the content of C^d is subjected to essential variations during the annual cycle and coordinated with variation of water level in the river.

2.4.4.2. Daily Variation of Organic Matter Concentrations in River Mouths

In October 1980 we carried out investigations of hydrochemical parameters; organic matter and micro-elements in the mouth of the Don river at semidiurnal stations (Figure 20), as well as at the section "Don mouth-Taganrog Bay" (see Chapter 3). As it is seen, the content of biogenous elements: silica, phosphate phosphorus, nitrate nitrogen, as well as suspension and micro-elements varied considerably through time both in surficial and bottom waters, which testifies to the variety in chemical composition of river waters during the day. At the same time content of C^d and C^p in the Don river mouth varies insignificantly during the same period. Concentration of C^p in the Pechora river mouth

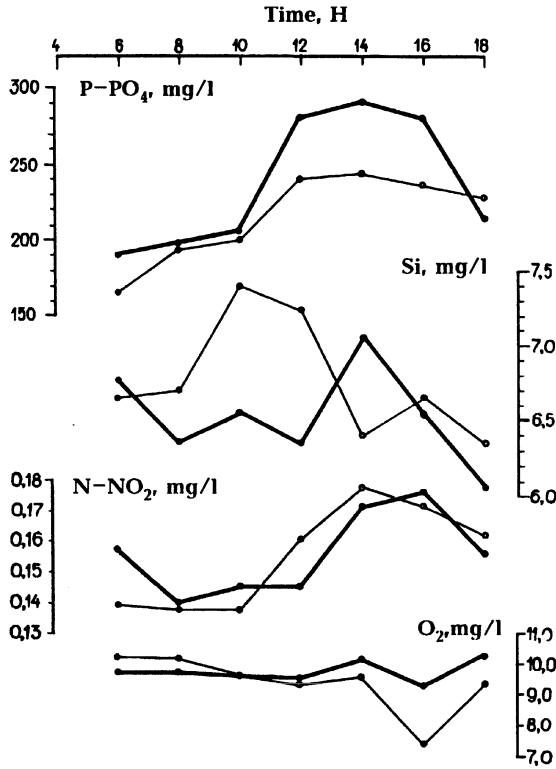


Fig. 20a. The change of biogenic elements, particulate matter, C^d , C^p and trace elements in the Don river mouth for a period of a day (October 1980).

was changed insignificantly during period of observations at semidiurnal station within the tide-uptide cycle (Table 17).

Variations in the concentrations of phosphates and nitrates in the mouth of the Don river were caused by economical activity but not by natural processes. If the variation in the concentrations of phosphates and nitrates in the river water were determined by remineralization of plankton skeleton residues it would affect C^d and C^p concentrations which is not observed.

Content of C^d and C^p in the mouth of the Don river varies insignificantly and amounts to 4.7–6.5 mg/l (average 5.7 mg/l) and 0.4–1.3 mg/l (average 0.7 mg/l) respectively. Dissolved organic matter exceeds particulate organic matter content, C^d/C^p varies from 4.9 to 14.2 and averages 9.5.

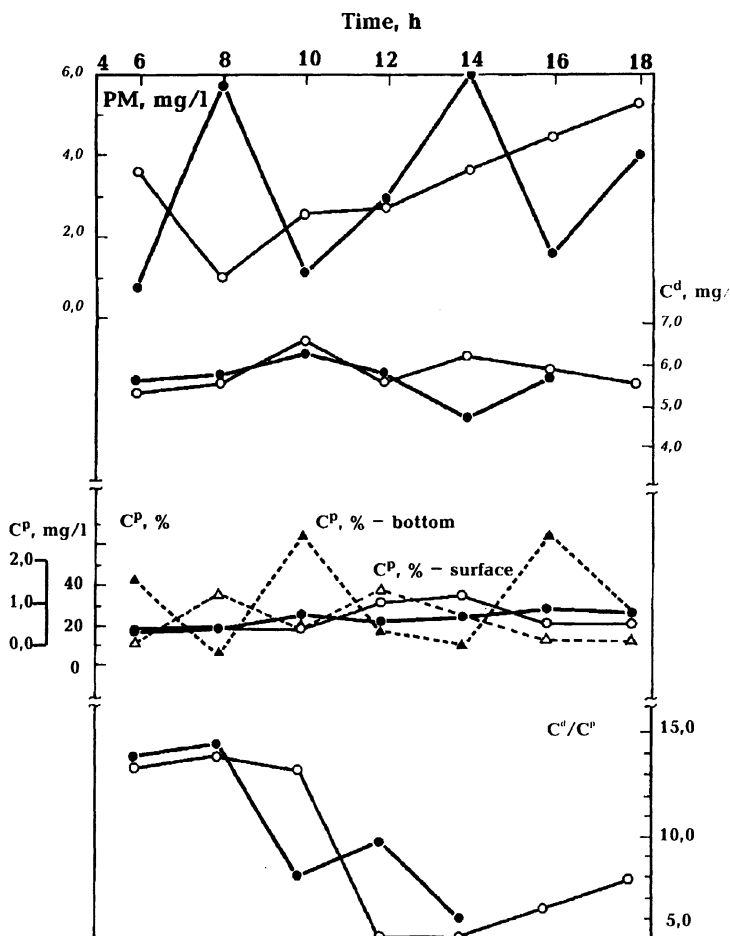


Fig. 20b.

Insignificant variations of C^d and C^p concentrations within the day in the mouths of the Don and Pechora rivers testify to the stability of dissolved and particulate organic matter contents in river mouths within a short period of time. Sharp variations of organic matter concentrations in river waters for a short period may, evidently, take place but not as a result of natural processes, regulating content of dissolved and particulate organic matter in river, but as a result of supply of technogenous pollutions into water (discharge of sewage, etc.).

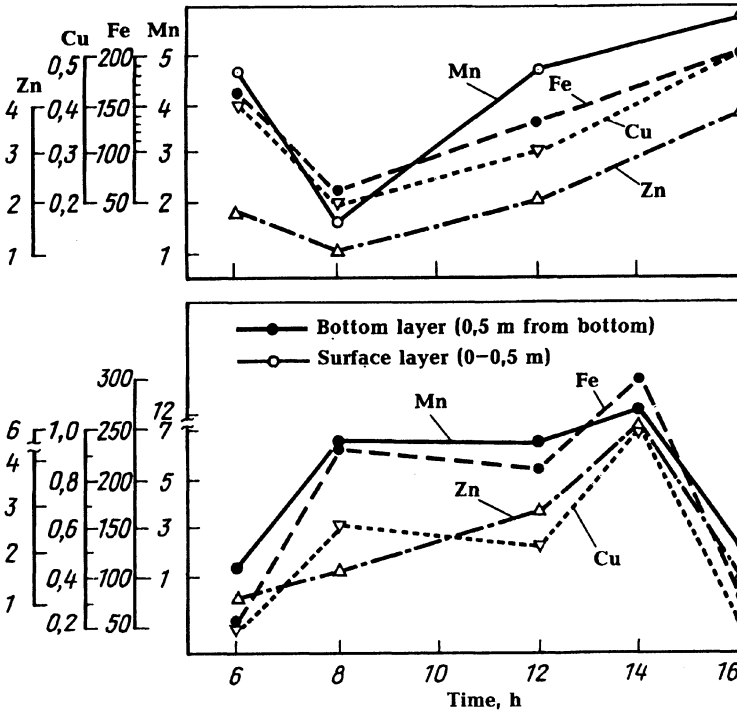


Fig. 20c.

2.4.5. COLLOID ORGANIC SUBSTANCE

Colloids occupy an intermediate place between suspended substance particles and proper dissolved substances. Conditional boundaries of colloid particles are within the limits of 0.001–1 nm. Colloid particles are formed as a result of condensation processes during which subcolloid particles are united in aggregates or as a result of dispersion processes during which coarse-grained material is fractured, converting into fine dispersed particles. Stability of colloids is partially bound up with their electrical charge.

Coulomb repulsions of similarly charged particles contributes to their separation, preventing in such a way their subsequent aggregation and sedimentation. Neutralization of these charges, for example, in case of adding an electrolyte to colloidal solution causes the disappearance of colloids. Deposition of colloids may take place in case of mixture of river and sea waters (Horn, 1972).

The biochemical value of natural colloid organic matter is determined by the fact that its composition includes large fractions of high-molecular organic matter of types such as polysaccharides, polypeptides, etc., which may serve as food for heterotrophic organisms.

Another part of colloid organic matter is represented by humic compounds of humic and fulvic acids type, the food value of which is considerably lower (they are hardly assimilated even by the simplest animals and bacteria).

As for the present day, few studies were carried out, concerning the behaviour of colloid organic matter in river waters and in the region of mixing of river and sea waters (Moore *et al.*, 1979; Sigleo *et al.*, 1982; Whitehouse *et al.*, 1989). According to the data (Whitehouse *et al.*, 1989), concentration of colloid organic matter in the Mackenzie river amounts to 20% of the sum of dissolved organic matter + particulate organic matter. In the opinion of these investigators in saline waters with concentration exceeding 5‰ colloid organic matter can be considered as close to zero. A part of high-molecular substance is strongly bound up with colloid micelles of iron oxide hydrate, forming flakes (aggregates) which are able to be deposited in estuaries. In the opinion of Moore *et al.* (1979) about 20% of terrigenous organic matter shall coagulate in estuaries. These suppositions were confirmed (and defined) in our investigations in the estuary of the Amazon (Artemyev and Shapiro, 1987).

Comparison of the absolute contents of various fractions of river and sea organic matter (Lyutsarev and Pashkova, 1984) showed that the actual dissolved organic matter is contained in almost equal concentrations both in river and sea water (Figure 21). In the opinion of the authors the small dimensions of molecules and their high hydrophillic potential give a possibility for dissolved organic matter of river water to pass the zone of river and sea waters mixing without noticeable coagulation. Proportion of various colloidal fractions in river and sea waters differs noticeably (Figure 21): river water contain considerably fewer low-molecular colloidal fractions and dissolved organic matter.

If it is accepted that colloidal organic matter in river drainage amounts to 80% of dissolved organic matter, and the river drainage of dissolved organic matter (global) to 204×10^{12} gC/year, the drainage of colloidal organic matter will amount to 170×10^{12} gC/year.

2.4.6. CONCLUSIONS

1. Organic matter is distributed in rivers of the world in accordance with climatic zonality and is represented in river water mainly in dissolved forms. The highest concentrations of C^d were found in rivers of the northern humid zone, which is bound up with the supply of organic matter of mainly humus genesis from podsollic and swampy soils of taiga-and-forest, forest-and-tundra and tundra zones.

2. The highest flows of both C^d and C^p are supplied with rivers to seas and oceans in the equatorial humid zone, respectively 75.8 and 90.2%. On the whole, rivers transport approximately equal quantities of C^d and C^p , 0.204×10^9 t/year and 0.184×10^9 t/year, respectively.

3. The spatial distribution of C^p in waters of river mouths vertically from the surface to the bottom and horizontally from one shore to another one are of very complicated character and are not characterized by any general regularities. Therefore, to obtain correct data on the concentrations of C^d and C^p in the river mouth it is necessary to take samples of water for analyses in three points of lateral section through the river bed: near

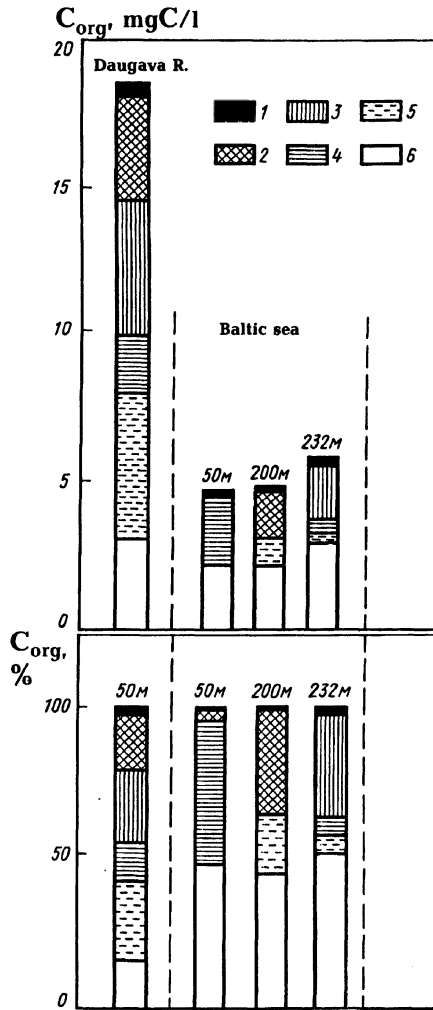


Fig. 21. C_{org} in the particulate matter, colloidal and dissolved substance in the Daugava river and the Baltic Sea (Lutzarev and Pashkova, 1984). 1. Particulate matter; 2-5. colloidal substance fractions; 6. dissolved organic matter (molecular weight $< 10^3$).

the right, left shores and from the middle of the river from surfacial, intermediate (when depth exceeds 3 m) and bottom horizons. The average value from all the obtained data will be the proper value of concentration of C^d and C^p in the river mouth.

4. Determination of the concentrations of C^d and C^p in the main bed of the Amazon, along the 2000 km stretch from the place of interflow of the Solimoiins and Negru rivers to the mouth and in its main tributaries, showed that no strongly expressed external contents of dissolved and particulate organic matter are observed in the basins of the rivers, which are not subjected to influence of anthropogenous effect (technogenous pollutions, etc.). The similar character of dissolved and particulate organic matter distribution along the river bed is evidently typical for rivers in which the basic sources of organic matter are mainly natural objects: soils, plankton, grass, macrophytes, etc.

5. The quantity and the composition of organic matter in rivers vary depending on the season and climate, stages of development of ground vegetation and sources of river supply. The highest concentrations of organic matter in river mouths of northern humid and moderate climatic zones is observed during the flood period. In river mouths of northern humid zone higher concentrations of C^p are also observed during the winter period, which is bound up with low rates of particulate organic matter destruction under conditions of low water temperature.

2.5. Composition of River Organic Matter

Composition of river organic matter is determined mainly by the supply of allochthonous organic matter, which includes organic compounds, discharged into water in the process of functioning and fracture of organisms (mainly polypeptides and polysaccharides), as well as products of polymerization of these organic matter – humic substances (HS), represented by the two main classes: humic and fulvic acids (HA and FA).

River water is a complex heterogenous multicomponent system. Table 23 contains the data about the content of the main classes of dissolved organic matter in river waters. As it is known, the natural waters are characterized by both exclusive variety of dissolved organic matter composition and a wide range of values for each of its components. The peculiarity of river dissolved organic matter composition is the denomination of natural substance of humic nature, humic and fulvic acids, inclined in solutions to association and formation of polydispersive systems with the range of molecular weight of 300–6000.

Humic and fulvic acids may amount to 60–80% of dissolved organic matter. As a rule, the content of fulvic acids is an order higher than the content of humic acids and totals 1–100 mg/l for mostly spread surfacial waters and more (Table 23).

2.5.1. AMINO ACIDS

Being supplied to water from soils by the process of plankton functioning, with atmospheric precipitations amino acids (AA), proteins take part in various chemical processes. Various organic and inorganic compounds being formed as a result, including such complex and specific ones as humus substances. The study of humic acids, polypeptides and proteins is necessary due to their tendency to form stable complexes with ions of many metals.

Table 23. Content of main classes of dissolved organic matter in river waters (Varshal *et al.*, 1979).

Class of natural OM	Concentration, mg/l
Carbonic and oxycarbonic acids of aliphatic line: formic and other	0.01–10
Humic acids	0.01–30
Fulvic acids	1–100
Alcohols	to 2
Aldehydes, ketones, polyfunctional carbonyl compounds	0.05–2.2
Phenols	0.001–0.060
Polyphenols	to 10
Reducing sugars	0.1–0.2
Polysaccharides	0.2–0.6
Esters, lipids, mono-, di- and triglycerides	10–200 $\mu\text{g-equiv/l}$
Amino acids	2–25 $\mu\text{g/l}$

2.5.1.1. Dissolved Amino Acids

Nearly all of the most important amino acids were found in river waters: glutamic and aspartic acids, glycerine, alanine, leucine, arginine, serine being met most often (Semenov, 1967; Ittekkot *et al.*, 1982, 1986).

The predominance of “bound”, i.e. unable for reaction, resistant to fracture, amino acids testifies their presence in river waters in the form of mainly humic compounds (Seifert and Ittekkot, 1985). The composition of free and bound amino acids in river waters varies essentially depending upon the season and is rather sensitive to the change of production process intensity, transformation, and consumption of organic matter (Semenov *et al.*, 1966b). The study of proteins in the rivers of Latvia showed that high concentrations of proteins in river waters are typical for summer, and the lowest are for winter (Table 24).

Such regularity is evidently bound up with the higher activity of phytoplankton which produce the organic matter in the summer–autumn period, contributing to dissolved organic matter accumulation and, in particular, accumulation of proteins in river water.

The connection of the content of proteins in river water with the process of primary production of organic matter by phytoplankton testifies to their autochthonous genesis.

2.5.1.2. Amino Acids of Suspension and Bottom Sediments

The results of studying suspended free amino acids in the Amazon showed that they amounted to 0.02–0.04% (0.03% on average) for calculation of dry mixture weight and 0.05–0.6 (average 0.2%) of organic matter (Tables 25 and 26).

Table 24. Proteins and C_{org} in rivers of Latvia (Laznik, 1987).

River, point	Months							Average per year	C ^d , mg/l	C ^p %
	II	IV	V	VII	X	XI	XII			
Gauya, above Sigulda	<u>168*</u>	<u>580</u>	<u>630</u>	<u>604</u>	<u>537</u>	<u>400</u>	–	<u>502</u>	11.9	4.2
	56	192	210	202	180	133		168		
Daugava, above Dkabpils	<u>420</u>	<u>534</u>	<u>453</u>	<u>672</u>	<u>540</u>	<u>408</u>	–	<u>530</u>	16.7	3.2
	140	178	151	224	180	136		177		
Lielupe, above Kalntsiems	<u>336</u>	<u>524</u>	<u>750</u>	<u>655</u>	–	<u>516</u>	<u>487</u>	<u>570</u>	20.0	2.0
	112	175	250	218		172	162	190		

*Nominator: concentration of proteins, $\mu\text{C/l}$; denominator: the same in $\mu\text{N/l}$.

Neutral amino acids – 46.3–55.0% (average 49.9%) of the sum of amino acids – prevailed essentially in the amino acids composition of the Amazon basin suspension. Studying the individual composition of amino acids in the suspension of the Amazon basin (Table 26) and other major rivers of the world (Ittekkot *et al.*, 1983) showed that glutamic and aspartic acids and glycerine prevail in suspended amino acids as well as in dissolved ones (Table 26).

Average contents of amino acids in bottom sediments of the Amazon basin river total 0.11–0.14% (average 0.12%), converting into dry weight of sediment and 2.0–3.5% (average 2.4%) of organic matter (Tables 27 and 28) which is 2–3 times higher than amino acids content in modern ocean sediments (Romankevich, 1977). Neutral amino acids (39.6%) prevail among amino acids groups in bottom sediments as in suspension also, and aspartic and glutamic acids prevail among individual amino acids. The summary content of amino acids in the bottom sediments of the Amazon basin is increased by 4–5 times, compared with suspension, content of amino acids containing sulphur is increased most intensively, by 16 times (Table 27). Similarity in the correlation of amino acids groups and set of individual amino acids in suspension and bottom sediment testifies their genetic relationship and the geochemical dependence of bottom sediments organic matter upon particulate organic matter composition. An increase of amino acids content in bottom sediments is bound up with the typical feature of organic matter transformation in the process of sedimentation including an increase of humic acids in organic matter composition.

2.5.2. CARBOHYDRATES

The results of analyses of carbohydrates in northern and southern rivers of the European part of Russia (Artemyev, 1981; Artemyev *et al.*, 1984) showed that carbon of particulate and dissolved carbohydrates in the waters of the North Dvina river (C_c^d and C_c^p amount respectively to 1.2 mg/l and 0.04–0.14 mg/l (average 0.09 mg/l). Thus, the example of the North Dvina river shows that carbohydrates in northern rivers are represented by mainly

Table 25. Group composition of amino acids in particulate matter of the Amazon basin and its estuary.

Ord. No.	River (Station numbers)	C _{org} , % (OM)	Content of amino acids, %																									
			main					neutral					acid					aromatic										
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Sum	% of sum of amino acids												
																		% from OM					sulph.cont.					
1.	Trombetas (1017)	12.3 (22.4)	0.005	0.013	0.005	0.003	0.001	0.027	0.12	18.0	49.2	18.0	11.1	3.7	0.027	0.12	18.0	49.2	18.0	11.1	3.7	0.027	0.12	18.0	49.2	18.0	11.1	3.7
2.	Shingu (1006-1008)	15.5 (28.2)	0.006	0.019	0.010	0.004	0.002	0.041	0.14	14.6	46.3	24.4	9.8	4.0	0.041	0.14	14.6	46.3	24.4	9.8	4.0	0.041	0.14	14.6	46.3	24.4	9.8	4.0
3.	Topazhos (1013)	20.5 (37.3)	0.004	0.014	0.004	0.002	0.001	0.025	0.06	16.0	56.0	16.0	8.0	4.0	0.025	0.06	16.0	56.0	16.0	8.0	4.0	0.025	0.06	16.0	56.0	16.0	8.0	4.0
4.	Amazon (1015, 1020)	2.0 (3.6)	0.004	0.011	0.005	0.002	0.001	0.023	0.64	17.4	47.8	21.7	8.7	4.4	0.023	0.64	17.4	47.8	21.7	8.7	4.4	0.023	0.64	17.4	47.8	21.7	8.7	4.4
5.	Negru (1028, 1033, 1034)	26.1 (47.5)	0.004	0.13	0.005	0.003	0.001	0.026	0.05	15.4	50.0	19.2	11.5	3.9	0.026	0.05	15.4	50.0	19.2	11.5	3.9	0.026	0.05	15.4	50.0	19.2	11.5	3.9
Limits		2.0-26.1	0.004-0.006	0.011-0.019	0.004-0.010	0.002-0.004	0.001-0.002	0.023-0.041	0.05-0.64	14.6-18.0	46.3-56.0	16.0-24.4	8.0-11.5	3.7-4.4	0.023-0.041	0.05-0.64	14.6-18.0	46.3-56.0	16.0-24.4	8.0-11.5	3.7-4.4	0.023-0.041	0.05-0.64	14.6-18.0	46.3-56.0	16.0-24.4	8.0-11.5	3.7-4.4
Average		15.3 (27.8)	0.005	0.014	0.006	0.003	0.001	0.028	0.20	16.3	49.9	19.9	9.8	4.0	0.028	0.20	16.3	49.9	19.9	9.8	4.0	0.028	0.20	16.3	49.9	19.9	9.8	4.0
Estuary: 1054		7.6 (13.8)	0.004	0.0011	0.005	0.002	0.001	0.023	0.17	17.4	47.8	21.8	8.7	4.3	0.023	0.17	17.4	47.8	21.8	8.7	4.3	0.023	0.17	17.4	47.8	21.8	8.7	4.3
1050		17.5 (31.8)	0.003	0.015	0.005	0.003	0.001	0.027	0.08	11.1	55.5	18.5	11.1	3.8	0.027	0.08	11.1	55.5	18.5	11.1	3.8	0.027	0.08	11.1	55.5	18.5	11.1	3.8
1049		24.9 (45.3)	0.003	0.015	0.005	0.003	0.002	0.027	0.06	11.1	55.5	18.5	11.1	3.8	0.027	0.06	11.1	55.5	18.5	11.1	3.8	0.027	0.06	11.1	55.5	18.5	11.1	3.8
1047, 1048		40.2 (73.2)	0.003	0.017	0.006	0.003	0.001	0.04	10.0	56.7	20.0	10.0	3.3	0.04	10.0	56.7	20.0	10.0	10.0	3.3	0.04	10.0	56.7	20.0	10.0	10.0	3.3	0.04
1045		-	0.003	0.016	0.005	0.003	0.001	0.028	-	10.7	57.2	17.6	10.7	3.8	0.028	-	10.7	57.2	17.6	10.7	3.8	0.028	-	10.7	57.2	17.6	10.7	3.8
Limits		7.6-40.2	0.003-0.004	0.011-0.017	0.005-0.006	0.003	0.001	0.023-0.030	0.04-0.17	10.0-17.4	47.8-57.2	17.6-21.8	8.7-11.1	3.3-4.3	0.023-0.030	0.04-0.17	10.0-17.4	47.8-57.2	17.6-21.8	8.7-11.1	3.3-4.3	0.023-0.030	0.04-0.17	10.0-17.4	47.8-57.2	17.6-21.8	8.7-11.1	3.3-4.3
Average		22.5	0.003	0.015	0.005	0.003	0.001	0.027	0.09	12.1	54.5	19.3	10.3	3.8	0.027	0.09	12.1	54.5	19.3	10.3	3.8	0.027	0.09	12.1	54.5	19.3	10.3	3.8

sulph.cont. = sulphur containing.

Table 26. "Free" amino acids ($10^{-4}\%$) in the particular matter of the basin and estuary of the Amazon.

Ord. No.	River	C _{org}	Main			Neutral			Acid			Aromatic			Sulph. cont. methionine	Sum total of AA	Quantity of AA						
			argi- nine	histi- dine	lisi- ne	ala- mine	vali- ne	gluci- ne	leu- cine	iso- leucine	pro- line	seri- line	aspartic acid	glutamic acid				tyro- sine	phenyl- alanine				
1	Trombetas	12.3	20	16	22	58	25	20	28	15	5	22	19	134	24	26	50	14	17	31	7	280	14
2	Shingu	15.5	20	17	20	57	32	28	38	27	7	37	20	189	49	51	100	19	26	45	16	407	15
3	Topazhos	20.5	12	10	17	39	25	18	28	22	6	29	17	145	21	24	45	18	18	18	9	256	14
4	Amazon	2.0	10	28	38	17	15	25	16	4	18	11	106	20	31	51	51	16	16	16	6	217	13
5	Negru	26.1	8	10	24	42	19	16	24	22	5	19	22	127	22	27	49	13	16	29	11	258	15
	Average	15.3	14	13	22	47	24	19	29	20	5	25	18	140	27	32	59	9	19	28	10	284	14
Estuary																							
6	1054	7.6	19	20	39	19	15	21	15	4	18	15	107	23	27	50	18	18	18	9	223	13	
7	1050	17.5	11	17	28	29	23	32	18	5	20	19	146	21	25	46	10	16	26	9	255	14	
8	1049	24.9	8	24	32	26	17	27	26	6	30	21	153	30	22	52	15	17	32	15	284	14	
9	1047, 1048	40.2	10	20	30	26	20	30	29	7	29	26	167	28	31	59	15	18	33	11	300	14	
10	1045	-	11	17	28	20	22	30	24	6	31	29	162	25	26	51	16	19	35	14	290	14	
	Average	22.5	12	0	20	31	24	19	28	22	6	26	22	147	25	26	52	11	18	29	12	270	14

sulph. cont. = sulphur containing.

Table 27. Variation in the composition of amino acids in the system "particulate matter-sediment".

Ord. No.	Station numbers,	Material	Content of amino acids in particulate matter and bottom sediments, 10 ⁻⁴ %					sulph. cont.	Sum
			main	neutral	acid	aromatic			
1	1006, Shingu	suspension	42	147	61	28	10	288	
		sediment	194	439	216	94	125	1068	
2	1013, Topazhos	suspension	39	145	45	18	9	256	
		sediment	204	419	288	128	117	1156	
3	1017, Trombetas	suspension	38	119	41	28	8	236	
		sediment	254	515	315	127	162	1373	
4	1023, 1034, Negro, above Manaus	suspension	42	127	49	29	11	258	
		sediment	196	508	242	131	164	1241	
5	Average	suspension	40	133	49	25	9	256	
		sediment	209	477	260	123	147	1216	

Table 28. Composition of bottom sediments amino acids in the Amazon basin.

Ord. No.	Station numbers, river	Sampling interval, cm	Content in sediment, %		HA % in OM	Content of AA × 10 ⁻⁴ %/OM × 10 ⁻²							
			Corg	HA		main				neutral			
						argi-nine	hys-tidine	lisi-ne	% of AA	ala-mine	va-line	gly-cocaine	leu-tine
1.	1006, Shingu	0-10	2.94	2.25	42.1	51	63	80	18.2	69	62	81	79
2.	1013, Topazhos	0-5	2.76	1.97	39.2	70	38	96	17.6	50	79	65	86
3.	1017, Trombetas	0-5	3.41	1.71	27.5	64	89	101	18.5	58	91	82	104
4.	1028, Rio Negro, above Manaus	0-5	1.81	2.47	75.1	63	40	72	15.1	77	82	60	96
5.	1034, Negro, below Manaus	0-5	3.55	3.54	54.8	73	60	84	16.4	78	78	91	112
Limits			1.81-3.55	1.71-3.54	27.5-75.1	51-73	38-89	72-101	15.1-18.5	50-78	62-91	60-91	79-112
Average			2.9	2.4	47.7	64	58	87	17.1	66	78	76	95

Table 28. (Continued)

Ord. no.	Content of AA × 10 ⁻⁴ %/OM × 10 ⁻²													% of OS
	neutral				acid			aromatic			sulphur containing			
	iso-leucine	pro-line	seri-ne	% of AA	aspar-acid	gluta-mine acid	% of AA	tyro-sine	phenyl-alanine	% of AA	methio-nine	cis-tine	% of AA	
	20	76	52	41.1	115	101	20.2	38	56	8.8	81	44	11.7	
2.	21	70	48	36.2	161	127	24.9	55	73	11.1	63	54	10.1	
3.	26	89	65	37.5	179	136	22.9	57	70	9.2	85	69	13.3	
4.	24	73	56	40.4	147	120	23.0	39	56	8.2	85	69	13.3	
5.	28	63	98	41.4	120	98	16.4	79	88	12.6	99	76	13.2	
Lim.	20-28	63-89	48-98	36.2-41.4	115-179	98-136	16.4-24.9	38-79	56-88	8.2-12.6	63-99	44-76	10.1-13.3	
Av.	24	74	64	39.3	144	116	21.5	54	69	10.0	84	63	12.0	

dissolved form (about 98%), C_c^p amounts to 11.7–20.0% (average 14.8% of C^p), and C_c^d to 3.5–12.3% (average 8.9% of C^d).

About 1/5 of the dissolved organic matter in southern plain rivers is represented by carbohydrates, a share of which amounts to 17.3–33.8% (average 21.7%). The total content of carbohydrates in rivers of southern seas of Russia totals, on average, 1.2 mg/l for plain rivers and 2.8 mg/l for mountain ones. In this case, if in plain rivers, carbohydrates are present mainly in dissolved form (average 68.5% of carbohydrates sum), particulate carbohydrates (70.1%) prevail in mountain rivers.

Content of carbohydrates in particulate organic matter of southern plain rivers is approximately the same as in particulate organic matter of the North Dvina river: C_c^p equals, on average, 15.5% of C^p . The ratio free/bound sugars in river waters is essentially higher than that in plankton organisms, which, as a result, contain negligible quantities of simple sugars (Artemyev, 1976). This may be connected with a preference of simple sugar formation rate in river waters over their consumption, as well as with excretion of low-molecular carbohydrates by developing algae. As it was shown by the studies of Semenov (1971) river waters differ essentially from each other by the composition of their carbohydrates. These variations are caused by many factors, the most important of which are the variation of composition of water organisms and the selectivity of consumption of various carbohydrates by them. Thus, only the study of organic matter composition and some of its components gives a possibility to estimate the trend and the intensity of biogeochemical processes in river waters controlled by organisms inhabiting the water medium. The data about relative content of labile components in river waters (amino acids and carbohydrates) may give ideas about the potential ability of organic matter for destruction. It was determined that the concentration of labile components in particulate organic matter composition in the majority of large rivers of the world does not exceed 12% (Degens and Ittekkot, 1985), i.e. the predominating part of particulate organic matter is represented by compounds which are resistant to degradation.

The proportion of labile and stable dissolved components in river and sea waters may be studied using the example of the Visla river and neighbouring waters of the Baltic Sea (Pempkowiak, 1985). It was shown that labile dissolved organic matter in river waters amounts to 20–30% and in sea waters it is equal to 30–40%. In this case the share of labile C^d in both river and sea waters during the seasons with lower average temperatures of water is higher than in summer months.

Seasonal variations of concentrations and composition in river mouths are typical for amino acids and carbohydrates as well as for other classes of organic matter, which testifies irregularity of supply of various classes of river organic matter to sea water, their qualitative variety being dependent upon the season. It was shown that variation of the share of amino acids and carbohydrates in river organic matter composition may be used as indicators of biogeochemical processes in river waters (Ittekkot *et al.*, 1985). Evidently, organic matter fractured by micro-organisms will contain relatively low quantities of these labile components. Investigation of seasonal variation of concentrations of amino acids and carbohydrates in the mouth of the Ganges (Ittekkot *et al.*, 1985, 1986) gave a possibility to determine that, in the case of an increase of river drainage, there is biodegradation of river organic matter as a result of biogeochemical processes. This is also borne out

by the decrease of content of labile components in it. The sequence of organic matter biodegradation or change of source of organic matter in river water is caused by seasonal variation in the composition of amino acids and carbohydrates (Ittekkot *et al.*, 1986).

2.5.3. HUMIC SUBSTANCES, BITUMOIDS

Some quantities of specific polyfunctional compounds are present virtually always in river waters (complex macro-molecular phenol carboxy acids), which are called humic or humine acids by the analogy with substances of soils and peats. It was found out that firstly, aqueous humic substances and in particular humic and fulvic acids demonstrate a number of properties, similar to the properties of soil and peat humic and fulvic acids, and secondly that a considerable part of humic substances is supplied to river waters directly from soils and peats by surfacial drainage (Beck *et al.*, 1974; Reuter and Perdue, 1977). An additional source of supply of humic substances to river waters may be the products of sewage waters, obtained as a result of processing polluted waters. These dead products are very similar to soil humic substances in their elementary composition, oxygen-containing groups and other parameters (Manka *et al.*, 1974). Contribution of such substances to the total sum of river organic matter may be very considerable for rivers flowing through large industrial centres.

2.5.3.1. Dissolved Humic Substances

Concentration of humic substances in river waters varies from less than 10 to 1000 mgC/l³ (Table 29). One may observe the clear zonality in latitudinal distribution of humic acids in river waters, determined by the influence of terrigenous material. The highest values of humic acids content were found in coloured waters of northern and Siberian rivers (Table 29), its supply being bound up with spring or autumn floods, i.e. supply of humic substances from the water collection area. It is known that seasonal variations of humic substances concentration, which are also determined by supply of terrigenous humus to rivers, have a connection with its water regime. All this is true for rivers, flowing in zones of excessive precipitation with a high development of forest, plants, well-drained podsollic soils, etc.

The results of the study of annual variation of concentrations of humic acids in the Don river showed (Semenov, 1971) that in the winter low water period concentrations of dissolved humic acids are low, and in spring flood and in autumn they reach their maximum values. Thus the concentration of humic acids in river waters of the moderate humid zone is determined mainly by organic matter supply from water drainage area and not within reservoir processes (Semenov, 1971).

From Table 29 we notice that the content of humic acids in plain river waters is increased regularly from the tundra group of landscape (Pechora river) to the taiga group (North Dvina, Daugave rivers) where it reaches its maximum values, and further to the south in the steppe zone it is decreased to the lowest values (Don, Kuban rivers).

³According to A.D. Semenov humic acids contains 56% of carbon.

Table 29. Content of humic and fulvic acids (mgC/l) in river waters of various latitude zones (Smirnoff *et al.*, 1978).

Hydrological phase	C _{HA}	C _{FA}	Typical river of drainage system basin
TUNDRA			
spring flood	339	2266	Pechora river
summer low water	236	1989	
winter low water	130	1048	
FOREST-TUNDRA			
spring flood	435	3371	
summer low water	180	2130	
winter low water	87	1495	
NORTHERN TAIGA			
spring flood	1020	5438	North Dvina
summer low water	180	2218	
winter low water	114	1572	
MEDIUM BELT TAIGA			
spring flood	1081	7173	
summer low water	303	3588	
winter low water	75	–	
SOUTHERN TAIGA AND MIXED WOOD			
spring flood	669	4927	Daugava
summer low water	182	3362	
winter low water	65	2158	
BROAD-LEAVED FORESTS, FOREST-STEPPE			
spring flood	305	2615	Don
summer low water	325	2848	
winter low water	68	961	
STEPPE			
spring flood	98	1046	Kuban
summer low water	17	602	
winter low water	18	578	

In spite of the fact that the largest part of coloured humic substances in river waters consists of fulvic acids, reliable information about the concentration of these substances is virtually absent in the literature. The few existing determinations of fulvic acids content in rivers showed that their quantity exceeds content of humic acids in river waters by several times (Tables 29 and 30). According to the data of Ertel *et al.* (1986) organic matter in

Table 30. Concentration of humic and fulvic acids in the Russian rivers and in the Amazon basin (mgC/l).

River	HA	FA
North Dvina	0.2	2.3
Neva	0.2	1.8
Dnieper	0.2	2.2
Volga	0.1	0.9
Amur	0.4	3.3
Amazon*	0.5	2.0
Negrú*	2.5	4.0

* Analyses were carried out in the Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of Russia.

the Amazon waters amounts to 60% of dissolved organic matter. The ratio FA/HA is, on average equal to 4.7 ± 1 . In the Solimoins river waters it is 5.4, in the Negrú river waters it is equal to 1.6. Dissolved humic substances, responsible for the colouring of the Negrú river waters, amount to about 1/2 of dissolved organic matter, the other part of dissolved organic matter are represented by colourless organic acids (Leenheer, 1980). The data of determining the elementary composition, infrared analysis, and other data show that the majority of non-humic dissolved organic matter is supplied to “black” waters as a result of drainage of the latosolic soils of the region.

Humic acids, found in “black”, “white” and “pure” waters of the Amazon may be compared with those supplied from podsollic and latosolic soils of the Amazon region (Leenheer, 1980). The maximum quantity of organic matter of humic type were found in “black” waters, where they are supplied as a result of underground waters drainage of podsollic soils covered with a thick layer of organic residue, accumulated on the surface. The study of the chemical composition of humic substances of Amazon “black” waters showed that they are the final products of organic matter destruction as a result of the humification process, which is carried on in tropical soils and waters more quickly than at more moderate latitudes (Leenheer, 1980).

Considerably lower quantities of humic substances are delivered into “pure” waters, passing through latosolic soils. These soils have no such layer as podsollic ones, which are enriched with organic matter and, moreover, coloured solutions of humic substances are adsorbed on clay minerals of latosolic soils.

Table 31. Bituminological characteristics of suspensions of the Amazon basin and estuary.

Ord. No.	Station No.	Content in suspension, %				bit. A _{cl} / bit. A alc.benz.	Group composition of OM, %			
		C _{org}	bitumoid "A"		HA		bitumoid "A"		HA	ROM
			chloroph.	alc.benz.			chloroph.	alc.benz.		
1.	1028, 1033, 1034	26.1	13.01	12.39	traces	1.01	27.4	26.1	-	46.5
2.	1017	12.3	5.53	12.95	not found	0.40	24.6	57.5	-	17.9
3.	1015, 1020	2.0	0.52	0.43	traces	1.20	14.4	11.9	-	73.7
4.	1013	20.5	7.80	12.12	not found	0.60	20.9	32.5	-	46.6
5.	1006-1008	15.5	7.05	13.20	traces	0.50	25.0	46.8	-	28.2
	Average	15.3	6.8	10.2	traces	0.70	22.5	35.0	-	42.6
Estuary										
6.	1054-1, 1054-2, 1054-3	7.6	1.32	7.24	not found	0.20	9.6	52.5	-	37.9
7.	1050	17.5	5.41	11.30	not found	0.50	17.0	35.5	-	47.5
8.	1049	24.9	3.39	13.40	not found	0.25	6.2	24.4	-	69.4
9.	1047, 1048	40.2	1.48	23.38	not found	0.06	2.7	42.6	-	54.7
10.	1045	-	2.39	13.60	not found	0.20	no data	-	-	-
	Average	22.5	2.89	13.78	not found	0.20	8.9	37.7	-	52.4

2.5.3.2. Humic Substances and Bitumoids of Particulate Matter and Bottom Sediments. Transformation of Organic Matter Composition in Line Soils-Suspension-Bottom Sediments

As it was shown by the studies (Table 31), humic acids in river suspension are either absent or are present in trace quantities. As a rule, more than 50% of river particulate organic matter is represented by bitumoids. Alcohol-benzol bitumoid "A" (bit. A_{al.b}) prevails in the Amazon suspension, content of that bitumoid tends to increase towards the river mouth, reaching almost 50% of organic matter. The sum of alcohol-benzol and chloroform bitumoid "A" (bit. A_{cl}) amounts to 25-80% in suspension of the Amazon, average 60% of organic matter. The remaining organic matter is represented by residual organic matter (ROM).

The main components of river bottom sediments are humic acids and residual organic matter. Humic acids are found in the terrigenous muds of the Amazon basin, where their concentration amounts to 1.71-3.54%, average 2.39% converting into dry weight, and 27.5-75.1%, average 47.7%, of the organic matter sum (Table 21). The high content of humic acids (average of 65% of organic substances) is typical for bottom sediments of the Negro river. According to the elementary composition of humic acids and other physico-chemical characteristics (Table 32) humic acids of bottom sediments in the studied rivers are formed by products of destruction of higher plants. Humic acids, found in aleurite-

Table 32. Physico-chemical characteristics of humine acids of bottom sediments and soils in the Amazon basin.

Station number, river	Type of sediment	C _{org} %	HA %	HA, % from OM	Content in HA, %					
					Ash	Moisture	Combustible mass			
							C	H	N	O+S
1006, Shingu	mud, pelite, terrigenous, grey	2.9	2.3	42.1	10.0	7.2	58.3	6.1	4.0	31.6
1006, Shingu	soil	2.7	0.8	16.5	34.1	7.2	48.7	6.1	–	45.2
1013, Topazhos	mud, pelite, terrigenous, grey	2.9	2.0	39.2	14.9	10.0	57.4	5.8	4.3	32.5
1013, Topazhos	soil	1.2	0.6	29.2	24.3	6.0	not determined			
1030, 1031, Negru	soil	1.0	0.3	18.7	29.8	5.7	not determined			
1028, 1034, Negru	mud, pelite, terrigenous	2.7	3.0	64.9	23.3	7.8	59.2	5.9	2.5	32.3

clay sediments of the North Dvina river amount, on average, to 20.4% of organic matter (Table 28).

Content of humic acids in soils taken on the Amazon basin rivers shores is below that in sediments (Table 32). Humic acids of soils are characterized by high ash-content, which in a number of cases makes it difficult to carry out their analysis. Humic acids were not found in terrigenous river sands in either the Amazon basin or the North Dvina river mouth (Tables 18 and 21).

Content of bit. A_{cl} and bit. A_{al–b} in both sands and muds of the Amazon basin decreases compared with suspension and total respectively to 13.6 and 3.7%. The predominating part of organic matter in sands is presented by residual organic matter: 86.4% on average. The share of residual organic matter in muds is on average equal to 48.6% of the sum of organic matter. Residual organic matter of aleurites in the North Dvina mouth is equal to 74.8%.

Variation of group composition of organic matter in sediments observed down the Amazon stream is quite regular and is determined by peculiarities of distribution and genesis of organic matter. So terrigenous sands of the Solimoins, Amazon and Tokantins rivers which are poor in organic matter are at the same time characterized by high content of bitumoids (up to 18%), typical for hydrobiontic organic matter (Artemyev and Danyushevskaya, 1988) and with the absence of humic acids (Table 21). Muds of the Negru river are characterized by the high level of humification of organic matter (up to 75%) and low bitumoid content (about 2%).

The studied river sediments of the Amazon river are clearly divided into two genetic groups. The first includes sediments enriched with organic matter pelite muds of the Negru, Trombetas, Shingu rivers. The second one includes organic matter poor sands of the Amazon, Solimoins, Madeira, Tokantins rivers. Evidently the basic source of organic

matter of the first group of sediments, which are characterized with high humification and low bitumoid content, are products of destruction of higher plants.

Practically the whole soluble part of organic matter in sediments of the second group is represented by bitumoid components, i.e. they are free of humic acids. Organic matter in these sediments is more polymerized (average content of residual organic matter is 86.4%, and 48.6% for sediments of the first group), and probably of hydrobionic type.

Bituminological studies are essentially supplemented by the results of physico-chemical studies of sediments and soils from the Amazon river system (Table 33). Bitumoids of river sediments, referred to by us as the first group, are characterized by high content of hetero-elements (O, N, S), average 15.7%, and their main carriers – resins and asphaltenes. The quantity of asphaltene components amounts, on average, to 25.0%, in the first group of sediments and it is equal to 52.8% in the second one. Bitumoids of the first group of sediments are poor in oils, in accordance with the enrichment of oxygen-containing compounds, the extremely low content of hydrocarbons is found in the composition of their organic matter (in 5–6 times less than that in the second group of sediments).

Thus, the data of element, group and hydrocarbon composition of bitumoids and their molecular structure is completely in agreement with the bituminological characteristics and reflect the presence of two basic types of organic matter in river sediments.

Comparison of physico-chemical characteristics of organic matter of sediments and soils (Tables 33 and 34) gives a possibility to note the features of differences among them. The data of element and hydrocarbons composition testify that soils contain higher quantities of aromatic compounds. Evidently, there is an enrichment of soils with oxygen-containing compounds, especially with asphaltenes and asphaltenic acids, the quantity of which reaches 51.7%, which is 6 times more than that of bottom sediments. There is no doubt that organic matter of soils is much poorer in the oil and hydrocarbons. The observed differences in the structure of bitumoids of soils and bottom sediments are related to the original organic material, being the source of organic matter formation. For soils these are mainly destructured vegetable residues, for bottom sediments it is hydrobionic material together with residues of higher plants.

Aleurite muds and sands from the North Dvina mouth are identical to muds and sands of the Amazon basin (Tables 18 and 35) by composition of organic matter and bitumoid A_{cl} .

2.5.4. LIGNIN

Lignin is a natural biopolymer, synthesized by higher ground plants. Content of lignin in various plants is equal to 25–30%. In pine wood its content is equal to 34%; content of it in beech wood is 22%, etc. Lignin is practically absent in sea organisms, thus it may serve as an indicator of land organic matter in seas and oceans.

Lignin is supplied to reservoirs with river drainage, eolic drainage and sewage from enterprises of the wood, chemical and paper industry. In the genesis of sediment lignin is more resistant to biodegradation compared to the other components of living organic matter, for example, proteins, lipids, carbohydrates.

Table 33. Physico-chemical characteristics of bottom sediments

Sampling place	Station numbers	Character of bottom sediments	Composition of bitumoid A_{cl} , %					
			Elementary			C/H	H/C	
			C	H	C+N+S			
Tokantins river	1002	terrigenous, grey sand	73.6	11.9	14.6	6.2	1.92	
Madeira river	1021	sand	74.5	12.0	13.5	6.2	1.93	
Amazon river	1009	sand	77.5	12.7	9.8	6.1	1.97	
Shingu river	1006	mud, pelite, terrigenous, grey	74.6	10.5	14.9	7.1	1.69	
Topazhos river	1013	mud, pelite, terrigenous, grey	75.2	11.8	13.0	6.4	1.88	
Trombetas river	1017	mud, pelite, terrigenous, grey	70.6	10.9	18.5	6.5	1.85	
Negru river	1028, 1034	mud, pelite, terrigenous, grey	71.7	11.6	16.7	6.1	1.94	
Estuary	1044	Sands {	Limits	73.6–77.5	11.8–12.7	9.8–14.6	6.1–6.2	1.92–1.97
			Average	75.2	12.2	12.6	6.2	1.94
		Muds {	Limits	70.6–75.2	10.5–11.8	13.0–18.5	6.1–7.1	1.69–1.94
			Average	73.0	11.2	15.8	6.5	1.84
		mud	Limits	70.5	11.6	17.9	6.1	1.97
			Average	74.9	11.9	13.2	6.3	1.91
1055	mud	70.0	11.6	8.4	6.0	1.99		
1061	mud	73.2	11.8	15.0	6.2	1.93		
		Limits	70.0–74.9	11.6–11.9	13.2–18.4	6.0–6.3	1.91–1.99	
		Average	72.1	11.7	16.1	6.2	1.95	

from the Amazon basin and estuary (March–April, 1963).

Composition of bitumoid, A _{cl} , %								
Groups			Hydrocarbons of oils			HC, %		% Me-Nf
Oils	Resins	Asphaltenes	Me-Nf	Ar	Me-Nf/Ar	in sediment	in OM	in OM
39.2	43.4	16.0	91.7	8.3	11.0	0.004	2.47	2.26
43.4	41.9	10.9	97.0	3.0	32.3	0.004	1.39	1.36
52.0	40.9	5.3	92.3	7.7	12.0	0.005	0.94	0.87
29.6	61.8	8.3	91.9	8.1	11.3	0.027	0.50	0.46
24.9	66.4	8.1	92.9	7.1	13.1	0.025	0.50	0.46
20.2	61.9	12.7	95.1	4.9	19.4	0.016	0.26	0.25
18.3	69.3	11.2	92.6	7.4	12.5	0.008	0.13	0.12
39.9–52.0	40.9–43.4	5.3–16.0	91.7–97.0	3.0–8.3	11.0–32.3	0.004–0.005	0.94–2.47	0.87–2.26
45.1	42.1	10.7	93.7	6.3	18.4	0.004	1.6	1.49
18.3–29.6	61.8–69.3	8.1–12.7	91.9–95.1	4.9–8.1	11.3–19.4	0.008–0.027	0.13–0.50	0.12–0.46
23.2	64.8	10.1	93.1	6.9	14.0	0.019	0.35	0.32
27.8	59.6	12.1	93.8	6.2	15.1	0.005	0.64	0.60
41.6	47.7	4.8	93.6	6.4	14.6	0.004	0.79	0.74
26.9	57.8	12.2	93.3	7.7	12.0	0.005	0.43	0.40
33.7	51.2	10.2	94.3	5.7	16.5	0.003	0.40	0.38
26.9–41.6	47.7–59.6	4.8–12.2	92.3–94.3	5.7–7.7	12.0–16.5	0.003–0.005	0.40–0.79	0.38–0.74
32.5	54.1	9.8	93.5	6.5	14.6	0.004	0.56	0.53

Table 33. Comparative characteristics of organic matter of soils, suspensions and bottom sediments from the Amazon basin and estuary.

Region of works	Object of studies	C _{org}	Group composition of organic matter, %			
			Bitumoid "A"		HA	ROM
			chloroform	alc.benz.		
River	Soils	1.6	1.6	1.6	21.5	75.3
	Suspension	15.3	22.5	35.0	not found	42.6
	Muds	2.9	1.3	2.4	47.7	48.6
	Sands	0.1	7.6	6.0	not found	86.4
Estuary	Suspension	22.5	8.9	33.7	not found	52.4
	Muds	0.5	1.8	2.0	6.4	87.7

Innumerable studies of lignin from the present day in river and sea bottom sediments permitted us to determine that the content of lignin destruction products (phenolic aldehydes, ketones, acids) in organic matter of bottom sediments varies from hundredth parts of a per cent to a several per cent. The total content of identified phenols in the studied sediments of North Dvina river mouth varies from 5.3 to 35.2 μg of aerial dry sediment, or from 0.06 to 2.88% of C_{org} (Figure 22).

High content of phenols was found in bottom sediments at four stations (4, 5, 6 and 2). High content of phenols in bottom sediments of station 4, remote from the sources of technogenous pollutions, may be caused by the supply of lignin from wood, stored at river shores as a result of washing out with rain waters. Higher content of lignin in bottom sediments, taken at the other three stations is, first of all, related to the supply of lignin-containing components with sewage waters of neighbouring plants. There is a trend for a decrease in the quantity of phenols with increasing distance. The lowest concentrations of phenols in bottom sediments were found at the stations remote from the place of sewage discharge.

Among the products of lignin oxidation, vanillin aldehyde predominates, as well as *p*-oxyacetophenone and *p*-oxybenzaldehyde. Their percentage in all the studied samples of bottom sediments of the North Dvina river mouth is considerably higher than that of other components. Higher content of vanillin aldehyde is bound up with its supply from coniferous forests, growing on the shores of the North Dvina river as well as from sewage products.

The source of *p*-oxybenzoic structures may be grass, as well as macrophytes. Higher content of vanillin and syringyl aldehyde is typical for angiosperms (Manskaya and Kudina, 1975). Vanillin prevails in lignin of monocotyledons and syringyl aldehyde prevails in lignin of bicotyledons.

Low concentration of syringyl aldehyde in the studied sediments, compared with vanillin aldehyde, may serve as the index of pollution of the studied region with industrial

Table 35. Physico-chemical characteristics of bottom sediments of the North Dvina river and Dvinsky Gulf.

Station no.	Type of sediment	Composition of chlorophormic bitumoid "A", %											
		Elementary			HC of oils, %			Sediment					
Sampling place	C	H	O+N+S	oils	resins	asphacid	Me-Nf	Ar	Me-Nf/Ar	HC, %	OM	% Me-Nf in OM	
North Dvina river	1 sand, medium-grained	n.f.	n.f.	n.f.	56.3	39.9	3.7	89.5	10.5	8.5	0.006	4.33	3.87
	2 sand, medium-grained	n.f.	n.f.	n.f.	41.6	52.7	5.5	84.8	15.2	5.6	0.004	1.66	1.41
	3 sand, medium-grained	n.f.	n.f.	n.f.	43.4	48.6	6.0	80.3	19.2	4.2	0.004	1.95	1.57
	4 sand, medium-grained	81.9	11.7	7.0	62.9	33.7	2.5	87.9	12.1	7.3	0.006	4.21	3.70
	5 aleurite	79.3	10.8	7.3	23.1	60.7	11.0	80.2	19.8	4.1	0.009	0.44	0.35
	6 aleurite	78.1	10.0	7.8	20.4	67.9	10.1	79.6	20.4	3.9	0.014	0.55	0.44
Sand	Limits	81.9	11.7	7.0	41.6-62.9	33.7-52.7	2.5-6.0	80.8-89.5	10.5-19.2	4.2-8.5	0.004-0.014	1.66-4.33	1.41-3.86
	Average	81.9	11.7	7.0	51.0	43.7	4.4	85.7	14.2	6.4	0.005	3.04	2.64
	Limits	78.1-79.3	10.0-10.8	7.3-7.8	20.4-23.1	60.7-67.9	10.1-11.0	79.6-80.2	19.8-20.4	3.9-4.1	0.009-0.014	0.44-0.55	0.35-0.44
Dvinsky Gulf	Aleurite	78.7	10.4	7.5	21.8	64.3	10.5	79.9	20.1	4.0	0.012	0.49	0.39
	sand with clay mud	81.3	12.1	6.7	49.2	45.3	5.3	86.5	13.5	6.4	0.010	1.13	0.98
	sand	82.3	12.3	6.7	51.6	35.4	12.8	84.3	15.7	5.4	0.10	1.75	1.47
9 sand	79.6	12.0	6.6	61.3	34.1	2.8	86.3	13.1	6.6	0.024	1.41	1.22	

n.f. = not found.

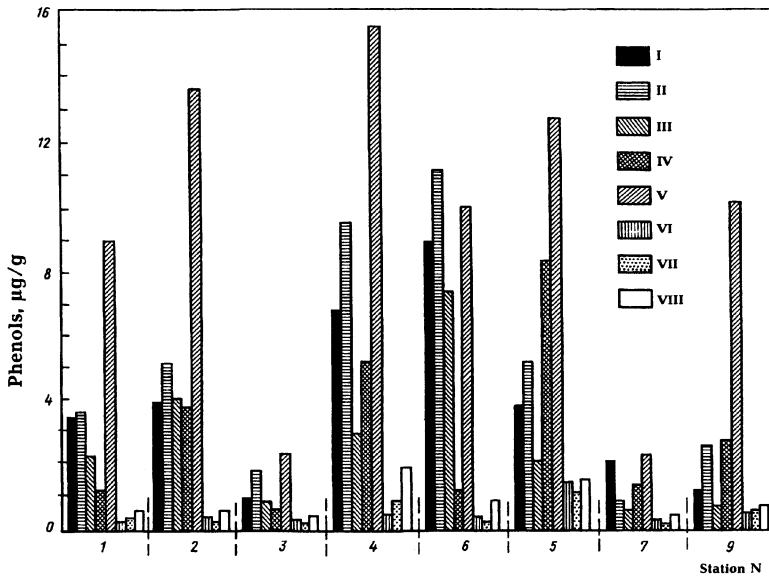


Fig. 22. The composition of lignin in bottom sediments at the profile "North Dvina river mouth-sea" (Peresypkin *et al.*, 1989). I. Benzoic acid, II. *p*-hydroxyacetophenon, III. *p*-hydroxybenzaldehyde, IV. *p*-hydroxybenzoic acid, V. vanillin, VI. vanillic acid, VII. syringyl aldehyde, VIII. syringic acid.

waste since syringyl structures are destructed firstly in processes of biodegradation, then vanillin ones.

Lignin is also supplied to river and estuary waters by the process of bark destruction when rafting wood, and its storage on the water surface. When bark is leached, various resin substances are also supplied into the surrounding water medium. The chromatogram (Figure 23) illustrates these high-molecular components which are now difficult to identify. Their content in the studied sediments, as it may be seen, considerably exceeds the concentration of phenols in lignin destruction products.

The main pollutions are delivered to sewage during production of cellulose in process of sulphite and sulphate boiling, washing, bleaching and processing of alkalies. Alkalies after boiling sulphate cellulose contain 22–28% of lignin in the form of lignin-sulphonate complex (Maksimov and Volf, 1969). The sulphate method of cellulose production pre-determines the presence of dissolved sulphate alkaline lignin in sewage waters (Bogomolov, 1973; Nepenin, 1963). Thus, lignin sulphates and sulphate alkali lignin are supplied to North Dvina waters with plant sewage, which in the process of purification are eliminated from sewage waters only to a very insignificant extent (Maksimov and Volf, 1969). In the process of destruction of these products, various phenols may be released into the surrounding medium and be buried in bottom sediments (depending upon the type of

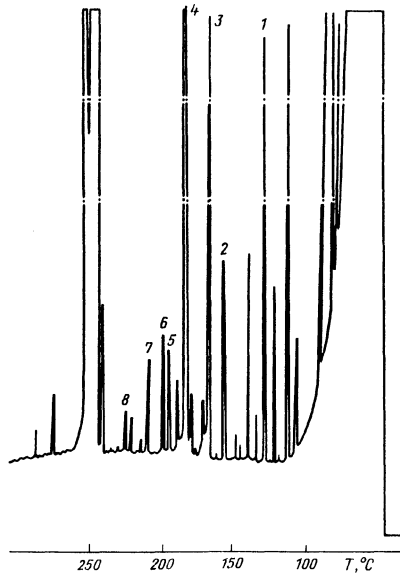


Fig. 23. Chromatogram of alkali-nitrobenzol oxidation products of bottom sediments organic matter from the Northern Dvina river mouth (Peresykin *et al.*, 1989). 1. Benzoic acid, 2. *p*-hydroxybenzaldehyde, 3. *p*-hydroxyacetophenon, 4. vanillin, 5. *p*-hydroxybenzoic acid, 6. syringyl aldehyde, 7. vanillic acid, 8. syringyl acid.

wood processing). High content of vanillin in the studied samples of bottom sediments indicates that coniferous wood is mainly subjected to such processing.

Lower (comparing with vanillin aldehydes) concentrations of *para*-oxybenzaldehyde in the studied samples testify the secondary role of grass for delivery of phenols to North Dvina waters. The ratios *p*-oxybenzaldehyde/vanillin aldehyde and syringyl aldehyde/vanillin aldehyde in the studied samples vary respectively from 0.5 to 1.9 and from 0.04 to 0.18, which indicates the permanent source of vanillin structures (comparing with *p*-oxybenzaldehyde and syringyl aldehyde) in waters of North Dvina river (st. 1–3). Low values of *p*-oxybenzaldehyde/vanillin aldehyde and syringyl aldehyde/vanillin aldehyde are related to bottom sediments, taken near CPP⁴ (Stations 1, 2). Aromatic acids (excluding syringic ones) were found in all samples, their concentrations being considerably lower than those of aldehydes (Figure 22).

The total content of lignin in bottom sediments, including unidentified compounds, may be determined by calculations, assuming that the vanillin aldehyde content is equal to 6% of the total content of lignin in bottom sediments (Gardner and Menzel, 1974).

⁴CPP = Cellulose-Paper Plant.

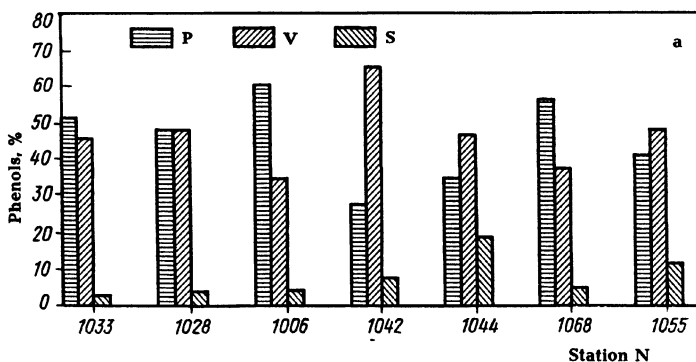


Fig. 24. Interrelation of lignin derivatives (phenols) in the particulate matter of the Amazon river basin and its estuary. P = paraoxybenzaldehyde, V = vanillin aldehyde, S = syringyl aldehyde.

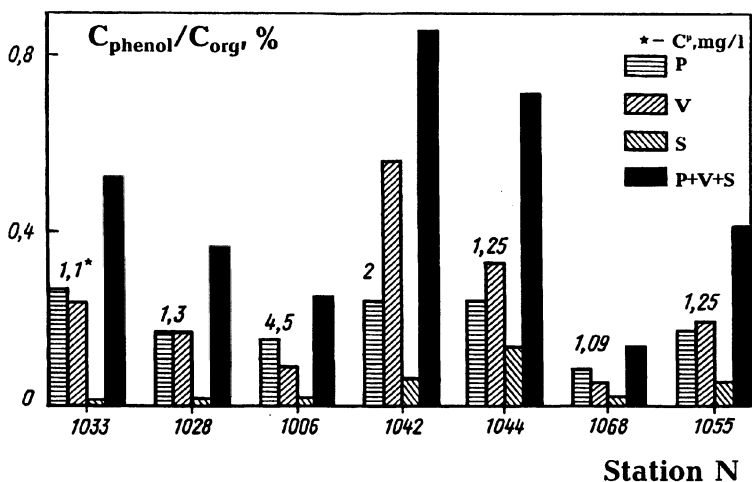


Fig. 25. Lignin derivatives (phenols) from particulate organic matter of the Amazon river basin and its estuary (see Figure 24).

Calculations showed that concentration of lignin in bottom sediments is equal to 37–256 $\mu\text{g/g}$ of dry sediment or 0.7–32% of C_{org} , which is comparable with the earlier obtained data (Hedges and Parker, 1976; Bobyleva, 1982; Bobyleva and Peresykin, 1987; Charriere *et al.*, 1991; Gough *et al.*, 1993).

Lignin was also studied by us in suspension and in bottom sediments of the Amazon basin. In suspension, para-oxybenzaldehyde and vanillin aldehyde predominate among phenols; they total about 90% of all phenols (Figure 24). The share of lignin (sum of

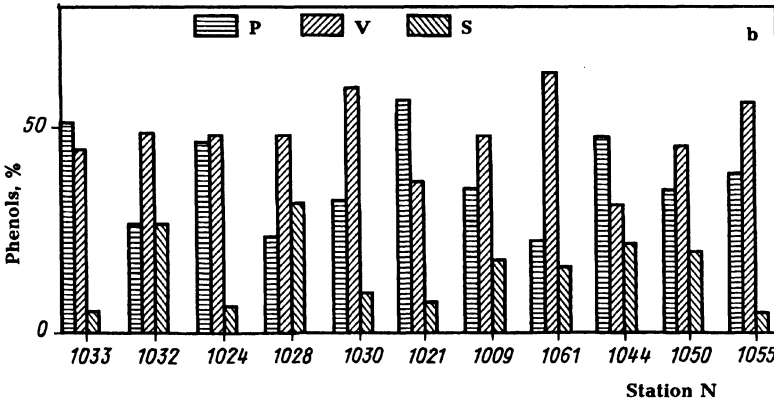


Fig. 26. The interrelation of lignin derivatives (phenols) in bottom sediments of the Amazon river basin and its estuary (see Figure 24).

phenols) in particulate organic matter composition in both the river and the estuary does not exceed 1% (Figure 25). The highest content of phenols was found in the mouth of the Amazon, which is associated with the accumulation of lignin-containing natural objects in the lower part of this river. High content of phenols was also found in suspension of the Negro river, which is, to a considerable extent, formed on the account of lignin-containing plants (Hedges *et al.*, 1986).

Comparing this with river suspension, the content of lignin in the composition of particulate organic matter in Amazon estuary is somewhat increased primarily on account of syringyl aldehyde.

p-Oxybenzaldehyde and vanillin aldehyde essentially predominate in the phenols of bottom sediments, as well as in suspension, and total 85% on average.

Thus, compared with the suspension, the share of vanillin aldehyde increases in the composition of lignin of bottom sediments of the Amazon basin and estuary. In this case, the share of lilac aldehyde in muds is higher and that of *p*-oxybenzaldehyde is lower than in sands (Figure 26).

Any essential changes in lignin composition of bottom sediments (muds) of the estuary (compared with river muds) were not observed. Content of lignin in bottom sediments of the Amazon is equal on average to 20 $\mu\text{g/g}$ for sands, and to 90 $\mu\text{g/g}$ of dry sediment for muds.

The absolute content of lignin in the estuary muds is less than in the river and is, on average, equal to 40 $\mu\text{g/g}$. The highest content of lignin among river sediments was found in the Negro river (Figure 27). However, content of lignin in the organic matter of muds is increased in the direction river–ocean (Figure 28), by average from 2 to 5%. Thus the same trend is traced in bottom sediments as in suspension: accumulation of lignin in the composition of organic matter in the direction river–estuary, testifying to genetic relationship of lignines in bottom sediments and in suspension.

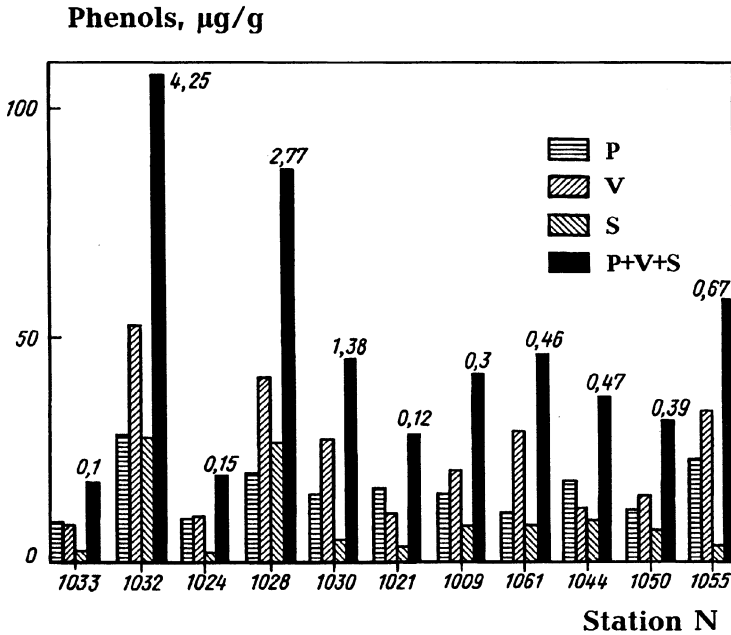


Fig. 27. The content of lignin derivatives (phenols) in bottom sediments of the Amazon river basin and its estuary (see Figure 24).

Higher content of lignin in the organic matter of river sands (compared with muds) is related to the fact that organic matter of sands is, on the whole, more stable, chemically inert and that its composition keeps mainly compounds of lignin type which are resistant to decomposition and mineralization.

2.5.5. CONCLUSIONS

Humic and fulvic acids predominate among organic matter of river waters, being equal to 60–80% of dissolved organic matter. As a rule, the content of fulvic acids exceeds the content of humic acids by an order. The highest content of humic substances is typical for waters of northern rivers of Russia and “black” waters of the Negru river (the Amazon basin). The remainder of river dissolved organic matter is represented by amino acids, carbohydrates and other organic compounds – products of activity of organisms. The content of labile components (amino acids + carbohydrates) in the majority of rivers of the world is equal to 30% of dissolved organic matter and 15% of particulate organic matter.

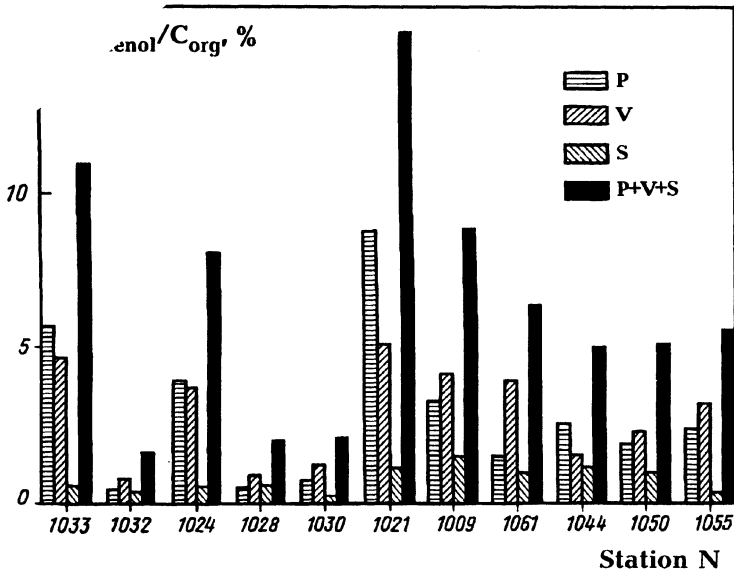


Fig. 28. The content of lignin derivatives (phenols) in bottom sediments organic matter of the Amazon river basin and its estuary (see Figure 24).

For river bottom sediments (the Amazon basin) amino acids amount to 2.4% of organic matter, on average, which is 2–3 times more than the content of amino acids in the modern ocean bottom sediments (Romankevich, 1977).

Summarizing the data of the study of organic matter of soils, suspension and river bottom sediments one should note the following:

1. The nature of organic matter of soils and bottom sediments is different: in soils they are preferably destructured vegetable residues; in bottom sediments they are planktonogenous material (together with residues of higher plants). Consequently, organic matter of river bottom sediments is formed to a considerable extent without noticeable influence of soil organic matter.

2. Composition of river particulate organic matter differs from the composition of organic matter of bottom sediments first of all by a higher content of bitumoids and by the absence of humic acids. Thus one of the main peculiarities of organic matter transformation in the line "river suspension–bottom sediments" is debittuminization, the utilization of bitumoid components in surficial layer of bottom sediments under the effect of bottom fauna and micro-organisms. In this case bitumoids are transformed into non-soluble complexes ("residual" organic matter) and may also form sorptional complexes with humic acids (Romankevich, 1977). Absence of humic acids in suspension does not allow the consideration of suspension as one of the sources of humic acids in river bottom sediments. Consequently, humic acids are formed in river terrigenous muds *in situ*. It

should also be noted that on the surface of river bottom sediments in the Amazon basin we observe the result of actively passing or recently completed process of humification, which is testified by the high content of humic acids in terrigenous muds (especially in muds of the Negro river, Table 21).

Organic matter of North Dvina muds is characterized by considerably lower content of humic acids, approximately by 3 times compared to muds of the Amazon (Table 18). This testifies to the fact that the organic matter humification process in river bottom sediments of northern humid zone passes far less actively than that under conditions of tropical climates. In river muds of the equatorial humid zone, conditions for humification of organic matter are more favourable than at northern latitudes due to the high temperature of water (average 29°C during the whole year) and more intensive (in this connection) activities of micro-organisms and bottom fauna on the transformation of organic matter in the surfacial layer of bottom sediments, leading to organic matter humification.

In spite of the fact that humic acids are mainly formed in the process of diagenetic transformation of organic matter in the surfacial layer of bottom sediments, humic acids of soil genesis may also be buried in bottom sediments. As we know, soil humic acids are transported to river water with rain flow, draining the soil, as well as directly from soils during floods, and they are present in river water in the dissolved form. Under certain conditions, dissolved humic acids may be a source of food for water organisms (Spitzky *et al.*, 1991), and consequently may get into the food chain and participate in the process of biosedimentation, incoming, for example, in the composition of pellet lumps, etc.

3. Independently from the climatic conditions of organic matter formation in both northern and southern humid zones, two types of bottom sediments shall be separated among the river bottom sediments by organic matter composition: terrigenous sands and terrigenous muds. River sands differ from muds by the absence of humic acids, higher content of bitumoids and "residual" organic matter, as well as by the composition of bitumoid A_{cl} (the content of oils is higher in bitumoid A_{cl} of sands). Consequently, it may be supposed that the organic matter of sands has passed the stage of humification and is at the stage of progressing formation of organic matter complexes, resistant to bio- and chemical degradation. Humic acids are evidently completely destroyed under sharply oxidizing conditions of the medium, or were not formed at all. The differences in composition of organic matter of sands and muds are bound up with differences in the "medium of life" of micro-accumulations of organic matter in the surfacial layer of bottom sediments, essentially differing from each other by granulometric composition. It is known that micro-accumulations of organic matter are mainly associated with clay sediments (Romankevich, 1977). The experimental studying of sorption of plankton decomposition products, organic matter of soils and ancient rocks, showed that clay minerals may adsorb 3–4 times more organic matter than they contain (Romankevich, 1977). The predominating part of this organic matter is strongly bound up with clay minerals and is not converted into dissolved form. This connection contributes to conservation of organic matter in case of micro-biological attack at earlier stages of diagenesis. In sands, particles of organic matter are in a free state and not bound with the mineral part of bottom sediments as strongly as in clay muds. As a consequence of this, organic matter particles

in sands are, to a higher extent, subjected to both mechanical destruction, moving under action of bottom streams, turbulent motion of water, etc. and to biodegradation.

4. It was determined that vanillin aldehyde and *p*-oxybenzaldehyde predominate among the products of lignin oxidation both in suspension and in river sediments. The sources of them are sewage of CPP, as well as coniferous trees and grassy vegetation. Content of lignin is increased in the direction of river-ocean (the Amazon estuary) in both suspension and bottom sediments. This fact testifies to the lignin resistance to destruction and to its selective preservation in the organic matter composition.

Chapter 3

GEOCHEMISTRY OF DISSOLVED AND SUSPENDED ORGANIC CARBON IN THE REGION OF RIVER AND SEA WATER INTERMIXTURE

3.1. The Region of Intermixture of River and Sea Waters as an Intermediate Link in the “River–Sea” System

3.1.1. DEFINITION AND SPECIFIC FEATURES

The region of river and sea water intermixture is, by definition, close to “estuary”. The word “estuary” originates from the Latin word “aestus” (tide). It is written in the English explanatory dictionary that an estuary is “a wide mouth of a river where its stream meets a sea and which is subjected to action of tides and ebb tides”. The literature contains various systems of classification of estuaries, depending on the base, chosen by authors, for its creation (Fairbridge, 1980). The most widely spread are two classifications, based respectively on geomorphological and hydrodynamic properties (Pritchard, 1987). The classification based on geomorphological properties subdivides estuaries into: flooded valleys of rivers (for example, Chesapic Bay on the Atlantic cost of U.S.A.), estuaries of fjord type, estuaries limited by banks, estuaries formed as a result of tectonic processes, and estuaries of river deltas (Odum, 1975).

As for the hydrodynamic classification, estuaries are subdivided into three basic types: estuaries with a stable salinity wedge, where the river run-off almost suppresses circulation completely (for example, the Mississippi estuary), estuaries with partial mixing of waters, and estuaries with well-mixed waters and insignificant variation of salinity from the surface to the bottom (Figure 29).

Thus an “estuary” is a wide definition which is traditionally applied to the mouth regions of rivers, inshore bays, tide dams (marsh), limans, in fact to all water areas where the sea water is mixed with fresh water, supplied from the continent. From these positions, the most precise definition of estuary is the definition made by Pritchard (1952, 1967a): “An estuary is a semiclosed inshore body of water, which has free communication with the open sea and inside which sea water is measurably diluted with fresh water, supplied after

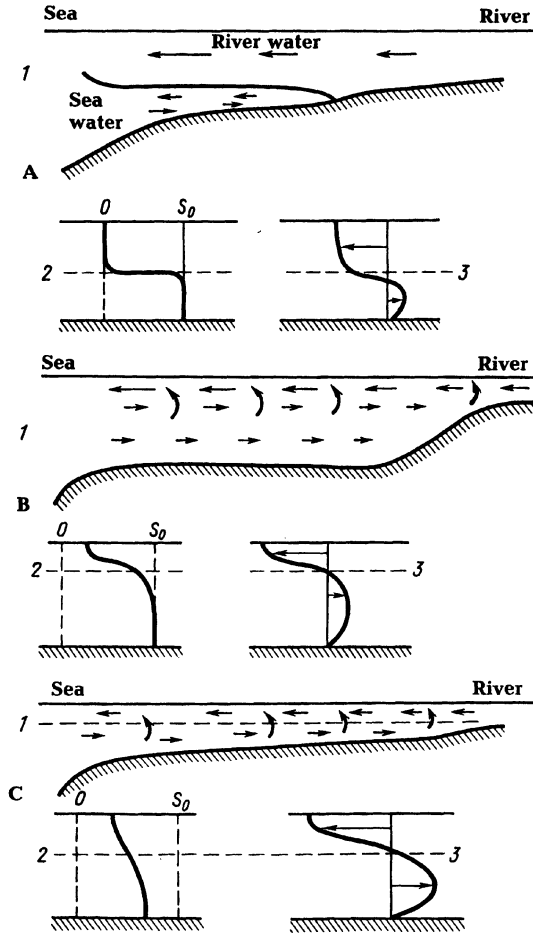


Fig. 29. Types of water circulation in estuaries (Bowden, 1975). 1. Profile through the estuary; 2. salinity; 3. velocity; A-C. types of estuaries (see text).

land surface drainage". Taking this definition as the basis, we shall consider the definition "region of river and sea water intermixture" as a special case of an estuary where sea water is mixed with not the whole body of fresh water, supplied from the land, but river only. In the present work we use both these definitions. However, the term "estuary" we use only in relation to the water areas which are traditionally defined as "estuaries". As it was noted by Odum (1975), estuaries may be considered as "transitive zones, or ecozones between fresh water and sea places of life". It is believed that the important contribution

Table 36. Estuaries of the World Ocean¹ system.

Measured parameter, natural object	Value	Author
Area of the Earth's surface	$510 \times 10^6 \text{ km}^2$	Lisitzin, 1974
Area of the World ocean	$361 \times 10^6 \text{ km}^2$	Lisitzin, 1974
Area of estuaries	$1.7 \times 10^6 \text{ km}^2$	Woodwell <i>et al.</i> , 1973
Volume of the World ocean	1 370 323 thous. km^3	Woodwell <i>et al.</i> , 1973
Volume of river waters	1.2 thous. km^3	Woodwell <i>et al.</i> , 1973
Volume of river run-off into the ocean from land	35 550 km^3/year	Lisitzin, 1974
Total primary production of phytoplankton	$30 \times 10^{15} \text{ gC/year}$	Romankevich, 1977
Net primary production of open ocean	$187 \times 10^{15} \text{ gC/year}$	Woodwell <i>et al.</i> , 1973
Primary production of phytobenthos	$0.1 \times 10^{15} \text{ gC/year}$	Romankevich, 1977
Net primary production of estuaries	$1.4 \times 10^{15} \text{ gC/year}$	Woodwell <i>et al.</i> , 1973

of estuary productivity is made by river run-off. However, this is true only in the case where the river run-off is enriched with biogenic elements. On the whole, rivers do not "fertilize" estuaries. Actually, mouths of rivers are less productive than bays and lagoons which have no large tributaries, but having a well-developed bottom flora.

According to the data obtained by Riley (1967) biogenic substances accumulated and renewed in estuaries are initially supplied from the sea. At the same time, estuaries often produce more than they may utilize. As a result, there is outwelling of biogenic substances and organic detritus into the ocean (Odum, 1975).

The following typical peculiarities of estuaries should be noted:

1. High sedimentation rate, exceeding those for the ocean as a whole by 1000–10 000 times.
2. Estuaries are areas of complex and active chemical processes, where sea water interacts with a large set of micro-elements and organic matter, delivered from huge areas of continental drainage systems. Complex chemical transformations also take place in bottom sediments.
3. Estuaries are subjected to active attack of such hydrodynamic factors as sea waves, tide-like variations of water level, river drainage, density stratification of waters, wind-generated currents, etc.
4. Estuaries occupy an area of 1.7 mln km^2 , which totals less than 0.4% of the ocean surface. However, they deliver more than 5% of net primary production (PP) of the ocean (Table 36). Estuaries have no equal to themselves among the sea localities on the net PP concentration (Table 37). The total vegetable mass of estuaries is equal to $0.63 \times 10^9 \text{ t}$ of organic carbon, which exceeds 1/3 of the total vegetable mass of

¹World Ocean – totality of oceans and seas of the Earth (Stepanov, V.N., *World Ocean. Dynamics and Properties of Waters*, Moscow, Znaniye publ., 1974, 255 pp. [in Russian].

Table 37. Net primary production in various zones of the ocean (McLusky, 1981).

	Open seas	Coast zone	Upwelling regions	Estuaries (and coral reefs)
% of ocean surface	90.0	9.4	0.1	0.5
Net PP, gC/m ² /year	50.0	100.0	300.0	1000.0
Net PP, 10 ⁹ tC/year	16.3	3.6	0.1	2.0

the World Ocean. The density of distribution of vegetable mass of estuaries is 2–3 orders greater than the density of distribution of the vegetable mass of the open ocean.

Estimation of the variety of ocean life conditions and the relative probability of life concentration showed that by this index estuaries exceed all the known ocean localities by many times (Aizatullin *et al.*, 1979). Unfortunately, for the last few years in the majority of the world's regions, estuaries were subjected to such strong action of people that it causes alarm for their future. The main hazard is the supply of various pollutants into estuaries as a result of drainage from continents and due to their supply from the open sea (Anikiev, 1987). "In the presently existing critical situation it is extremely important that the unique properties of estuaries would be understood widely" (Odum, 1975).

The region of intermixture of river and sea waters is at the same time a boundary of separation of river and sea waters in the river–sea system, characterized by scales measured in both tens and hundreds of metres, and sometimes by hundreds of kilometres.

The regions of river and sea water mixture also have their own inner hydrodynamic, physico-chemical and biological processes, characterized by wide variety in time and space. The rhythm of variety of hydrodynamic regime in the river–sea system is predetermined by tides, seasonal variations of river drainage and wind. In the region of the mixture of river and sea waters, the gradients of physico-chemical parameters arise, which are an integral part of the geochemical barrier in the river–sea system. The following parameters are changed as a result of the transition from river water to sea: proportion of components of basic salt composition, ionic force of solution, concentration and composition of suspension, organic matter, etc.

A distinctive peculiarity of estuaries with partially mixed and well-mixed waters is the presence of a so-called "turbidity maximum" or higher concentration of suspension in the bottom layer of waters and its accumulation near the bottom, generally in the middle part of an estuary. This is associated with the character of water circulation in the estuaries of that type. Fresh water drainage forms a current directed to sea in the upper layer of water and the lower layer of the water mass is occupied with sea water, the current of which is directed towards the land. River particles, lowered into this layer are taken by the current directed towards the land and deposited on the surface of estuary bottom sediments (Martin and Gordeev, 1981).

3.1.2. HYDROLOGY AND HYDROCHEMISTRY

Integration of river and sea waters occur in different ways in each estuary, which causes specific peculiarities of hydrological and hydrodynamic regimes of waters. However, there are also properties of the waters' regime formation which are common for regions of river and sea water mixture. The physical and chemical processes in the estuaries are interlinked and it is impossible without serious study of the problems of hydrology and hydrochemistry in these water areas to explain sufficiently the other phenomena (such as biological, physical, geochemical, etc.) since the dynamics of waters is the energetic basis of transportation and interaction of dissolved substances (Semenov, 1969).

However, it would be a mistake to suppose that variations of dissolved substance concentrations in the estuaries are predetermined only by the dynamics of water. Chemical transformations in estuary waters are of great value, due to the extent of the saturation of waters with carbonates, dependent on variations in salinity, mutual chemical adsorption at the "water-suspension" boundary and deposition of the formed aggregates (Alekin and Moricheva, 1959, 1961).

Therefore, the process of intermixture of fresh and sea waters is more complicated than simple mechanical stirring of salts, dissolved in water.

The problem of chemical interaction of river and sea waters is closely bound up with the problems of studying the sedimentation process under conditions of intermixture of river and sea waters.

It was theoretically determined and confirmed by observations that "transformation" of river water into sea water is going on in such a way that the basic qualitative jump is performed within the salinity range of 1–2‰ when river water mineralization is up to 0.25 g/l. In this case it is important that the jump area is determined independently upon the sea water salinity and is the common regularity.

The value of active reaction pH in the regions of sea and river water mixing varies during that process from values typical for river water to higher values in sea water. Since deep salt waters with high values of pH take part in the mixing process, the surface waters of the mixing region are characterized by local extremes, predetermined by dynamic properties.

The river and sea water mixing regions are characterized by transformation of salt composition of continental waters. When mixing river hydrocarbonic water (composition of ions: $\text{HCO}_3 > \text{SO}_4 > \text{Cl}$ and $\text{Ca} > \text{Mg} > \text{Na} + \text{K}$) and sea water (composition of ions: $\text{Cl} + \text{Br} > \text{SO}_4 > \text{HCO}_3$ and $\text{Na} + \text{K} > \text{Mg} > \text{Ca}$) in these regions and especially in large bays and limans, it is possible to trace all the intermediate stages of ionic ratio (Figure 30).

As it is seen, transformation of hydrocarbonate Don river waters into chloride-potassium sea waters generally takes place when the salinity is equal to 1–2‰. Similar variations of ionic composition in the case of the mixture of river and sea waters take place also in other seas (Almazov, 1962, 1967; Pakhomova and Zatuchina, 1966). Therefore, an isohaline of 2‰ is considered the hydrochemical boundary between river and sea water, although transformation of ionic composition of water goes on actively up to 6‰, varying to a lesser extent up to 10‰. Ionic composition of water of higher salinity is practically not changed (Figures 30 and 31).

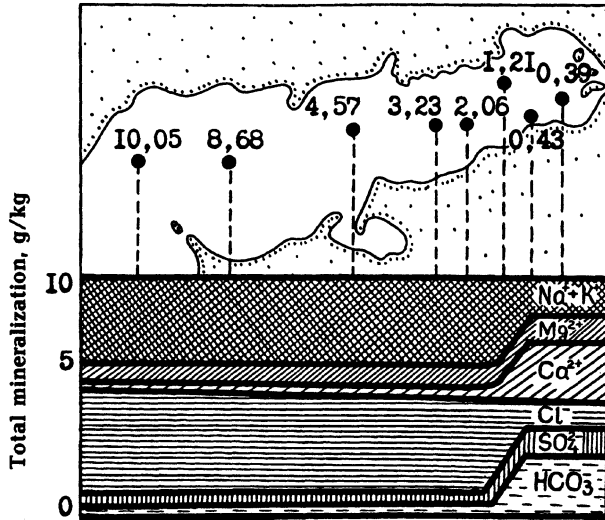


Fig. 30. The change of ion composition of Taganrog Bay water at the mixing of river and sea waters (Tzurikova and Shulgina, 1964).

Hydrochemical parameters are subjected to considerable temporal variations in estuaries, which are associated with variation of the river run-off value, piling up-and-piling down phenomena and the conditional hydrochemical boundary of river and sea water separation may vary its position in space depending upon hydro- and meteorological conditions.

One of the main factors forming hydrochemical and geochemical regimes of river and sea water mixing regions is the river run-off. However, the main role in forming biological, chemical and biogeochemical regimes of water mixing regions belongs to processes of mixing of fresh and salt waters, which actually form the specific natural medium, differing from both river and sea.

In the case of the mixing of river and sea waters, not only salinity is changed but so is the concentration of various ions, especially those which predominate in river or sea water. So, in the case of desalinification of sea water, the relative content of HCO_3^- and calcium ion is sharply decreased (Almazov, 1962). Variation of salinity in the considered region is also influenced by evaporation, atmospheric precipitation and vital activities of water organisms. The vital activity of water organisms, photosynthetic processes in which water plants (phytoplankton, higher water plants) take part, cause an essential effect on the hydrochemical regime of the areas of sea and river water mixing.

Table 38 contains the data for the oxygen content and pH value in the surfacial layer of water of the mouth regions of the northern coast of the Black Sea. In the lower parts of rivers, as well as in the near-mouth shelf where phytoplankton are relatively insufficiently

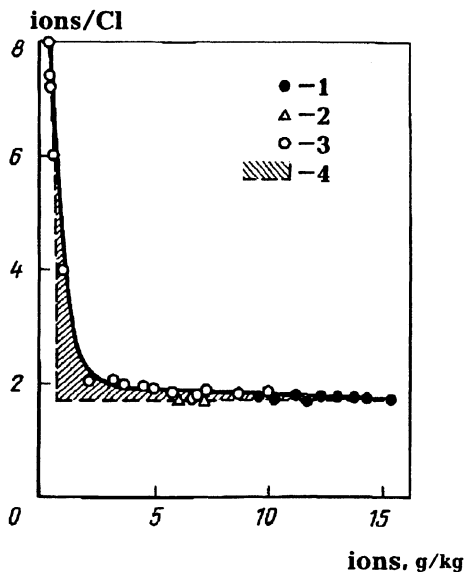


Fig. 31. The interrelation of summary mineralization and its relation to chlorine in the Azov Sea (Tzurikova and Shulgina, 1964). 1. Open sea; 2. near Kuban river waters; 3. Taganrog Bay; 4. the area of river and sea water mixing.

Table 38. Dissolved oxygen and pH in surficial waters of the mouth regions of the northern part of the Black Sea (Almazov, 1962).

Area	Oxygen		pH
	mg/l	%	
Lower part of Danube	7-12	85-95	7.7-8.4
Lower part of Dnestr	6-14	65-95	7.8-8.5
Lower part of Dnieper	6-15	75-105	7.6-8.6
Lower part of South Bug	-	-	7.2-8.3
Dnestrovsky liman	7-17	80-190	8.1-8.9
Dnieper-Bug liman	7-17	80-190	7.6-9.9
North-western part of the Black Sea	4-13	80-105	7.8-8.7

developed, the upper limits of oxygen content in water do not usually exceed 100% saturation and the pH value does not exceed 8.6. In open limans, where phytoplankton are sufficiently developed, the oxygen content reaches 190% of saturation as a result

of photosynthetic processes; dissolved carbonic acid is confined completely and pH is increased to 9.

The effect of river waters on the composition of water, formed as a result of its mixing with sea water drops quickly with dilution. So in the case of 5‰ salinity, when sea water represents only 1/7 of the total volume of water, only 2% of dissolved salts of river genesis and 98% of sea genesis were found (Eisma, 1988).

Usually, concentrations of silicates, compounds of nitrogen and phosphates are higher in river waters than in sea waters. They are supplied into river water from eroded rocks and soils, and nitrogenous compounds are partially supplied from the atmosphere by rain. Side by side with other factors (sun light, water, CO₂, some metals, etc.) these so-called nutrient substances are necessary for the growth of plants. Phosphates and nitrates with CO₂ are required for forming organic matter, silicates for forming skeletons of diatoms, radiolarians, etc. Since the nutrient salts are required for the growth of phytoplankton, behaviour of phosphates and nitrates during estuary mixing is often non-conservative.

Since the rivers make an essential contribution to the delivery of nutrient substances to the sea, river mouths and neighbouring coastal waters are usually the regions with relatively high contents of nutrient substances, which may cause intensive bioproduction. In the majority of estuaries and mouth areas, one may also observe a high content of suspension. The turbidity of waters prevents the penetration of light in the water and controls the growth of phytoplankton.

Under conditions of rapid and turbulent mixing of waters, plankton communities have no time for growth since conditions in the water mass change too quickly. In such regions, populations of algae have a chance to develop at a sufficient distance from the river mouth, where water mixing is very weak. Solely due to these reasons (high turbidity and strong stirring) the PP maximum is often found at some distance out from the river mouth.

3.1.3. PHYSICO-CHEMICAL PROCESSES

Behaviour of dissolved components in the case of mixture of fresh and sea waters may be "conservative" when it is determined exclusively by dilution of waters of low and high salinity with various concentrations of elements; it may be "non-conservative" when the processes of elimination or addition of substances as a result of physico-chemical and/or biological processes are observed (Figure 32).

If some component contained in river or sea water is conservative, i.e. its total concentration is changed only as a result of physical stirring, its total concentration will depend only linearly upon the salinity (or chlorine content). However, if the component is eliminated or added to the water medium as a result of some processes (physical, chemical, biological) there will be a deviation from the theoretical curve of dilution (depending upon the salinity). Thus variation of total concentration of the component as a function of salinity will give a possibility to determine if its behaviour is conservative or not.

Large (more than 1–2 μm) particles supplied to the estuary maintain their dimensions, and their deposition is controlled by hydrodynamic factors. As for particles of smaller sizes and colloids, their behaviour is controlled by the processes causing coagulation and, in some cases, subsequent disaggregation of flocculated material. It was determined that in

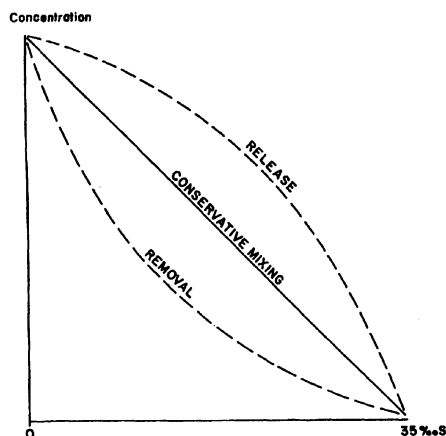


Fig. 32. The scheme of dissolved organic matter behaviour at the mixing of river and sea waters (Eisma, 1988).

fresh water solid particles of 1–2 μm (mainly clays and colloids) are usually characterized by an excessive negative surface charge, as a result of which repulsive forces prevail between these particles. This charge is balanced by a double layer of positive ions; its thickness depends, first of all, upon the ionic force of water, as well as upon the temperature and pH. When a charged particle is supplied to a solution of high ionic force, the double electric layer is compressed and the surface negative charge is neutralized (due to the sorption of cations of the double layer). Decrease of the repulsive barrier between particles create closer contact between them and contributes to the formation of aggregates (Eisma 1981) or new formations of suspended particles; the higher their concentration the more frequent their collisions. Transition to positive charges is met in cases of salinities, typical for early stages of mixing (2–10‰) (Martin *et al.*, 1971).

The process of enlargement of particles in the dispersive systems, with liquid or gaseous dispersive media is called flocculation. The main subject of flocculation is colloid organic matter of river genesis. The process of flocculation is also typical for Fe hydroxides, when they are eliminated from the solution together with organic matter and micro-elements bound up with them (Sholkovitz, 1976, 1978). It was determined that flocculation is the main mechanisms for extraction of dissolved elements during estuary mixing (Sholkovitz *et al.*, 1977, 1978; Sholkovitz and Coplang, 1981). The phenomenon of flocculation of organic matter of river genesis in the presence of sea water was discovered as far back as in the forties (Skopintsev, 1946, 1947), but it was studied in detail only considerably later, and first of all Sholkovitz and his colleagues (1976, 1978, 1980, 1981). Experiments performed by Sholkovitz showed that flocculation takes place in water within the range of salinity from 0 to 15–20‰ and that dissolved organic matter plays the important role in controlling non-conservative behaviour of inorganic components. The study of the

flocculation mechanism showed that flocculation takes place as a result of electrostatic and chemical interactions of the main sea salts with the river colloid humic substances (Eckert and Sholkovitz, 1976; Pempkowiak *et al.*, 1979; Pempkowiak and Kupryazewski, 1980; Pocklington and Pempkowiak, 1983).

The results of laboratory experiments performed by Sholkovitz were later confirmed by both laboratory experiments (Artemyev and Shapiro, 1987) and numerous data obtained in the expeditions. It was shown that organic matter is not only able to pass from the dissolved into the suspended form in the regions of river and sea water mixing (Sholkovitz *et al.*, 1978; Eisma *et al.*, 1978, 1980, 1983; Artemyev *et al.*, 1981, 1984, 1986, 1987) but helps coagulation of inorganic components (Sholkovitz, 1976; Artemyev, 1983; Eisma, 1981; Artemyev *et al.*, 1982; Demina and Artemyev, 1984; Martin *et al.*, 1993). It was also found that some types of planktonic algae are able to form aggregates with clay particles in the presence of electrolytes (Avnimelech *et al.*, 1982).

Obtaining data about this quantity of dissolved organic matter, subjected to flocculation during mixing of river and sea waters, is extremely important for estimating the real deliveries of both dissolved and suspended organic matter from rivers to seas and oceans. Taking the important role of organic matter in the processes of formation of complexes with inorganic components dissolved in water (metals, clay particles), such information is required for the calculation of supplies of all materials with the river run-off into the World Ocean.

Yurkovsky and Rugaine (1986) interpreted the formation of floccules during mixing of river and sea water as "induced by cations coagulation of negatively charged colloids of terrigenous humus, bound up with iron and other elements". Since even small quantities of dissolved organic matter are sufficient for stabilization of iron in solution, and the total mass of iron is equal to no less than 1/3 of the total mass of floccules (Boyle *et al.*, 1974, 1977), relative "losses" of dissolved organic matter due to coagulation in estuaries (as considered by Yurkovsky and Rugaine, 1986) should be relatively low. In accordance with the data of these investigations, about 10% of the total mass of dissolved coloured organic matter flocculate in the Bay of Riga.

In the case of the interaction of dissolved and suspended material during mixing in estuaries, there is adsorption of dissolved material on solid particles: lithogenic minerals, living and detrital material either releasing material into solution from suspended phases by dissolution, desorption or from respiratory biological processes. The balance of sorption and desorption processes in estuaries is still insufficiently studied. The freshly introduced particles, such as clays and iron hydroxides, are able to adsorb many components from solution. In the estuary, in the case of the introduction of particles of river genesis to waters of higher salinity, some material may be released which had been adsorbed at an earlier stage, during weathering and transition processes (Eisma *et al.*, 1991). Unfortunately, at present the information about the scale of sedimentation of material, supplied with river run-off in estuaries, is insufficient.

It is also necessary to solve a number of problems concerning organic matter behaviour in estuaries, associated with processes of flocculation, sorption and desorption of elements and chemical compounds during mixing of waters.

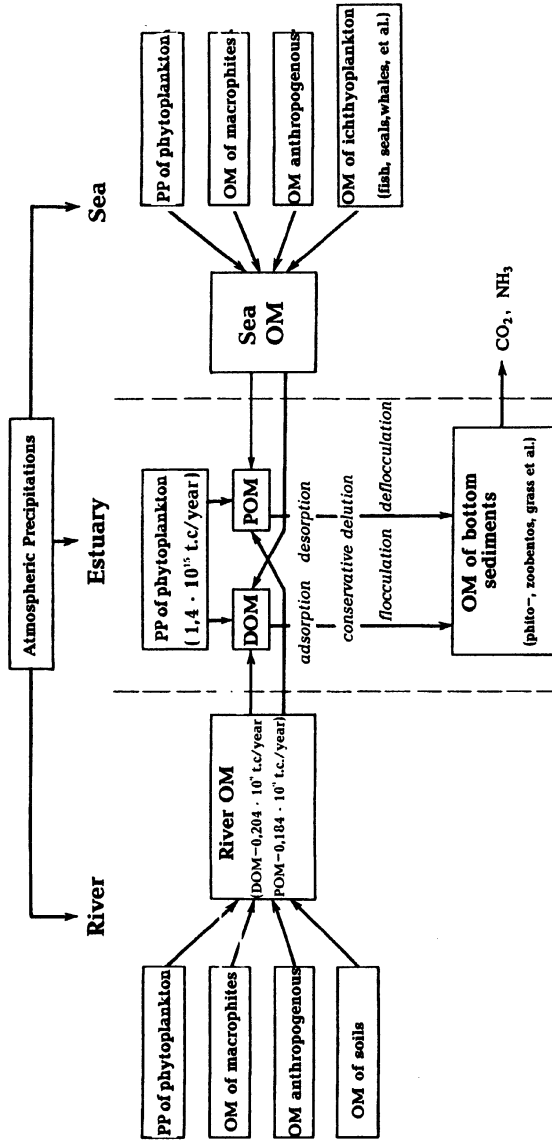


Fig. 33. Paths of organic matter input and transformation in the river-estuary-ocean system (Mantoura, 1986; Laane and Ruardij, 1988; and the author).

Table 39. Primary production of phytoplankton in the estuary at the South-West of the Netherlands (Wolff, 1980).

Salinity, ‰	16	3	fresh water
Potential production	80	20	75 mgC/m ³ /2 hours
Products <i>in situ</i>	175	90	310 mgC/m ² /2 hours

3.1.4. SOURCES OF ORGANIC MATTER, BIOPRODUCTION AND MICRO-ORGANISMS

The basic sources of organic matter and the processes of its transformation in estuaries are shown in Figure 33. Estimation of the contribution from the atmospheric precipitations to the delivery of organic matter into estuaries is unreliable due to an absence of reliable information about the concentration of organic matter in rain (Laane and Ruardij, 1988).

It is practically impossible to measure the flow of organic matter in the section estuary–sea. It can only be supposed that the flow of river organic matter into estuaries will not be the same as the flow of organic matter from the estuary to the sea.

The concentration of organic matter in the estuary is permanently affected by hydrodynamic and hydrometeorological factors (streams, tides, ebb tides, wind), physical, chemical and biological interactions between organic and inorganic material. On the whole, estuaries contain more living organisms than any other region of the sea or ocean (Wolff, 1980). Due to this reason, organisms affect estuary chemistry much more intensively than in other parts of the sea. Many animals (fish, seals, whales, mollusks, etc.) migrate actively between the sea and the neighbouring estuary. Some species of fish spawn in fresh water, and adult individuals live in the estuary or in the sea (anadromous). In contrast to this fact, other individuals of fish spawn in the sea and live in fresh water (catadromous).

The basic ecological groups of photosynthesizing primary producers in estuaries are: phytoplankton, phytobenthos and vascular plants (sea grass). Phytoplankton in estuaries are usually a mixture of phytoplankton from adjacent seas and rivers entering the estuary. Many species of phytoplankton are able to grow and breed in water with a rather wide range of salinity; however, there are optimal typical conditions for normal functioning (Wolff, 1980).

The value of PP in estuaries depends upon the water residence time in them. The longer it is, the more intensive is the development of autochthonous estuary plankton. If there is insufficient residence time of water in the estuary, sea and fresh water plankton die, resulting in low values of PP. Intensive atrophy of phytoplankton in estuaries with a short residence time of water, as expected, is met in intermediate water salinities, which are characterized by low values of PP. These suppositions were confirmed during measurement of PP in one of the estuaries of the Netherlands (Table 39).

Another reason for low PP in salty waters of estuaries may also be due to the high turbidity of water. The factors restraining development and growth of phytoplankton may also include the temperature of the water, shortage of light, biogenic elements, processes

Table 40. Primary production of phytoplankton in estuaries, gC/m²/year (Wolff, 1980).

Estuary	Primary production
Long Island Sound, U.S.A.	380
Cochin Bay, India	124
St. Margaret's Bay, Canada	190
Loch Etive, Scotland	70
Wadden Sea, Netherlands	100–200
Estuary of Ems river, Netherlands	13–55
Estuary of Grevelingen, Netherlands	146–200

of mixing of the waters and interaction of all these factors. In this case, one should bear in mind that various types of phytoplankton require different quantities and proportions of biogenic elements. Nutrient salts, limiting the growth of some types, may be useful for other types. Consumption (eating away) of phytoplankton by zooplankton and zoobenthos may also limit the PP value.

Growth and development of phytoplankton is one of the main biological processes acting on the estuary chemistry. The concentration of CO₂, phosphates, nitrates, ammonia and sometimes silica may be decreased as a result of photosynthesis. At the same time, the content of oxygen increases and often reaches oversaturation. As it was shown by measurements, the value of PP in estuaries varies within the limits of 10–400 gC/m²/year (Table 40).

Phytobenthos forming in estuaries belong to various groups, including unicellular and multicellular plants with lengths of several metres. The data concerning PP of phytobenthos in estuaries is given in Table 41.

Sea grasses (macrophytes) are vascular plants, living under water in inshore waters and estuaries. For example, *Zostera*, *Thalassia* and *Cymodocea* grow at high salinities and *Ruppia* and *Zannichellia* are typical for salty waters. The biomass of sea grass may be very high being up to 2000 gC/m²/year (Figure 34).

Mann (1972), in his review of the productivity of sea grass, indicates values of 58–1500 gC/m²/year. The highest values of sea grass production are typical for tropical and subtropical waters. High values of production make sea grass the main producer of organic matter in some estuaries. So, for example, according to Barsdata *et al.* (1974), 90% of PP in the Aizembeck lagoon (Alaska) is produced by *Zostera* algae. At moderate latitudes, the production is provided by macro-algae such as *Macrocystis*, *Laminaria*, *Fucus* and *Ascophyllum* and sea grasses such as *Spartina*, *Zostera* and *Thalassia*. In tropical estuaries mangroves predominate. Large quantities of dissolved and particulate organic matter are discharged in waters of estuaries as a result of macrophyte vegetation (Sieburth and Jensen, 1970). The quantity of C^D discharged by macro-algae reaches 7–15 gC/m²/day.

Table 41. Primary production of phytobenthos in estuaries gC/m²/year (Wolff, 1980).

Estuary	Primary production
Sapelo Island, U.S.A.	180
Fjords of Denmark	116
Wadden Sea, Denmark	115-173
False Bay, U.S.A.	143-226
Uthan Estuary, Scotland	31
Southern New England, U.S.A.	81
Wadden Sea, Netherlands	101 ± 39
Delaware, U.S.A.	160

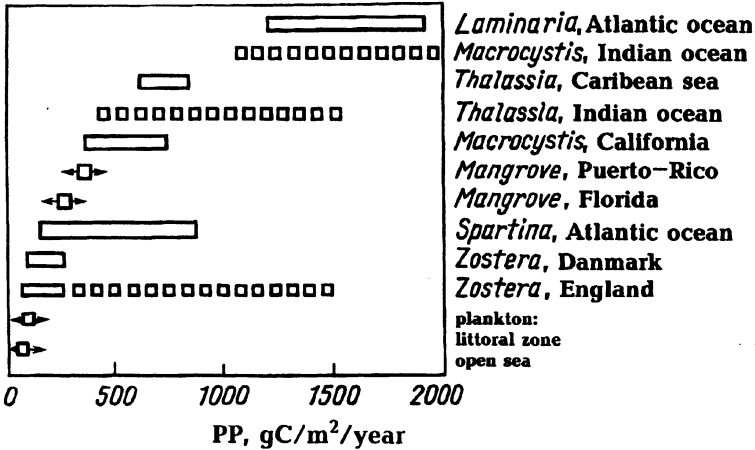


Fig. 34. The production of phytoplankton and basic sea macrophytes in estuaries (Mann, 1972).

As it was shown by various investigations (Wood, 1974), an important role in inshore ecosystems and estuaries in various links of the food chain is played by micro-organisms, which may be the basic consumers of organic matter. The largest quantity of micro-organisms in seas is concentrated in river mouths and regions of river and sea water mixing.

The action of river run-off on the production of micro-organisms is observed at a distance of tens and hundreds of kilometres from river mouths (Zobell, 1946; Lebedeva, 1958; Novozhylova, 1973). The higher content of micro-organisms in waters of mouth regions, estuaries and regions of river and sea water mixing, as well as a great biomass of phyto- and zooplankton in these regions (Aldakimova *et al.*, 1977), are predetermined by

the heavy (rich) supply of mineral and organic substances with river run-off, as well as by good aeration and heating of the water.

Living organisms change the biochemical parameters of estuary medium, discharging into it the products of exchange of substances and various organic compounds, and consuming macro- and micro-elements, leading to a change in the substance composition of the suspension and bottom sediments.

3.1.5. SEDIMENTATION AND SEDIMENT FORMATION

Within the limits of the shore zone and shelf, the region of maximum sedimentation of terrigenous material are the delta and mouth regions. The most intensive rates of present day sedimentation are noted in deltas, and the thickness of sediments of ancient deltas often exceed 10 km (delta of Irravadi river, Bengal delta, etc.): see Chystyakov and Scherbakov (1983). The processes of sedimentation in the regions of river and sea water mixing depend upon the physico-geographical situation existing at the water drainage areas, as well as upon the hydrodynamic regime predetermining directed motion of water masses of various salt composition and salinity. Within the boundaries of avandelta, where the area of river and sea water mixing is usually placed, the sudden decrease of the velocity of river streams causes the accumulation of poorly sorted, mainly terrigenous bottom sediments with a wide size range, from sand to clay mud. The intensity of sedimentation from suspended and traction detrital deposits in deltas and foremouth shelves is extremely non-uniform and is determined by the distribution of solid and liquid run-off along branches, the character of the underwater slope, other morphological peculiarities, and hydrodynamic regime (Chystyakov, 1980).

The basic hydrodynamic parameters, determining the fate of terrigenous material, are stream run-off, waveness, piling up and piling down. The areas of river and sea water mixing are characterized by the large-scale accumulation and processing of the material supplied by river drainage. Lisitzin (1982) referred mouth regions to the first global belt of avalanche-type sedimentation. Avalanche-type sedimentation is the process of very quick accumulation of sedimentary material at the bottoms of reservoirs, which leads to the appearance of new properties of sedimentary formation. Such processes take place in deltas, estuaries, limans and marginal seas which are traps for sedimentary substances (Lisitzin, 1982).

Almost a quarter of a century ago, opinion held that about 80% of river run-off material is deposited in river mouths and on the ocean periphery (Vinogradov, 1967).

Estimating the losses of suspended substances of rivers in deltas, the majority of authors came to the conclusion that more than 50% of river suspension is deposited in river mouths and does not penetrate into seas and oceans (Sokolov, 1980); according to the data presented by Lisitzin it totals up to 92%.

Numerous data on the distribution of suspension in seas and oceans showed that its concentration is at a maximum near the river mouth (Lisitzin, 1982).

The rate of sedimentation in these regions is 1–2 orders higher than that in the pelagic zone and reaches tens of centimetres per thousand years. A very important feature is that in the case of avalanche-like sedimentation, organic matter has no chance to be decomposed

in the water thickness or in the surface layer of bottom sediments. Organic matter of sea genesis is added to terrigenous organic matter near river mouths, that finally causes the noticeable enrichment of deposit with various organic matter.

High rates of sedimentation, leading to quick accumulation of huge masses of material in the regions of river and sea water mixing, results in isostatic sinking of sedimentary formations and an increase in their temperature. Thermobaric transformation of organic matter, thermocatalysis, takes place and at a certain combination of temperature (60–200°C) and depth (more than 1.5 km) oil- (and then gas-) formation is started within the sedimentary column (Vassoevich *et al.*, 1970, 1972; Sokolov, 1980).

The regions of avalanche-like sedimentation in a number of cases become oil-and-gas-bearing zones that warranted significant activity in studying them for the last few years (Lisitzin, 1982).

3.2. Transformation Mechanisms for Dissolved and Suspended Organic Carbon in the Region of River and Sea Water Mixing (the Amazon Estuary – Atlantic Ocean

3.2.1. HYDROLOGY, HYDROCHEMISTRY, OPTICAL CHARACTERISTICS, SUSPENSION AND BIOGENOUS ELEMENTS

Propagation of the Amazon water stream, entering the Atlantic is predetermined mainly by two factors; firstly, by the Guyana current, moving to the north-west over the continental slope and external shelf; secondly, by tides.

According to data from Meade *et al.* (1979), the average current velocity decreases to the north-west from the Amazon mouth, from 1.8 m/sec to 0.4 m/sec at 4°N.

The tidal currents are directed mainly across the shelf, especially in the upper layer. They are most intensive near the mouth, 1.2 m/sec, the velocity of the tidal currents decreasing to the north-west. To study the effect of tide on the changeability of various characteristics in the Amazon estuary, a daily station (Figure 35) was arranged during the period of Russian expedition investigations in 1983 in the Amazon and its estuary (March–April 1983). At that time the tide was syzygeous, the level difference being equal to 3.5 m.

It is clearly illustrated in Figure 36 that during the overwhelming part of time the whole mass of water is occupied by river waters (salinity less than 1‰). Only at moments of maximum water level freshened waters (salinity 6–7‰) arrive from the ocean side, and they exist on the surface for 1.5 hours. Change of salinity proceeds in jumps and the front, differing by colour, salinity and other characteristics, comes at the very end of the water lift from the ocean side.

The maps – diagrams of salinity distribution on the surface for high and low water seasons – are shown in Figure 37. During the high water season, 35‰ isohaline is at a distance of 270 km from the river mouth. During the low water season the area of mixed waters (salinity from 1 to 30‰) moves towards the river for approximately 50 km due to decrease of river run-off, but salt waters do not penetrate into the river mouth. Figure 38 illustrates the distribution of salinity and standard density on the main section river–

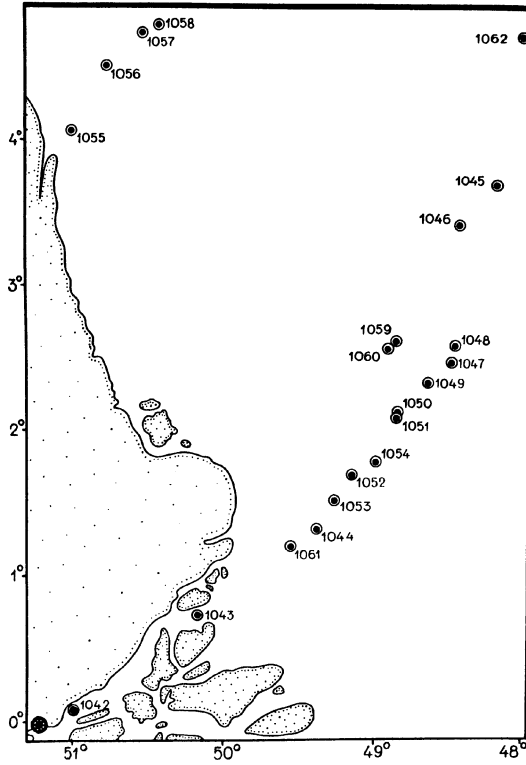


Fig. 35. Sampling stations in the Amazon river estuary (March–April 1983).

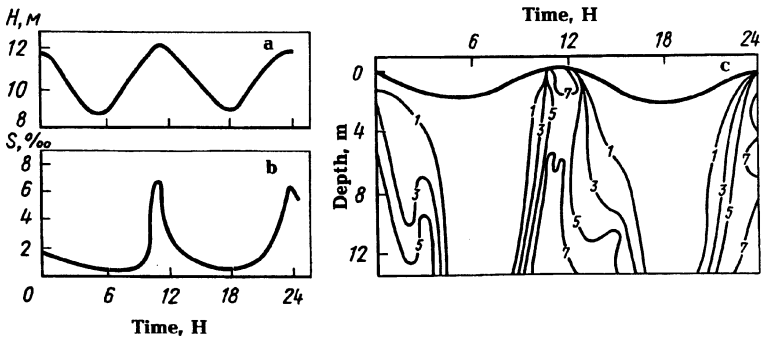


Fig. 36. The daily change of water level and salinity in the surfacial and deep waters at 1044 station (see Figure 35) (Gordeev *et al.*, 1988)

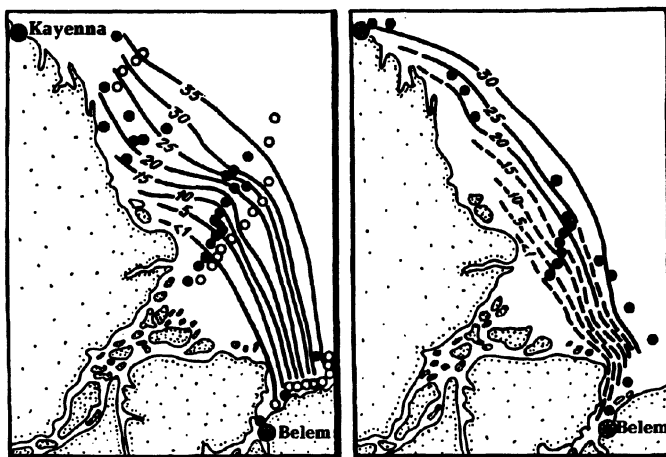


Fig. 37. The distribution of salinity (‰) at the surface of waters in the Amazon river estuary in a high water (left) and low water season (Monin *et al.*, 1986).

ocean in the Amazon estuary during the high water season. Near the mouth, inclination of isohaline is considerably less than those far away from it. In this area we observe intensive turbulent mixing, caused by interaction of river water streams and powerful tidal currents. Here we registered the minimal vertical gradients of salinity and relative density. The maximum values of both vertical and horizontal gradients at the considered section were registered near stations 1049 and 1050 in the medium part of the section. The vertical gradients of salinity and relative density are distributed here almost uniformly through the whole 20 m thickness of water, and amount to approximately 1‰ and 0.8 of relative density unit per 1 m.

Complex processes of water mixing is well illustrated in Figure 39. This process is characterized by alternation of waters which are weakly and strongly saturated with oxygen. Moving from the shore, river waters are incrementally saturated with oxygen, up to 100% at a distance of 250 km from the mouth. The zone of water oversaturated with oxygen (up to 110%), associated with high bioproductivity, is observed in waters with salinities of 15‰.

Horizontal gradients of salinity are insignificantly in the Amazon estuary waters, remote from the mouth, but at the same time vertical gradients (Figure 40) increase sharply. Their maximum values for salinity and relative density are equal to 3‰ and 1 unit of relative density per 1 m.

The temperature of water in the Amazon and neighbouring regions of the Atlantic is equal to $29 \pm 1^\circ\text{C}$. The values of pH in the Amazon mouth are equal to 7.4 and vary within the limits of 7.4–8.2 in the whole area of mixing of river and sea waters.

The Amazon transports 1.2×10^9 t of sedimentary material per year to the Atlantic (Meade *et al.*, 1985)). Distribution of suspension in the surface layer of the Amazon

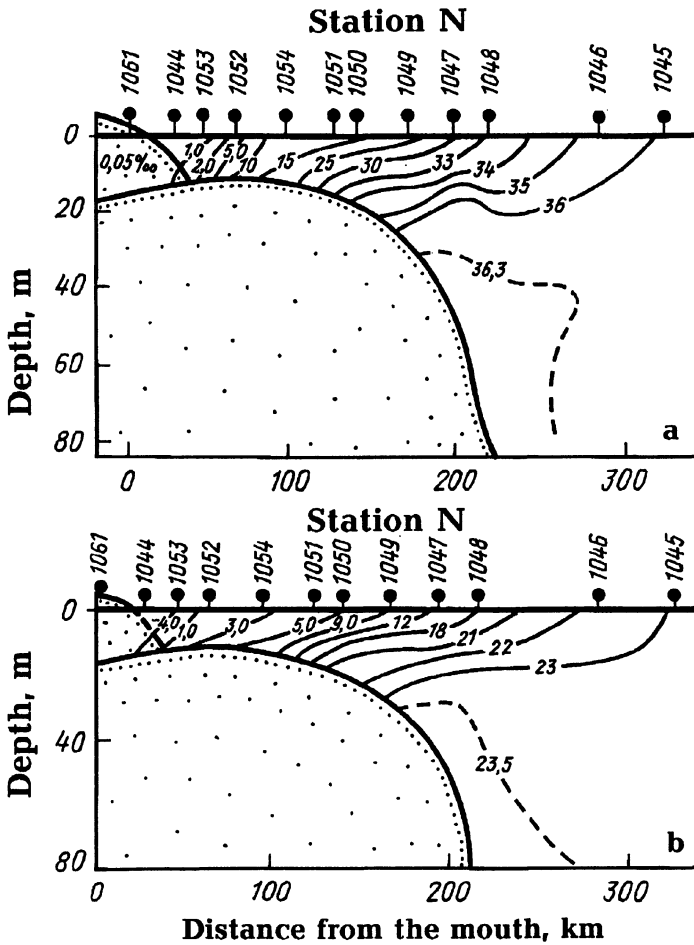


Fig. 38. The distribution of salinity (a) and density (b) at the profile "Amazon river mouth-sea" (see Figure 35) (March–April 1983).

estuary water during the high water period is shown in Figure 41. The principal character of suspension distribution is not changed during the period of low water (Gibbs, 1973). The typical feature of distribution is the elongation of isolines along the shore to the north-west, just like salinity isolines.

In the area of inshore shelf over the near-mouth bar, attention is drawn to the zone of high concentrations of suspension, with values on the water surface equal to 200–400 mg/l and in the bottom layer equal to 1500–4000 mg/l, which far exceeds the concentration of

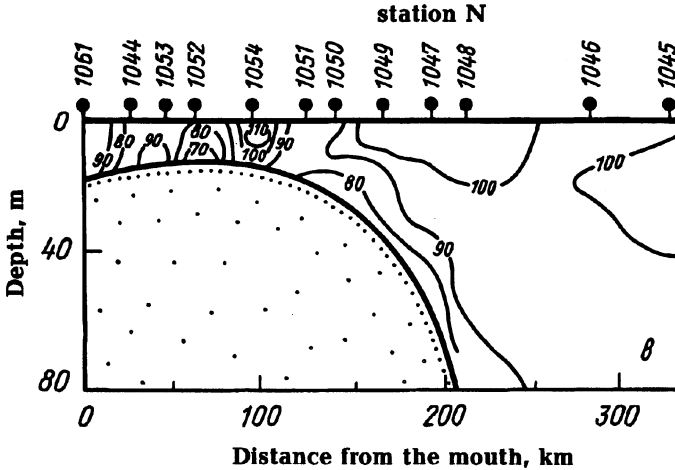


Fig. 39. Vertical distribution of oxygen (%) at the profile "Amazon river mouth-ocean" (March-April 1983).

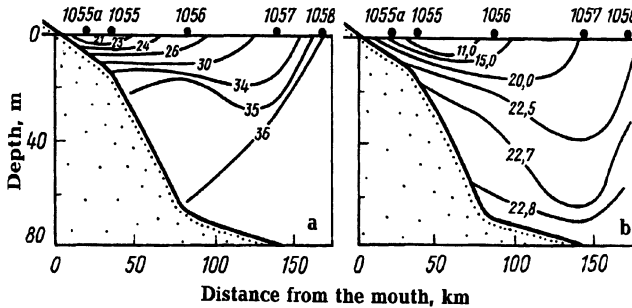


Fig. 40. The distribution of salinity (a) and density (b) at the profile land-ocean in the north-western part of the Amazon river estuary (see Figure 35) (March-April 1983).

suspension in the Amazon moth (110 mg/l). In accordance with optical characteristics, these waters may be characterized as exclusively turbid ones. It may be supposed that the reason for their originating is the rolling of bottom sediments by strong turbulent motions during the interaction of the river water stream and powerful tidal currents.

The processes of rolling bottom sediments are clearly traced on the daily station (1044, Figure 35). Variations of the suspension concentration is surfacial and bottom layers of water due to the variation of the water level during tide/ebb tide cycle are shown in Figure 42. We may see that the concentration of suspension is changed by more than two times on the surface, and by more than an order near the bottom, depending upon the tide phase.

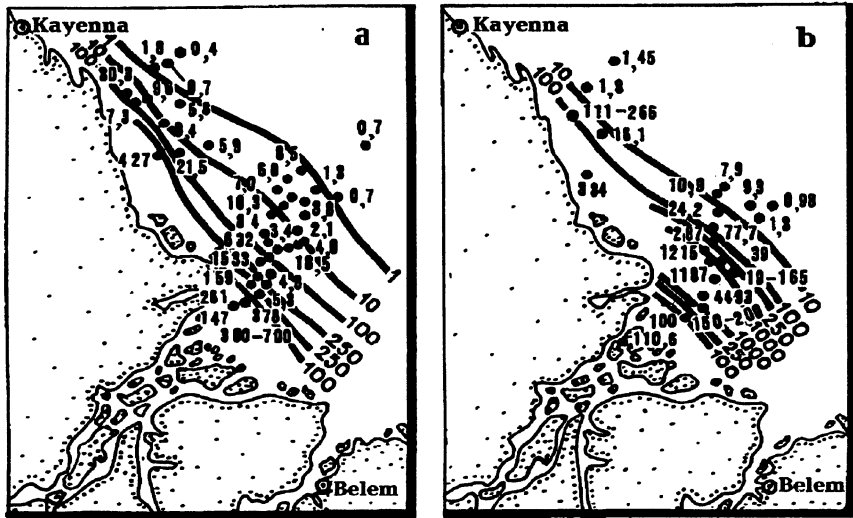


Fig. 41. The distribution of particulate matter (mg/l) in surficial (left) and near-bottom waters in a period of high water in the Amazon estuary (Monin *et al.*, 1986).

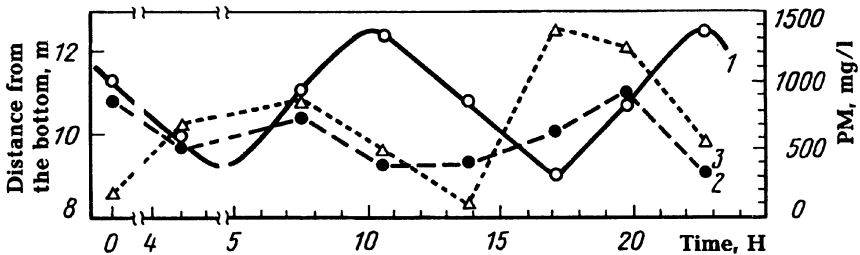


Fig. 42. The daily change of particulate matter concentration in the Amazon estuary. 1. Ocean water level; 2. particulate matter concentration at the surface of water; 3. same at 1 m from bottom surface (Gordeev *et al.*, 1988).

The Amazon estuary waters may be subdivided into four groups by colour (Monin and Kopelevich, 1983): yellow-brown, yellow, green and blue. Yellow-brown waters are located over the inner part of near-mouth bar and are characterized by the maximum values of suspension concentration and optical characteristics. The salinity of these waters does not exceed 1‰. In the case of transition to yellow waters, the salinity is increased stepwise to 5–6‰ and the values of optical characteristics are lower. The boundary between yellow and green waters is a sharp one, its position corresponding to the end of the near-mouth bar and to the beginning of an increase in depth.

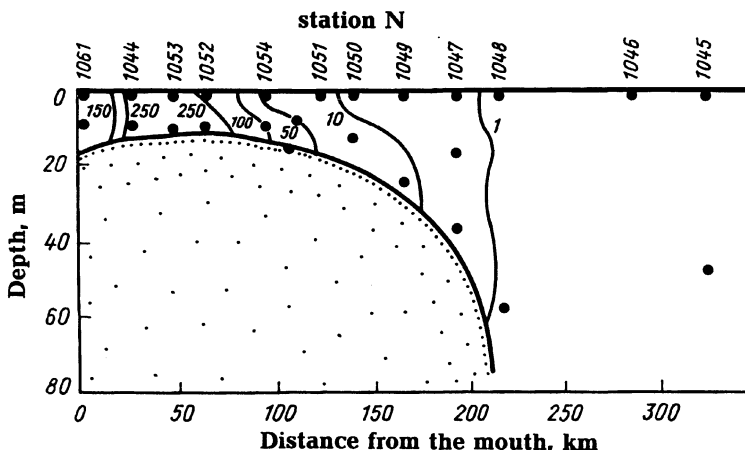


Fig. 43. Vertical distribution of particulate matter (mg/l) at the profile "Amazon river mouth-ocean" (March-April 1983).

It should be noted that we are speaking about the average position of boundaries and zones, which may vary depending upon the tide phase and may move by tens of kilometres. At the boundary between yellow and green waters we observe the next stepwise change of optical characteristics with decreasing values. The green water zones are characterized by the further decreasing of suspension concentration and optical indexes (slackening, dispersion, adsorption). Transition from green to blue waters is a smooth one.

Vertical distribution of the suspension on the section "Amazon mouth-ocean" is shown in Figure 43. Comparing this data with the distribution of salinity (Figure 38), one may note that the concentration of suspension in the surface increases from the values of 100–150 mg/l near the Amazon mouth to 300–700 mg/l in the zone of strong rolling of bottom sediments, and then drops to 5–10 mg/l in waters with a salinity of 10‰. On further increasing of salinity, concentration of suspension is gradually reduced to 1 mg/l and lower. It is also obvious from Figure 43 that the bottom layer of water on the section "Amazon mouth-ocean" is much more turbid than the surfacial one, which is bound up with both rolling the surfacial layers of bottom sediments and with the deposition of suspension from the surfacial layer of waters.

Variations of suspension concentration in the Amazon estuary are, to a considerable extent, bound up with processes of mechanical and mineralogical differentiation of suspended material. The comparison of results of river and ocean water suspension granulometric composition analyses shows that the Amazon suspension corresponds to pelite and aleurite-pelite muds (Table 42).

The granulometric spectrum of oceanic suspension is characterized by the high content of pelite fraction (less than 0.01 mm); content of subcolloid substances (particles less than

Table 42. Granulometric composition of river and ocean suspension in the Amazon basin and estuary (Monin *et al.*, 1986).

Location of stations	Station number	Content of fractions, in %				Granulometric type (by Bezrukov's and Lisitzin's classification)
		> 0.1 mm	0.1–0.05 mm	< 0.01 mm	< 0.001 mm	
Madeira river	1021	0.34	23.90	75.76	15.12	Pelite mud
Madeira river	1022	0.15	25.00	74.85	14.98	Pelite mud
Shingu river	1041-1	0.11	38.29	61.60	7.21	Aleurite-pelite mud
Amazon river near Obidos	1015	2.12	22.38	75.50	20.93	Pelite mud
Amazon river below Santaren	1040	0.35	30.90	68.75	8.61	Aleurite-pelite mud
Zone river–ocean	1044-4	0.10	5.10	94.80	39.20	Pelite mud
Zone river–ocean	1061	1.75	17.38	80.97	13.95	Pelite mud

0.001 mm) is higher than that in river suspension, and the quantity of aleurite particles in it is less than in rivers.

The main part of the suspension consists of clay minerals, kaolinite and montmorillonite prevailing. The share of heavy fractions (sp. gravity exceeding 2.9) is very low. In the Amazon they are represented by amphibole-pyroxene-epidote-zirconium associations; there are also black non-transparent minerals. The quantity of heavy metals is sharply decreased in the Amazon suspension. Such minerals as zircon, epidote, pyroxene, hornblende, garnet, rutile and tourmaline were met in the form of single grains, and the recorded quantities of black ore minerals were more impressive (Monin *et al.*, 1986).

The distribution of nitrates in the Amazon estuary is characterized by the following peculiarities: considerable variations in fresh waters, maximum at a water salinity of 5‰, a sharp drop of concentration in the salinity range of 10–15‰ (as a result of active assimilation by phytoplankton) and comparatively low and non-varying concentrations at salinities of 15‰ and more (Figure 44).

The behaviour of phosphates in the Amazon estuary is in many cases similar to that of nitrates, but it is characterized by a great spread of data on the diagram for their relationship with salinity (Figure 45), as well as a relative enrichment of salt edge waters with phosphates. The balance between dissolved and suspended material showed that almost all phosphorus, evidently, passes into solution in salt wedge waters or on bottom sediment surfaces (Edmond *et al.*, 1981). Suspended phosphorus was found in high concentrations when salinity is about 10‰ and enrichment of the suspension with phosphorus is the greatest compared to other macro-components (Sholkovitz and Price, 1986).

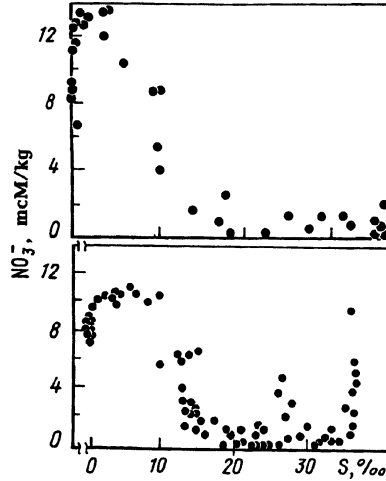


Fig. 44. Dependence of nitrates content from salinity in the Amazon estuary (data of Institute of Oceanology expedition in 1983 and Edmond *et al.*, 1981 (lower)).

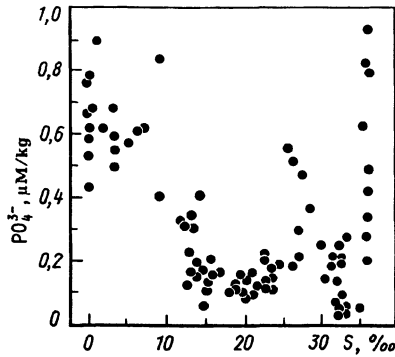


Fig. 45. Dependence of phosphates content on salinity in the Amazon estuary (Edmond *et al.*, 1981).

3.2.2. FACTORS DETERMINING BEHAVIOUR OF C^d AND C^p DEPENDING ON WATER SALINITY

One of the aims of our investigations in the Amazon estuary and neighbouring regions of the Atlantic was to determine the regularities of dissolved and particulate organic matter behaviour as a function of the salinity of the waters. As it was already noted, deviations from simple dilution of river organic matter with oceanic waters may be caused by both physico-chemical and biological processes.

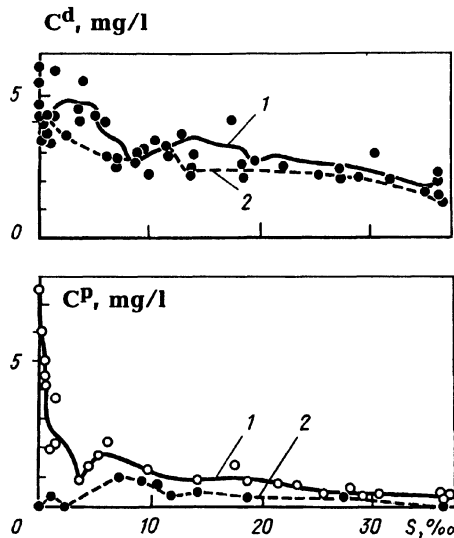


Fig. 46. Dependence of C^d and C^p concentrations on salinity in Amazon estuary (Artemyev and Shapiro, 1987). 1. Field (natural) data; 2. experimental data.

Among the physico-chemical processes, the basic role is played by flocculation of dissolved organic matter, transported by river run-off, in presence of sea water salts; among the biological processes, the production of organic matter by phytoplankton plays the major role.

3.2.2.1. Results of Experimental Mixing of the Amazon and Atlantic Waters

To estimate the role of flocculation in processes of organic matter transformation in the region of the Amazon and the Atlantic water mixture, we performed experiments of mixing river and ocean waters and then comparative analysis of the experimental data and the results of natural observations. The experiment was carried out during the period of the expedition of the 9th voyage of the scientific-and-research ship "Professor Shtokman" using the methods of Sholkovitz (1976).

Natural observations were performed in parallel. The results of the experiment showed that the process of forming of organic floccules proceeds at all stages of the mixing of waters, from slightly salted (less than 1‰) to practically oceanic ones (about 30‰). It is evident from Figure 46 and Table 43, that the most intensive process of floccule formation takes place in the salinity range of 5–10‰. The content of organic carbon in floccules (C^f) varies from 0.0 to 1.0 mg/l and reaches a maximum when the salinity is equal to 7.1‰, being equal to 27.7% of the content of carbon in the mixed water sample. Organic floccules, formed as a result of artificial mixing of river and ocean waters, are equal to

Table 43. Organic carbon in samples for the experiment on mixing of the Amazon and Atlantic waters (Artemyev and Lazareva, 1986).

Ord. No.	River water: :ocean water	S ‰	C ^f mg/l	C ^d _{exp} * mg/l	(C ^f + C ^d _{exp}) mg/l	C ^f , % from the sum (C ^f + C ^d _{exp})
1	river water	0.01	0.0	4.2	4.2	0.0
2	40:1	0.90	0.2	4.2	4.4	4.7
3	15:1	2.40	0.0	3.5	3.5	0.0
4	4:1	7.10	1.0	2.6	3.6	27.7
5	3:1	8.90	0.8	2.8	3.6	22.2
6	2:1	11.70	0.4	3.1	3.5	11.4
7	1.7:1	14.00	0.5	2.3	2.8	17.8
8	1:1	18.60	0.3	2.2	2.5	12.0
9	1:3	27.50	0.3	2.2	2.5	12.0
10	ocean water	36.40	0.0	1.2	1.2	
Average			0.3	2.8	3.2	10.8

*C^f = organic carbon in floccules;

C^f_{exp} = organic carbon in sample of mixed water after the filtration of floccules.

Table 44. Variations of concentrations of dissolved organic carbon (C^d), "stable" C^d (C^d_{st}), "labile" C^d (C^d_l) and humic acids carbon (C_{HA}) in the case of mixing of the Visla river and the Baltic Sea waters (Pempkowiak, 1985).

Object of research	Salinity ‰	C ^d		C ^d _{st}		C ^d _l		C _{HA}	
		mg/l	%	mg/l	%	mg/l	%	mg/l	%
River water		8.6	100	6.1	100	2.5	100	3.8	100
River + sea water	3	—	—	—	—	2.6	104	3.5	92
River + sea water	5	7.4	86	5.0	82	2.4	96	3.0	80
River + sea water	7	—	—	—	—	2.3	91	2.5	66
River + sea water	9	6.6	77	4.2	70	2.2	88	2.3	60

0.0–27.7%, average 10.8%, of the total content of organic carbon in the sample. Since the experiment data correlates satisfactory with the results of natural observations (coefficient of correlation is 0.7–0.8) one may prove that the process of floccule formation takes place not only in the case of artificial mixture between fresh and salt waters, but also under natural conditions.

Our experimental data on the mixture of waters of the Amazon and the Atlantic correlate well with the results of the experiment on mixing waters of the Visla river and the Baltic Sea (Table 44), where it was shown that more than 20% of C^d of mixed water

and sea waters are transformed into C^p (basically into humic substances). Labile organic matter and “non-humic” organic matter, resistant to decomposition and mineralization, flocculate in small quantities, 12 and 7% respectively (Pempkowiak, 1985).

3.2.2.2. Peculiarities of C^d and C^p Behaviour under Natural Conditions and “Losses” of River Organic Matter in the Estuary

To estimate the reliability of the character of C^d and C^p behaviour in the case of mixing of river and sea waters (“conservative”, “non-conservative”) the data, obtained during natural observations, was subjected to “smoothing” by means of the method of “moving average” by 3 and 5 points (Artemyev and Shapiro, 1987). It is obvious from Figure 46 that the resulting curve of C^d distribution against salinity in the studied waters does not correspond to the line of simple dilution, the equation of which, obtained by the method of least squares, has the form $C^d = 4.46 - 0.078S$.

To prove the significance of deviations, we performed statistic estimations of zero-hypothesis about the fact that natural data lie on the straight line of sample dilution. Calculations, performed by the method of Livovsky (1982), showed that the hypothesis on simple dilution may be rejected with 95% confidence probability. Thus, ideas of “conservative” behaviour of dissolved organic matter in the regions of river and sea water mixture (Sholkovitz, 1978; Fox, 1983; Mantoura, 1986; Mantoura and Woodward, 1983; Michaelis *et al.*, 1986) are not confirmed. In addition, the analysis of actual data, included in the above-mentioned papers, does not permit us to agree with the authors’ conclusions completely, due to a whole number of reasons (unequal study of river–sea sections, absence of definitions of C^p parallel to those for C^d , insufficient sampling for reliable interpretation of the obtained data, quantity of taken samples of water on sections, etc.). As it was shown by our investigations, as well as by the data obtained by a number of foreign researchers, conservative behaviour of dissolved organic matter in estuaries may take place, but this, more likely, is an exception, and not a rule. Content of C^d and C^p as the distance from the Amazon mouth to the ocean generally decreases on average from 5.0 to 2.0 mg/l and from 6.7 to 0.4 mg/l respectively (Figure 46).

At the initial stage of mixing of waters (within the range of salinity of less than 1‰ to 12‰) higher and lower concentrations of C^d and C^p alternate. In this case, as a rule, an increase of C^d concentration is accompanied by a C^p concentration decrease, and *vice versa*. To quantitatively estimate the observed fluctuations in organic matter behaviour at different stages of water mixing and to clarify their nature, we performed calculations of “losses” and “new formations”² of dissolved and particulate organic matter under natural conditions, and compared the obtained data with the results of laboratory experiments.

Existing individual data on calculations of “losses” of dissolved substances, transported by river run-off to the ocean are based on the one-dimensional model (Boyle *et al.*, 1974; Officer, 1979), suitable for the estuary, in which diffusion flow of substances is considered to be directed by axial currents. Such a model is unlikely for the Amazon estuary waters

²Conventional terms, actually meaning transition of organic matter from one form into another one under the action of physical, chemical and biological processes [V.A.].

Table 45. Integral losses of dissolved (C^d) and particulate (C^p) organic carbon in the region of mixing waters of the Amazon and the ocean, depending upon their salinity.

Ord. No.	S, ‰	Zone	"Losses", % from river DOM	S, ‰	Zone	"Losses", % from river POM
1	0.05		8	0.05		10
2	0.12		1	0.12		0
3	0.37	I	18	0.35	I	17
4	0.62		25	0.52		31
5	0.90		21	0.70		46
6	1.38		10	0.93		54
7	2.18	II	4	1.39		61
8	2.92		0	2.18	II	68
9	3.77		0	2.92		71
10	4.48		2	3.77		78
11	5.11		5	4.48		77
12	6.05	III	16	5.47	III	73
13	7.38		27	7.09		73
14	8.58		36	8.99		75
15	10.04		34	11.59	IV	79
16	11.40		30	14.14		79
17	12.88	IV	21	19.03		75
18	14.88		12	19.03		75
19	16.68		16	21.10	V	78
20	12.50		18	23.34		82
21	20.17	V	23	25.52		83
22	21.74		21			
23	23.65		23			
24	25.59		25			

I-V see Figure 47.

as Guyana Current results in an "elongation" of the mixed water plume along the shore (Gibbs, 1970) and, consequently, the transverse diffusion intensity will considerably exceed that of the longitudinal one.

We proposed the stationary quasi-one-dimensional model, taking into account the advective streams, and streams predetermined by turbulent diffusion transversed to the current (Artemyev and Shapiro, 1987).

Integral "losses" of river dissolved and particulate organic matter depending upon the salinity are shown in Table 45 and in Figure 47. Figure 48 contains "differential losses" of organic matter. It is obvious that "losses" for dissolved and particulate organic matter (positive values Q) alternate with the "new formation" of organic matter.

Depending upon the direction of these processes, five zones may be separated in the area of the Amazon and the ocean water mixing. The first zone (waters with salinity of

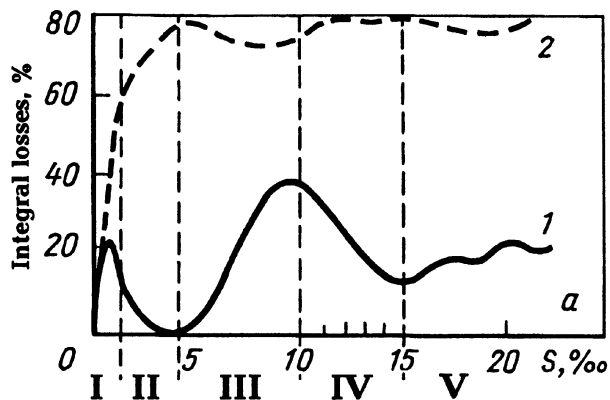


Fig. 47. Integral “losses” of river organic matter (1) and particulate organic matter (2) in a process of mixing of Amazon river and ocean waters (Artemyev and Shapiro, 1987).

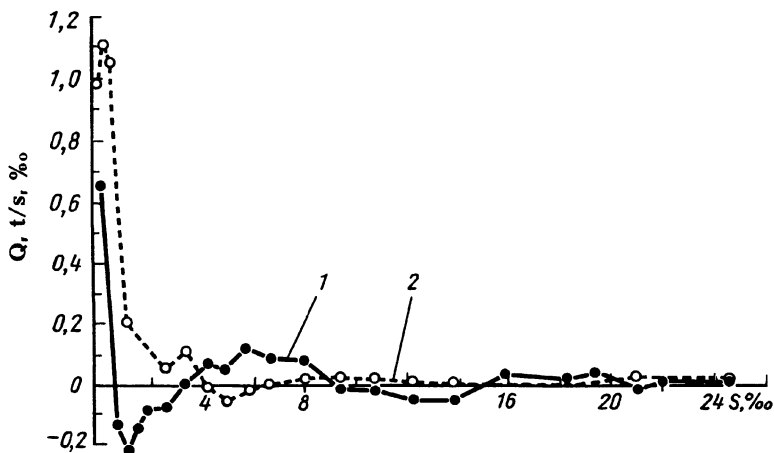


Fig. 48. The intensity of differential “losses” of dissolved organic matter (1) and particulate organic matter (2) in the Amazon estuary (Artemyev and Shapiro, 1987).

0.01–1‰) is characterized by “losses” of both dissolved and particulate organic matter (as a result of transformation into suspended form in processes of flocculation, deposition on the bottom, etc.) reaching respectively 25% (first maximum of dissolved organic matter “losses”) and 54% from the initial river organic matter.³

³Here and subsequently the quantity of relative losses (%) calculated following Boyle *et al.* (1979) is shown.

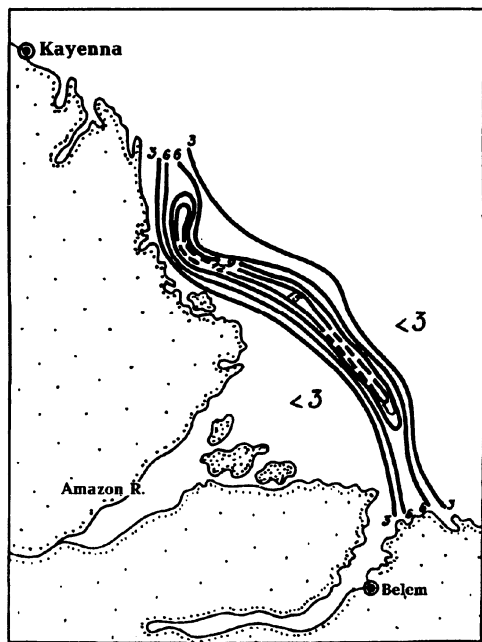


Fig. 49. The distribution of chlorophyll (mg/m^3) at the surface of Amazon estuary waters in a season of high water (Monin *et al.*, 1986).

The second zone (waters with salinity of 1–4‰) is characterized by “new formations” of dissolved organic matter (“losses” decrease to zero) also in this case “losses” of particulate organic matter are still increasing to 78% in waters with salinity of 4‰. The main source of dissolved organic matter in this zone is, evidently, organic matter supplied from suspension during desorption. Additional sources of organic matter for dissolved and particulate organic matter in the waters, studied by us, might be the primary production of phytoplankton. However, as it was shown by optical studies carried out during our expedition (Monin and Kopelevich, 1983), the favourable conditions for development of phytoplankton in the Amazon estuary are created in transparent (“green”) waters with salinities exceeding 15‰, where the maximum of chlorophyll “a” consumption was determined (Figure 49).

In the third zone, from 4 to 10‰, “losses” of dissolved organic matter increase again (to 36%), but at the same time losses of particulate organic matter decrease. As it was shown by comparing the data of natural observations and experiments, one of the sources of particulate organic matter in this case is the flocculation of dissolved organic matter. As is obvious, the process of forming organic floccules proceeds at all stages of mixing, from

slightly saline to oceanic waters, but it proceeds most intensively in waters with salinities of 7–8‰.

Since the data of the experiment correlate satisfactory with the results of natural observations, it is possible to prove that the process of forming of floccules takes place not only in the case of artificial mixing between fresh and salt waters, but also under natural conditions.

Suspended organic particles, formed as a result of flocculation, may total up to 60% of particulate organic matter. It is obvious from Figure 47 that “losses” of dissolved organic matter in the third zone are not completely compensated by new formation of particulate organic matter. Evidently, part of the suspended particles formed as a result of flocculation are lowered to the bottom and buried in bottom sediments.

In the fourth zone (waters with salinity from 10–15‰) we observed again an increase of dissolved and a decrease of particulate organic matter, probably as a result of desorption processes. Finally, in the fifth zone (water salinity exceeding 15‰) the processes of transformation of organic matter are practically completely levelled.

Calculations of losses of river organic matter in the area of mixing of the Amazon and the Atlantic waters show that 75% of river dissolved organic matter and 20% of particulate organic matter are finally supplied to the ocean.

3.2.2.3. Primary Production

As it is known, biological productivity of waters is predetermined mainly by two factors: supply of solar radiation, required for photosynthesis and the presence of biogenous elements (nutrient substances) in the photic layer. The quantity of solar energy, supplied to the water surface in the tropical belt, is sufficiently high but penetration of this energy into water depth depends upon the quality and the quantity of substances contained in it and on their hydro-optical characteristics (Kopelevich, 1983).

As it was noted above, yellow-brown and yellow waters of the Amazon estuary (with salinities up to 12‰) are characterized by higher turbidity due to great supply of river suspension and the rolling of the surface layer of bottom sediments by strong turbulent waters. In the zone of green waters, removed from the river mouth by more than 100 km the concentration of suspension is essentially decreased, the water transparency is increased, which creates favourable conditions for the development of phytoplankton. Existence (in the Amazon estuary) of waters with high productivity of phytoplankton but removed considerably from the river mouth, was noted in earlier literature (Edmond *et al.*, 1981). According to the data, obtained by the French expedition on the research vessel “Calypso” (May, 1983) the highest concentration of chlorophyll (more than 20 mg/m³) was found in transparent (green) waters of the estuary with salinity of 10–12‰ (Figure 50), when the values of the index of vertical weakening of light are sharply decreased and water becomes acceptable for penetration of sun light. Intensive blooming of algae in the Amazon estuary at salinities of about 10‰ was also noted by Cai *et al.* (1983). The presence of phytoplankton in the same waters was also found by using the spectra of light adsorption, the appearance of maximum of consumption of chlorophyll “a” at 675–678 nm

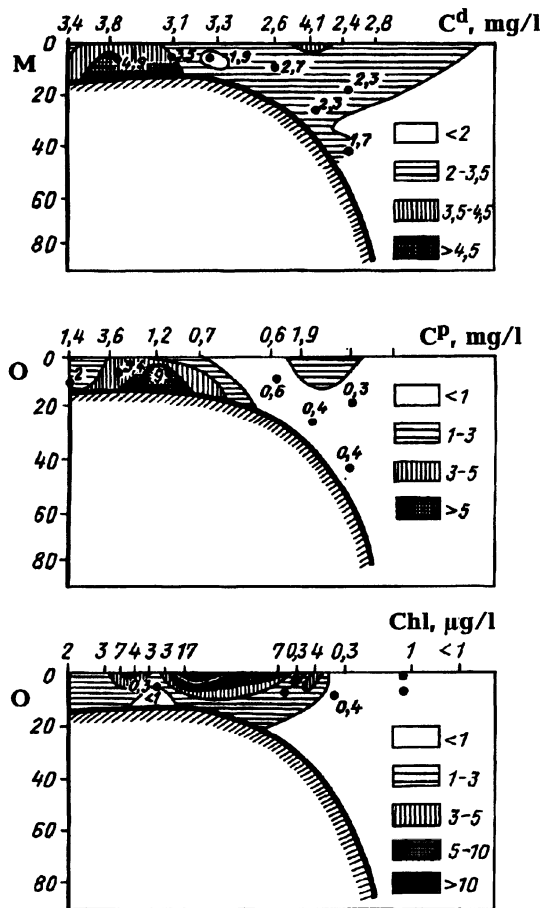


Fig. 50. Vertical distribution of C^d , C^p and chlorophyll at the profile "Amazon river mouth-river" (Monin *et al.*, 1986).

(Monin and Kopelevich, 1983). Evidently, the high content of C^d in "green" waters of the Amazon estuary is bound up with development of phytoplankton (Figure 46).

Thus, the favourable conditions for the development of phytoplankton in the estuary of one of the largest rivers of the world, i.e. the Amazon, are possible only at a considerable distance from the river mouth. Near the river mouth under conditions of quick and intensive mixing of waters, plankton communities have no time for growth and therefore are forced to breed only far away from the river mouth, where mixing of waters decreases (Eisma, 1988).

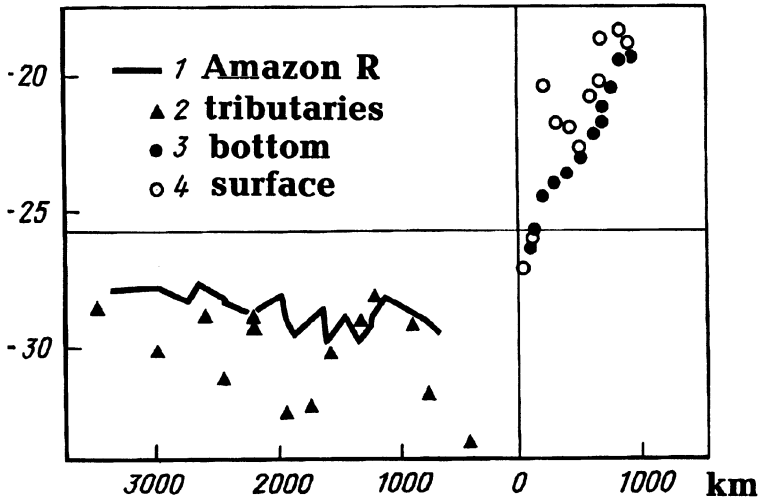


Fig. 51. Change of $\delta^{13}C^P$ in Amazon river basin waters and its estuary (Cai *et al.*, 1988).

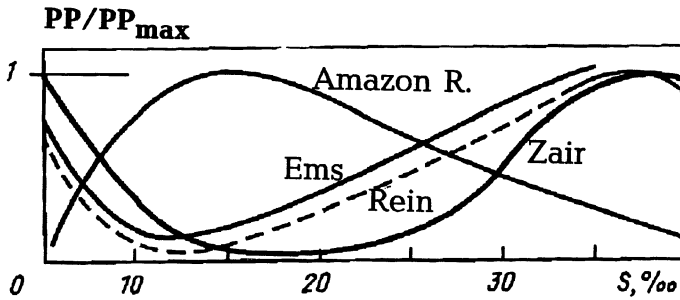


Fig. 52. Dependence of the relation PP/PP_{max} on salinity in estuaries (Eisma, 1988; Cadee, 1982).

Figure 51 illustrates the variation of $\delta^{13}C$ for C^P from the main bed and tributaries of the Amazon, where these values average 29.3‰, to the Amazon estuary where the values $\delta^{13}C$ increase to 18‰ which is typical for sea plankton. The estuarine waters which are most favourable for the development of phytoplanktonic organisms may be located at varying distances from the river mouth. In this case, the determining factor is the transparency of waters, their accessibility for penetration of sun light, but not high concentrations of biogenous elements (Eisma, 1988). As it is obvious from Figure 52, high values of primary production may be met in both the medium part of the estuary (the Amazon) and at its periphery (Zaire river) and outside its boundaries (Ems river, Rhine river).

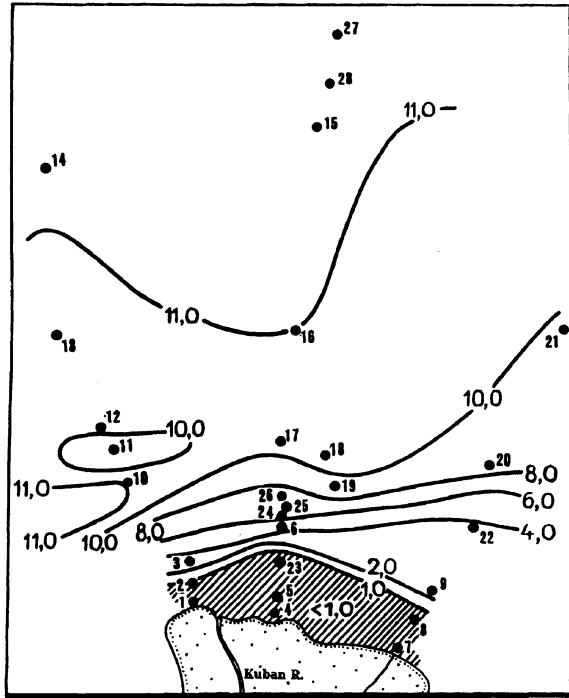


Fig. 53. Sampling stations and salinity in the area of Kuban river and sea waters mixing (April–May 1979) (Artemyev *et al.*, 1982).

3.2.3. CONCLUSIONS

The results of experiments in the mixing of the Amazon and ocean waters and data of natural observations in the Amazon estuary showed that the process of dissolved and particulate organic matter formation as a result of flocculation is present at all stages of water mixing, but most actively in waters with salinities of 5–10‰.

Calculations showed that C^d behaviour in the studied waters depending upon the salinity does not correspond to the line of sample dilution, and is of a “non-conservative” character as a result of its transformation into the suspended form and back into dissolved one at various stages of river and ocean water mixing the under effect of physico-chemical processes (flocculation, adsorption-desorption).

By means of the model worked out by us we made an estimation of “losses” of river organic matter in the case of mixing of river and ocean waters: for dissolved organic matter 25% and for particulate organic matter 80%.

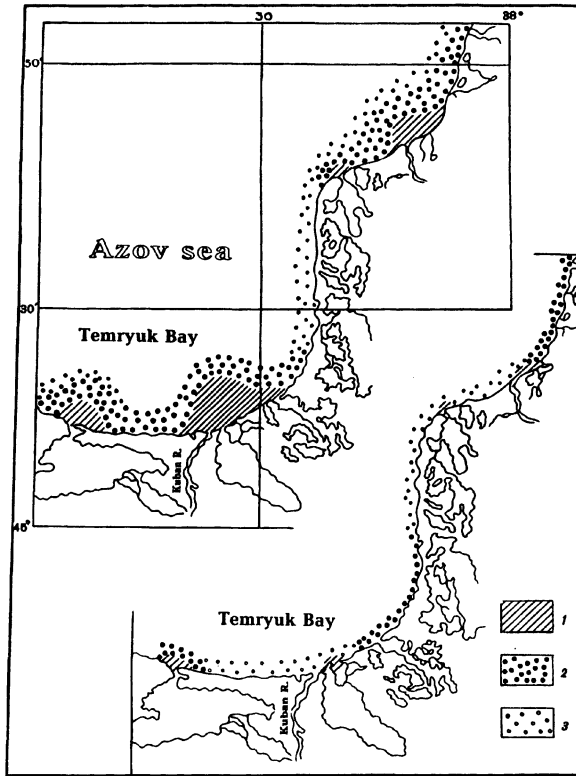


Fig. 54. Distribution of particulate matter at the area of Kuban river and sea waters mixing under south-eastern (up) and north-western (down) winds (Shulgina, 1955). 1. River water; 2. mixed river and sea water; 3. sea water.

Comparative consideration of factors, determining organic matter behaviour in the Amazon estuary, showed that physico-chemical processes (flocculation, adsorption-desorption) are, primarily responsible for variation of dissolved and particulate organic matter ratio at the initial stages of water mixing, in waters with salinity of up to 10‰. The effect of biological processes and mainly primary production of organic matter by organisms of phytoplankton on variation of concentrations and transformation of organic matter in the Amazon estuary is actively revealed only at a considerable distance from the river mouth in transparent waters, accessible for light penetration.

The area of the Amazon and the ocean water mixing is separated in the various zones, corresponding to stages of water mixing and characterized by various intensity and direc-

tivity of transformation processes of forms (dissolved, suspended) and the composition of organic matter.

3.3. Behaviour of Organic Matter, Micro-Elements and Primary Production at Various Stages of Water Mixing (Temryuk Bay, Azov Sea)

3.3.1. BIOGENIC ELEMENTS, PRIMARY PRODUCTION AND SUSPENSION

During our investigations in the Temryuk Bay in the region of mixing of the Kuban river and sea waters (Artemyev *et al.*, 1982) we observed clear change from fresh (less than 1‰), to mixed (1–11‰) and salt waters (11‰ and more) on the surface of the water area studied (Figure 53). Such a distribution of salinity in the surface water (Figure 54) of the studied region was observed in the case of south and south-eastern winds. In this case waters of the Kuban river are moved towards the bay for 1–2 km (Figures 53 and 54).

The distribution of nitrates and phosphates in the studied area, dependent upon the salinity, is characterized by the decrease of their content by passage from river to sea waters (from 50 to 5 mg/l). High concentrations of nutrient salts in the Kuban mouth might stimulate active growth of organic matter by organisms such as phytoplankton as was observed in the Temryuk Bay (see next section). But the activity of phytoplankton in the Temryuk Bay at the early stages of mixing of river and sea waters (as in the Amazon estuary) is prevented by the water turbidity (Figures 55 and 56). Due to this fact the primary production value does not reach high values here, but shows maximum values in the middle part of the river and sea water mixing area, when the water salinity is equal to 7‰. Concentration of suspension in these waters is essentially lower by a factor of three in comparison to the near-mouth region when the waters become more transparent and accessible for penetration of sun light.

The value of primary production decreases noticeably with an increase of the distance from the shore, which may be caused by the deficit of nutrient salts, but as the boundary with sea waters this value sharply increases. The increase of phytoplankton primary production at the boundary of river and sea waters is related to the mass development of phytoplankton, observed in the region of hydrofronts. In the same boundary waters an increase of “production” of bacteria was discovered (Ivanov, 1967).

Content of suspension in waters studied change from 11 to 66 mg/l and averages 27 mg/l, decreasing towards river mouth–sea. The leading factor of terrigenous material sedimentation at the premouth shelf of the Kuban river is the wind regime. The quantity and propagation area of suspended material of the river depend upon the intensity and direction of wind (Figure 54). A considerable part of suspension (about 60%) is deposited in the mouth area of the Kuban (Table 46), 10–20% of terrigenous pelite material being deposited as a result of coagulation (Simonov, 1969).

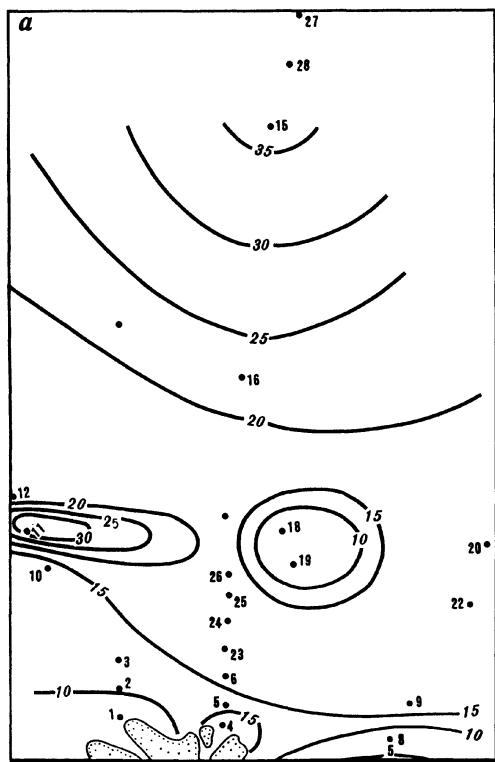


Fig. 55. Distribution of primary production (mgC/l/day) in the area of Kuban river and sea waters mixing (April-May 1979).

Table 46. Sedimentation of terrigenous material fractions (mln t) into delta and in the coastal waters near Kuban R. (Khrustalev, 1989).

Fraction, mm	Supply of suspended and traction material (1936-1972)	Sedimentation of terrigenous material		Flux into sea
		Delta	Beach	
Less than 0.01	3.95	1.23	0.71	2.01
0.01-0.05	1.68	0.50	0.59	0.59
0.05-0.25	0.91	0.22	0.69	0.00
More than 0.25	0.19	0.08	0.11	0.00
Total	6.73	2.03	2.10	2.60

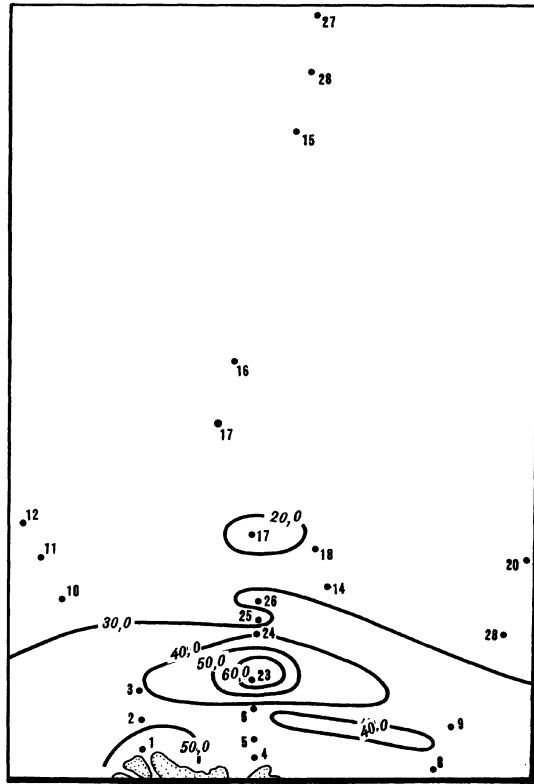


Fig. 56. Distribution of particulate matter in the area of Kuban river and sea waters mixing (mg/l) (April–May 1979).

3.3.2. RELATIONSHIP BETWEEN C^p , MICRO-ELEMENTS AND PRIMARY PRODUCTION

Content of organic matter in the area of mixing of the Kuban river and Temryuk Bay waters varies from 0.23 to 1.62 mg/l and averages 0.74 mg/l. The share of particulate organic matter in suspension is equal to 1.6–10.7%, average 4.9%, i.e. suspension is represented mainly by mineral components. Distribution of organic matter depending upon the salinity is characterized by three maxima: a near-mouth maximum, a maximum in the central part of the river and sea water mixing region, and a maximum at the boundary with sea waters.

As it is obvious from Figures 55 and 57, distribution of C^p and primary production is similar, which indicates the determining contribution of phytoplankton to the delivery of particulate organic matter to the studied waters.

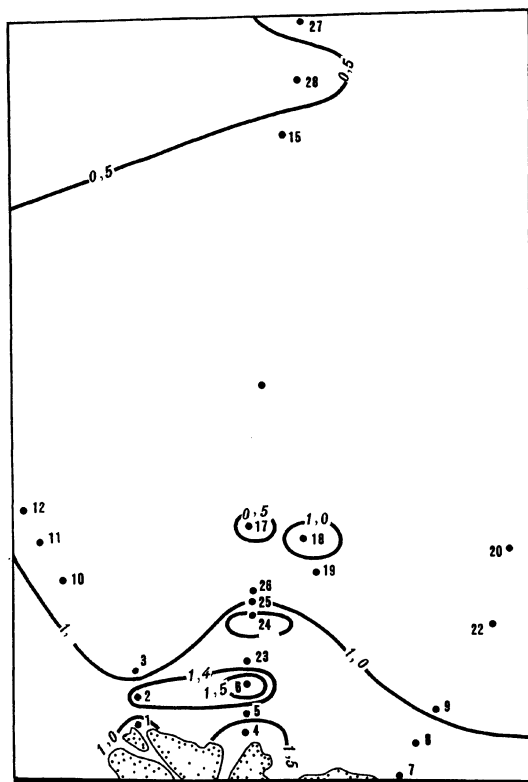


Fig. 57. Distribution of CP (mg/l) in the area of Kuban river and sea waters mixing (April–May 1979).

One of the important problems of estuarine biogeochemistry, which has been a subject of attention over the last few years, is the behaviour and interaction of organic matter and micro-elements in the river–sea system. There is a lot of evidence for the deposition of dissolved and colloid micro-elements during the process of water mixing in estuaries in cases of both low salinity and salinity of 20‰ (Gordeev, 1983; Anikeev, 1987; Anikeev *et al.*, 1985; Martin *et al.*, 1993). The preferable mechanism of transition of organic matter and micro-elements from the dissolved into the suspended state is the formation of floccules “iron oxide–organic matter” and connection with such aggregates of other micro-elements (Boyle *et al.*, 1977; Bowers and Yeats, 1981). A number of works proves similarity in behaviour of metals and organic matter, especially humic substances, in areas of mixing of river and sea waters, where it has been shown that flocculation of metals and humic substances takes place (Boyle *et al.*, 1977; Eckert and Sholkovitz, 1976; Sholkovitz, 1976, 1978; Sholkovitz *et al.*, 1977, 1978).

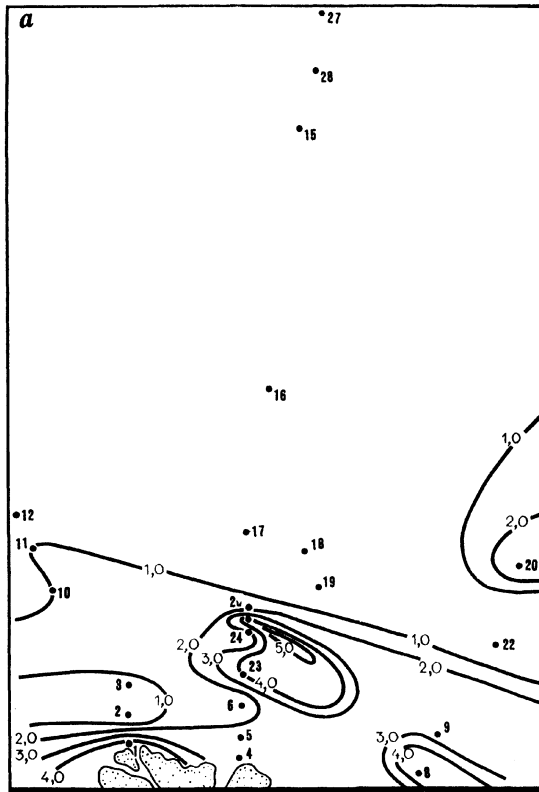


Fig. 58. Distribution of particulate Cu (mg/l) in the area of Kuban river and sea waters mixing (May 1979).

A considerable part of micro-elements in river and sea waters is adsorbed by organic suspensions and transported by suspended substances (Lisitzin and Gordeev, 1974; Turekian, 1971; Wallace *et al.*, 1977). It was shown by experiments that suspended organic particles are able to adsorb ions of sea waters effectively. The formed absorption complex micro-elements–organic matter is able to react and may be actively included in further chemical transformation during the process of sedimentation.

In spite of the fact that problems of interaction of organic matter and micro-elements during intermixture of river and sea waters were considered in a number of works (for example, Martin *et al.*, 1971; Sholkovitz *et al.*, 1978; Montgomery and Santiago, 1978; Gordeev *et al.*, 1985), their behaviour under natural conditions remains insufficiently studied. With this in mind we studied the peculiarities of the behaviour of organic matter and micro-elements in the regions of river and sea water intermixture in the Temryuk Bay

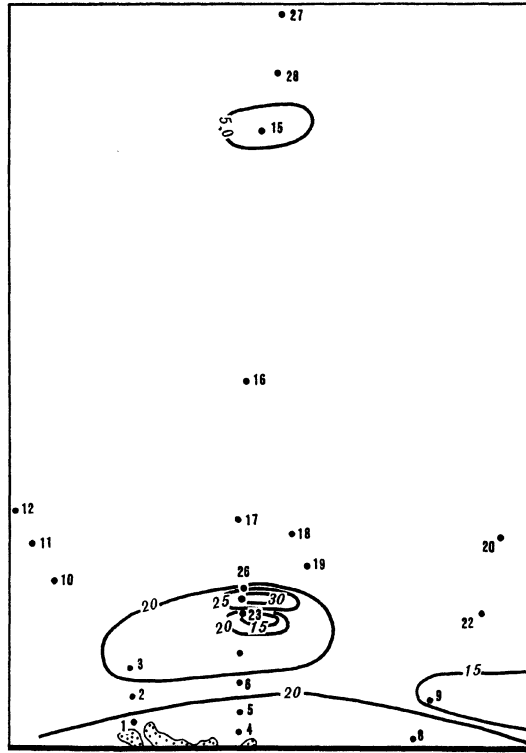


Fig. 59. Distribution of particulate Ni (mg/l) in the area of Kuban river and sea waters mixing (May 1979).

(Artemyev *et al.*, 1982) and the southern part of the Riga Bay (Artemyev and Gorshkov, 1982; Demina and Artemyev, 1984).

The study of micro-elements in suspension at the section “mouth of Kuban river–Temryuk Bay” showed that their concentration, as well as C^P and primary production, decreases in direction of the river–sea. However, on the background of the general trend to decreasing content of micro-elements, the maximum concentration of copper, nickel and cadmium is clearly separated in the central part of water intermixture area at the salinity of 5.5–7.0‰, i.e. in the area where high values of primary production and C^P (Figures 58 and 59) were found. If we suppose that the enrichment of suspension with the above-mentioned micro-elements is bound up only with the activity of primary producers, concentrating micro-elements in their tissues in process of their development, one should expect an increase of concentration of suspended micro-elements at the boundary of river and sea water intermixture area. Just here we noted the maximum (third one) of primary production value. However, the content of micro-elements is steadily decreasing seawards

after the maximum concentrations in the central part of the waters intermixture region. Thus, the residues of tissues dying or dead phytoplankton organisms are not the only reason for high concentrations of micro-elements in suspension in the central part of water mixing areas. Since the noted maximum content of micro-elements in suspension is located several kilometres from the river mouth (where their concentration is lower), the river run-off also cannot be the reason for that extreme.

As it was noted earlier (Demina *et al.*, 1973; Sholkovitz *et al.*, 1976, 1978), in the case of intermixture of river and sea waters micro-elements are removed from the dissolved into the suspended state as a result of flocculation of colloid particles. Apparently, extreme concentrations of micro-elements in the area of intermixture of waters of the Kuban river and Azov Sea area also primarily caused by flocculation.

The contribution of phytoplankton primary production to the deliver of micro-elements into suspension of water intermixture area takes place too, although it plays a secondary role in the studied waters.

3.3.3. CONCLUSIONS

1. While water salinity is increased, the content of phosphates and nitrates is progressively decreased from 50 and 25 mg/l respectively in the Kuban river mouth to 20 and 5 mg/l in sea waters.

2. Distribution of primary production of phytoplankton in the area of river and sea water intermixture is characterized by the presence of 2 maxima: in the central part of the river and sea water intermixture area (waters with salinity of 5–6‰) and on the boundary with sea waters, in the region of hydrofront (waters with salinity of 11‰).

3. Content of C^P and suspended micro-elements (copper, nickel) is increased in the direction river–sea but it is characterized by the presence of a number of maxima and minima, bound up with the physico-chemical (flocculation, adsorption-desorption) and biological processes (primary production of organic matter by phytoplankton). The sharp increase of content of C^P and micro-elements in the central part of the water intermixture area is caused by activity of primary producers, as well as by flocculation of dissolved organic matter and micro-elements bound up with it.

4. Behaviour of particulate organic matter and micro-elements of suspension (copper, nickel) dependent upon the salinity in the studied waters is of similar character, which testifies to their migration in a form of organic matter–metal complexes.

3.4. Dissolved and Suspended Organic Carbon and Primary Production in Non-Stratified Estuary (The Taganrog Bay)

3.4.1. BIOGENIC ELEMENTS, PRIMARY PRODUCTION, AND SUSPENSION

In October 1980 we performed biochemical studies at the section “Don river mouth–Taganrog Bay” (Figures 60 and 61). One of the typical peculiarities of waters in the studied region was the absence of any kind of stratification along the whole section river–

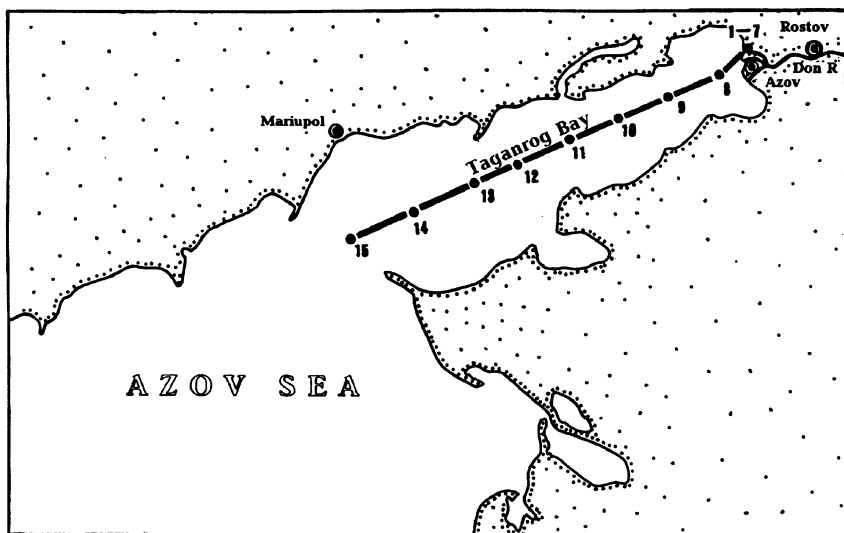


Fig. 60. Sampling stations in Taganrog Bay (October 1980).

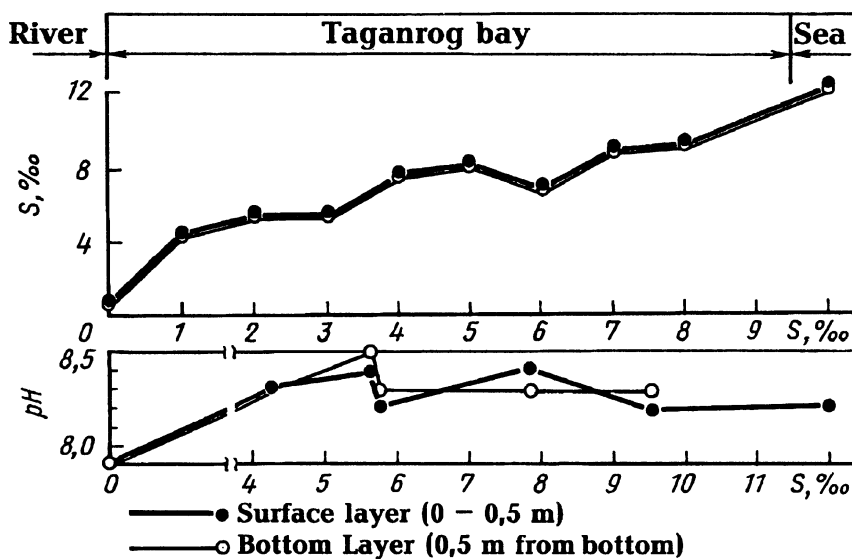


Fig. 61a. Hydrochemical and biogeochemical components at the profile "Don river mouth-sea" (October 1980).

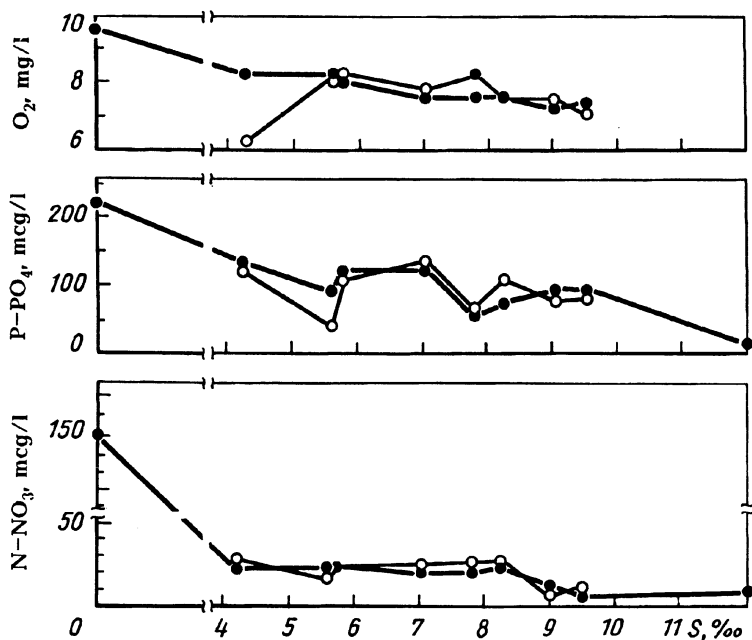


Fig. 61b.

sea (Figure 61). Good intermixture of the whole water mass caused practically the same distribution of the majority of considered components in surface and bottom waters.

The values of pH in the direction river-sea increase from 7.9 to 8.1. The distribution of oxygen and biogenic elements (phosphorus, nitrogen and silica) is characterized by the peculiarities, typical for the mouth shelf of the Don river and Taganrog Bay (Simonov, 1969): a decrease in concentrations by the transition from fresh to salt waters, sharpest in waters with salinities of 0.5 to 4‰. Activation of processes of primary production of organic matter by phytoplankton organisms takes place in the same waters in the early stages of mixture of river and sea waters at relatively low turbidity of waters (concentration of suspension is about 10 mg/l). Using the data from Khrustalev (1989), it is seen that diatomic complexes are mainly developed in October in the Taganrog Bay. This causes a sharp increase of primary production value, by more than an order compared with river waters, in waters with a salinity of about 4‰ (Figure 61). Thus, a decrease of concentration of nutrient salts in the area of contact of river and sea water is caused to a considerable extent by their consumption by phytoplankton. The further decrease in the intensity of organic matter produced by algae towards the sea (from 750 to 70 mgC/m³/day) is bound up with the shortage of biogenic nutrient salts, and an increase of concentration of suspended particles in water, which nevertheless allows for the upkeep of primary

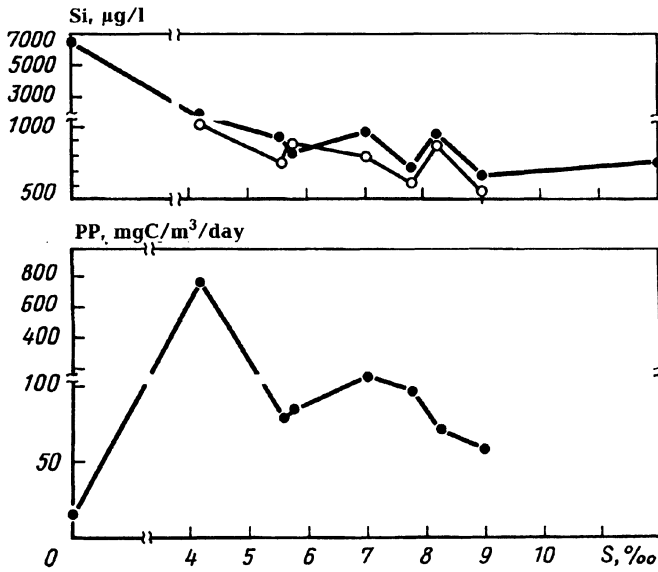


Fig. 61c.

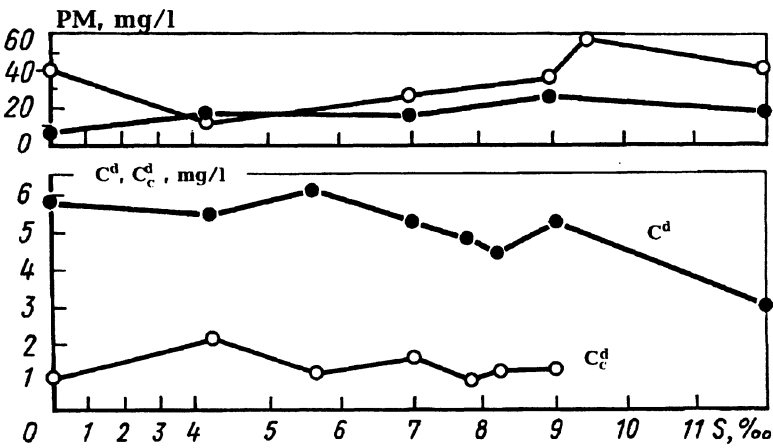


Fig. 61d.

production at the level of 70–100 $\text{mgC/m}^3/\text{day}$. When approaching the boundary with sea waters, the primary production value decreases to 50 $\text{mgC/m}^3/\text{day}$.

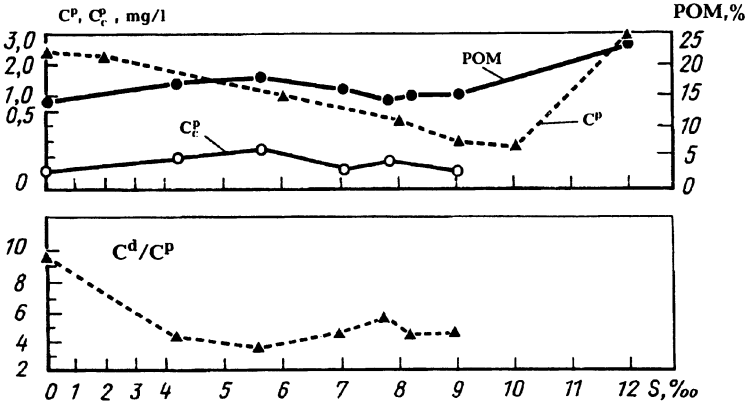


Fig. 61e.

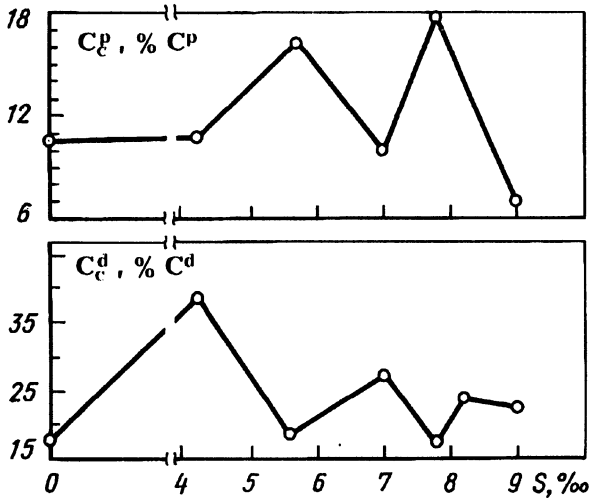


Fig. 61f.

As it is obvious from the example of the Taganrog Bay, the river run-off may have a fundamental effect on the primary production value in the area of intermixture of river and sea waters, and is one of the factors controlling primary production in these waters.

The concentration of suspension within the studied period in the Taganrog Bay varied from 11 to 53 mg/l with an average of 25 mg/l. When moving from the river mouth to the sea the content of suspension was increased step by step, from less than 4 mg/l in the river mouth to several tens of mg/l in the sea part of section. An increase of the content

Table 47. Seasonal distribution of suspension and particulate organic matter in Taganrog Bay (Khrustalev *et al.*, 1982).

Month	Suspension, 10 ⁶ t		Sum total
	Inorganic	Organic*	
April	2.9	<u>0.8</u> ** 21.6	3.7
June	1.2	<u>0.5</u> 29.4	1.7
July	1.1	<u>0.3</u> 21.4	1.4
August	0.4	<u>0.1</u> 20.0	0.5
October	0.5	<u>0.2</u> 28.6	0.7

* Content of particulate organic matter was determined by means of bichromatic oxidation.

** Numerator = mln t; denominator = %.

of suspension in the area of intermixture of the waters of the Don river and Taganrog Bay (compared with river waters) within the studied period is bound up with its supply to the water as a result of rolling of the surfacial layer of bottom sediments under conditions of intensive wind mixing of the whole 3–4 m thick water mass. The share of organic matter in the composition of suspension is equal to 5.9–21.5%, averaging 11.2%, which is also confirmed by the data presented by Khrustalev (Table 47).

3.4.2. FACTORS DETERMINING THE BEHAVIOUR OF DISSOLVED AND SUSPENDED ORGANIC CARBON AND LABILE ORGANIC SUBSTANCE

Content of C^d and C^p in the studied waters is equal respectively to 3.22–8.5 mg/l, average 5.4 mg/l and 0.7–2.3 mg/l, average 1.3 mg/l (converting into particulate organic matter – 1.3–4.2 mg/l, average 2.4 mg/l, Figure 61). The dissolved form of organic matter predominates in waters of the Taganrog Bay (74.0–88.6%, average 80.9%). The basic and most labile component of particulate organic matter in the Taganrog Bay and the Azov Sea is detritus, represented by residues of planktonic plants (Table 48).

A specific group is formed by organic-mineral aggregates, consisting of clay minerals and products of heavy decomposition of vegetable residues. The content of living organisms in particulate organic matter is extremely low. As it is obvious from Table 48, the particulate organic matter concentration is usually at a maximum in regions adjoining the Don mouth. The effect of river run-off is revealed in the increase of allochthonous genesis vegetable detritus content in the suspension, as well as in high concentrations of nutrient salts (Figure 61).

Table 48. Seasonal variation of particulate organic matter composition in the Taganrog Bay of the Azov Sea in 1977, mg/l (Khrustalev *et al.*, 1982).

Region	Particulate organic matter						Sum total	
	Phytoplankton			Living bacterio-	Living zoo-	Deeply mineralized		
	Living	Fresh detritus	Sum total	plankton	plankton			
Taganrog Bay:								
April	eastern	0.14	1.27	1.41	0.04	0.04	3.47	4.96
	central	0.04	1.48	1.52	0.03	0.00	1.29	2.84
	western	0.03	0.76	0.79	0.03	0.00	0.96	1.78
	sea	0.01	0.38	0.39	0.05	0.01	1.10	1.55
Taganrog Bay:								
July	eastern	0.45	2.64	3.09	0.17	0.02	0.72	10.00
	central	0.36	0.81	1.17	0.10	0.00	5.22	6.49
	western	0.01	1.45	1.46	0.08	0.01	3.54	5.09
	sea	0.03	0.63	0.66	0.11	0.03	2.08	2.88
Taganrog Bay:								
October	eastern	0.81	1.32	2.13	0.01	0.04	2.68	4.86
	central	0.24	0.63	0.87	0.03	0.01	1.92	2.83
	western	0.05	0.62	0.67	0.02	0.00	0.80	1.49
	sea	0.04	0.78	0.82	0.04	--	1.09	1.95

However, behaviour of organic matter in the Taganrog Bay may be of different character, since concentrations of dissolved and particulate organic matter in surface and bottom layers of water, and distribution of these components by the section river–sea are influenced by water hydrodynamics. So, during the period of our investigations when the whole thickness of water from the surface to the bottom was mixed well, i.e. under conditions of “non-stratified” estuary distribution of C^d and C^p on the section “river mouth–sea” was of “calm” type in the Taganrog Bay, without clearly expressed extremes. Nevertheless, in the case of passage from fresh waters to waters of intermixture, C^p more than doubled. Evidently (Figure 61), this is bound up with a sharp increase of primary production value in these waters.

It is obvious from Figure 62, that the content of particulate organic matter, as well as the suspension and biomass of phytoplankton is subjected to noticeable variations within 24 hours. As is obvious, there is no direct connection between organic matter and biomass of phytoplankton, which can be explained by the fact that the majority of particulate organic matter is presented by “mineralized” organic matter (Table 48).

Behaviour of C^d and C^p in the near-mouth section of the area of intermixture of the Don river and Taganrog Bay waters are mutually opposite: the increase of C^p is followed by

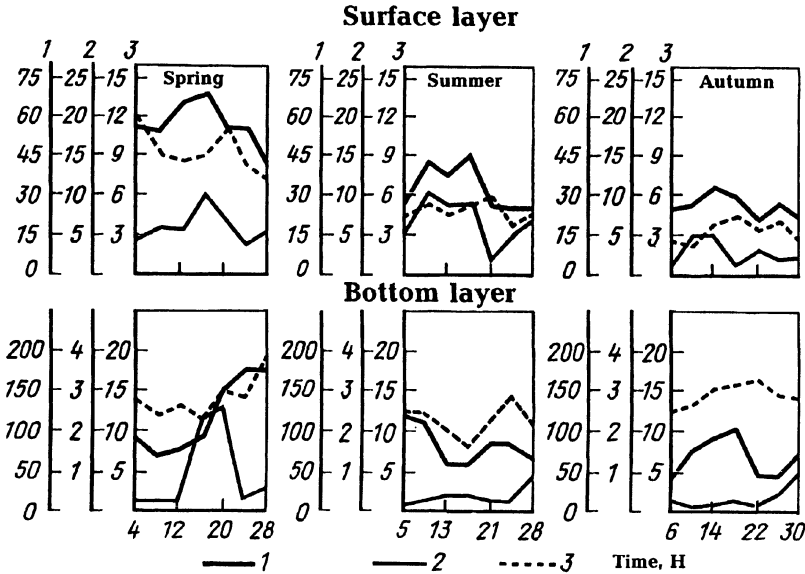


Fig. 62. The daily dynamics of particulate matter (1) content (mg/l), phytoplankton biomass (2), g/m^3 , and particulate organic matter (mg/l) in Taganrog Bay waters (Khrustalev, 1989).

C^d decrease. This is also testified by the character of variation of C^d/C^p ratio at the section river–sea: in waters with salinity of 0.5–4‰ the ratio C^d/C^p more than halves, from 9.5 to 4.5, while in waters with higher salinity this value does not vary with an increase in distance from the shore (Figure 61).

The most probable reason for C^d concentration decrease at the initial stage of mixture of river and sea waters, in waters with salinity of 0–4‰, is flocculation of dissolved organic matter and its transformation into the suspended form. In this case the decrease of C^d content cannot be bound up in any way with the activity of primary producers. On the contrary, in these waters, as it was noted earlier, the processes of organic matter production by phytoplankton, were activated, as well as processes of discharging of dissolved organic matter into water.

Composition of organic matter (dissolved and particulate organic matter) in waters of the Taganrog Bay is noticeably changed when moving away from the Don mouth to the sea, which was very noticeable in the curves of the distribution of dissolved and particulate carbohydrates on the section river–sea.

Since the main source of natural organic matter in the studied waters over the entire length of the section river–sea is diatomic plankton, changes in composition of dissolved and particulate organic matter may be, primarily, bound up with vital activity of planktonic organisms. It follows from Figure 61 that at the early stage of intermixture of waters in the

Taganrog Bay during the period of active production of organic matter by phytoplankton, the content of carbohydrates in dissolved organic matter composition is increased considerably, from 17.5% in fresh waters to 38% in waters with a salinity of about 4‰. Their content decreases again with the increase of distance from the shore.

It is necessary to pay attention to the fact that the character of variation of relative content of dissolved carbohydrates in the composition of dissolved organic matter (C_c^d , % of C^d) and primary production on the section river–sea coincide almost completely. Consequently, primary production is the main source of dissolved carbohydrates in the studied waters. As for the variation in the dissolved and particulate organic matter composition on the section “Don river–Taganrog Bay”, the content of dissolved carbohydrates in dissolved organic matter varies from the particulate carbohydrates content in particulate organic matter in a contrasting way. The obtained results of studying the carbohydrates in the area of intermixture of waters of the Don river and the Taganrog Bay correlate with the data (Laane and Ittekkot, 1985) of dissolved carbohydrates concentration (of the same order) in the Ems river (average 18.4% of dissolved organic matter).

3.4.3. CONCLUSIONS

Content of C^d and C^p in the studied waters average respectively 5.4 and 1.3 mg/l. Dissolved forms of organic matter prevail and total 74.0–88.6%, with an average 80.9% of the sum of dissolved and particulate organic matter. The share of particulate organic matter in the suspension composition is equal to 5.9–21.5%, average 11.2%.

Under conditions of good stratification of waters in the bay (as a rule in summer and autumn seasons) increased concentrations of particulate organic matter are seen in the waters adjacent to the Don mouth and bound up with the delivery of particulate organic matter with river run-off. In the case of intensive mixing of waters by wind, and the absence of water mass stratification, the behaviour of dissolved and particulate organic matter is determined by physico-chemical (flocculation) and biological (primary production of organic matter by phytoplankton) processes in the area of intermixture of river and sea waters.

Variety of dissolved and particulate organic matter composition on the section river–sea is bound up with the functioning of phytoplankton, which play the main role in delivery of dissolved carbohydrates into water.

3.5. Biogeochemical Aspects of C^d and C^p Behaviour at the Boundary of River and Sea Water Intermixture (Riga Bay)

3.5.1. FEATURES OF HYDROCHEMICAL REGIME OF THE BAY IN THE AREA OF RIVER RUN-OFF INFLUENCE

The main feature of the hydrochemical regime of the southern part of the Riga Bay is the essential refreshing of sea waters with river run-off. The Riga Bay includes four groups of sea water classified by the degree of refreshing: highly refreshed (salinity up to 3‰),

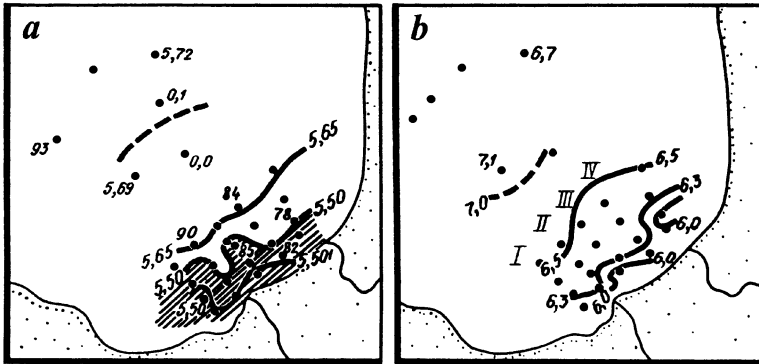


Fig. 63. Distribution of salinity in a surficial (a) and near-bottom (b) layer of Riga Bay waters (Artemyev *et al.*, 1981).

medium refreshed (salinity 3.0–4.5‰), weakly refreshed (salinity 4.5–5.5‰), relatively non-refreshed (salinity exceeds 5.5‰) (Matisone, 1974; Matisone and Trautmanis, 1982). Highly refreshed sea water is typical only for the premouth shelf of the Daugava. Medium refreshed sea water is observed on the river mouth shelf of the Daugava and Gauya rivers. The area of propagation of these waters may reach a 20 m isobath. Weakly refreshed sea waters predominate in the rest of the water area of the bay. Weakly refreshed and non-refreshed sea waters are typical for the bottom horizon of the southern part of the Riga Bay.

Studies of the geochemistry of organic substance in the southern part of the Riga Bay were carried out by us twice: in September 1977 and in July 1978 (Artemyev and Gorshkov, 1982; Artemyev *et al.*, 1981; Demina and Artemyev, 1984). Detailed data of the structure of water thickness in the area of effect of waters of the Lielupe, Daugava and Gauya rivers on the water of the Riga Bay (by the data of temperature and salinity measurements) were obtained in July 1978 during the 26th cruise of the research vessel “Akademik Kurchatov” (Figures 63 and 64). It was obvious that surficial weakly refreshed waters on the southern part of the Bay spread from the mouth area of the Daugava river north-west and north-east, and waters of higher salinity (about 6.5‰) from the open part of the bay edged into insufficiently refreshed waters to a distance of 35–45 km from mouth of the rivers and spread over surficial waters just up to the shore (Figure 64).

It is obvious from the curves of vertical distribution of temperature and salinity (Figure 64) that poorly refreshed waters nearest to the shore stations of sections II and III in the zone of influence of river run-off of the Daugava river have thicknesses of 8–12 m and are edged at a distance of 25–45 km from the shore. On section IV, some distance from the Daugava river mouth, the thickness of the layer of poorly refreshed waters nearest the shore stations is about 5 m, and the distance of their propagation does not exceed 10 miles. Consequently, water thickness in the north-east part of the studied water area is represented mainly by sea waters of the bay.

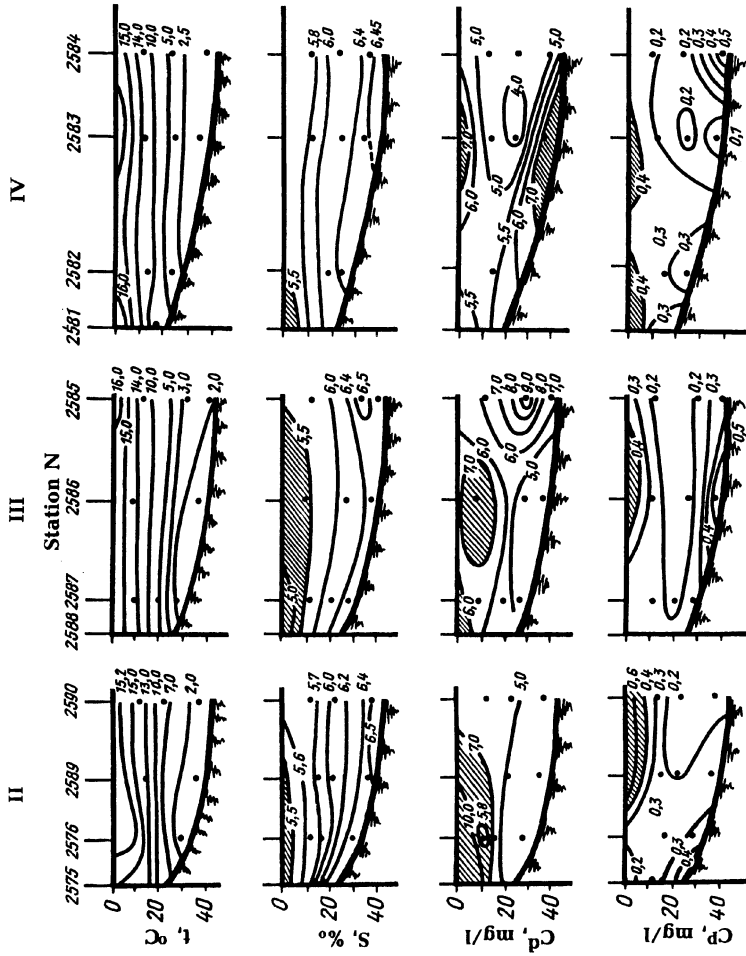


Fig. 64. Vertical distribution of T°, salinity, Cd and Cb at profiles river-sea in the southern part of the Riga Bay in July 1978 (Artemyev *et al.*, 1981).

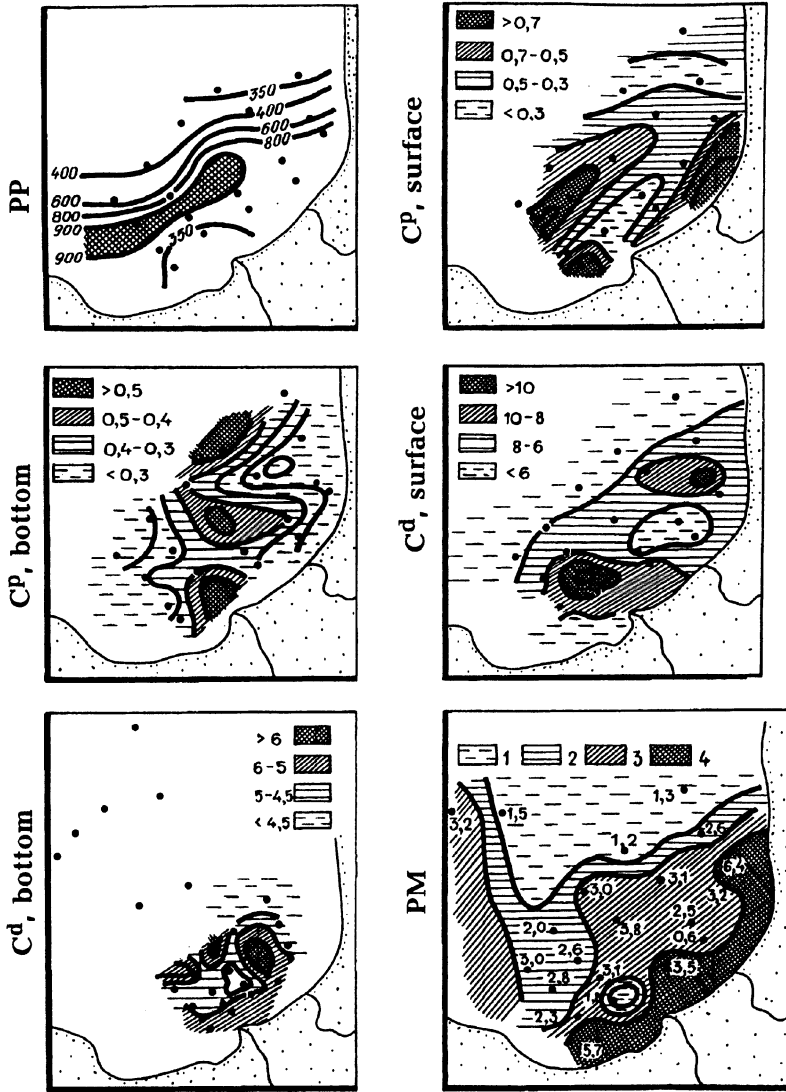


Fig. 65. Primary production (mgC/m³/day), C^p, C^d and particulate matter (e), mg/l, in a surfacial and near-bottom layer of the southern part of the Riga Bay waters (Artemyev *et al.*, 1981; Dymina and Artemyev, 1984).

3.5.2. SPATIAL DISTRIBUTION OF C^d

Organic carbon in the studied waters is mainly in dissolved form (85–98%, average 94% of the sum of C^d and C^p). Content of C^d varies from 3.1 to 18.1 mg/l and averages 7.2 mg/l. The highest content of C^d was found in refreshed waters in the Daugava river mouth and bound up with the supply of organic matter by river run-off (Figure 65). The area of propagation of refreshed waters, enriched to the maximum extent with organic matter of river origin is limited within a narrow area, propagating from the Daugava river mouth mainly to the north-west (Figure 63). It should be noted that a spot of higher concentrations of C^d (10–15 mg/l), due evidently to contamination, was found in the north-east part of the studied water area on the background of low C^d concentrations and outside the zone of river run-off effect.

C^d is distributed vertically in accordance with the water stratification (Figure 64). So, for example, in the Daugava river mouth the thickness of the upper layers of water with high concentrations of C^d (more than 7 mg/l) regularly decreases in the direction from the shore towards the bay, edging towards water surface approximately in the same places where the boundary of poorly refreshed waters pass. On section IV, where the effect of river run-off is practically absent and all the studied thickness of waters is represented by the most saline waters of the bay, C^d vertical distribution is, on the whole, characterized by slightly varying values.

High concentrations of C^d as well as C^p in the waters of the southern part of the Riga Bay, some distance from the Daugava river mouth are bound up with the processes of primary production of organic matter by phytoplankton organisms (Figure 65).

The study of dissolved organic “yellow” substance in the Daugava river mouth and in the open part of the Riga Bay showed (Pelevina, 1980) that its relative concentrations are equal to $3.6\text{--}6\text{ m}^{-1}$ and $0.4\text{--}1.5\text{ m}^{-1}$ respectively.

Evidently, the main source of these organic compounds is the river run-off. By the data of Yurkovsky and Rugaine (1985) the highest concentration of dissolved coloured organic matter (DCOM) (and C^d , by our data) was found in the region of the Daugava river mouth (6.3 mg/l). For comparison, the bottom waters of the bay and surface waters of the Baltic Sea contain about 1 mg/l of dissolved coloured organic matter. Dissolved and suspended coloured organic matter are equal to 17–41% of dissolved organic matter and 2–14% of particulate organic matter respectively.

3.5.3. SUSPENDED ORGANIC MATTER AND FACTORS DETERMINING THE BEHAVIOUR OF C^d AND C^p

The composition of studied suspension includes 1.9–42.1% of C^p , average 15.3%, or 3.5–76.6%, average 27.8% of organic matter. Thus, in the majority of samples a considerable part of suspension is represented by mineral particles, mainly terrigenous (Pustelnikov, 1976). Distribution of particulate organic matter on the surface of the studied water surface is similar to the distribution of primary production of phytoplankton (Figure 65). The similarity of areas of high concentrations of C^d and primary production on the surface of studied water area in the zone of transition from refreshed waters to sea water, testifies

to the fact that considerable parts of C^P in the area of mixture are characterized by phytoplankton genesis. High concentrations of C^P in surface waters in the region of the Lielupe and Gauya rivers are bound up with the delivery of particulate organic matter with river run-off.

Content of C^P is, as a rule, decreasing with increasing depth (Figures 64 and 65). However, high concentrations of C^P were noted in some bottom samples of suspension, which were not found in respective surficial layers of water. The source of this suspension are waters, propagated from the open part of the bay towards the Daugava river mouth (Figure 64). On the other hand, the high content of C^P in surface waters of the region of river and sea water intermixture is not accompanied by the same high concentrations of C^P in bottom layers (Figure 65).

This is bound up with the fact that processes of sedimentation in the stratified estuary, which is the studied water area of the northern part of the Riga Bay, are subjected to influence not only of hydrological factors (direction and velocity of currents, wind, etc.) but also by different genesis of surface mainly refreshed waters, and bottom, mainly sea waters. These peculiarities of the waters of the southern part of the Riga Bay determine the direction of transportation and place of deposition of suspended organic particles on the surface of bottom sediments.

High concentrations of C^P in the zone of transition from refreshed (mixed) waters to sea waters of the bay are accompanied with low concentrations of C^d (Figure 65). It is possible to suppose that a part of the dissolved (colloid) organic matter coagulates during mixture of refreshed and sea waters, increasing the content of particulate organic matter with the formation of floccules. As it was obvious from Figure 65 there is a principal difference in the behaviour of C^d in surficial and bottom waters: maxima of C^d content in surface waters corresponds to minima of concentrations of C^P in bottom waters and *vice versa*. This fact may also serve as indirect evidence of the presence of dissolved organic matter flocculation process and its transformation into the suspended form during sea and river water intermixture.

“Non-conservative” character of dissolved organic matter behaviour on the section “Daugava river mouth–Riga Bay” is testified by the results of studying of dissolved “coloured” dissolved and particulate organic matter (Figure 66). In this case, as considered by Yurkovsky and Rugaine (1986), only a part of these components may be eliminated from solution by flocculation. In the opinion of some authors, the character of the behaviour of “coloured” dissolved and suspended organic matter dependency upon salinity is determined by the concentration of organic matter in river water. Under comparatively low concentrations of organic matter the relationship between dissolved coloured organic matter and salinity is represented by a line which is virtually straight and dissolved organic matter behaviour depends upon the law of simple dilution during mixing between river and sea waters.

According to the data of Yurkovsky and Rugaine (1986) “losses” of dissolved organic matter brought from the land totals up to 10% in the southern part of the Riga Bay.

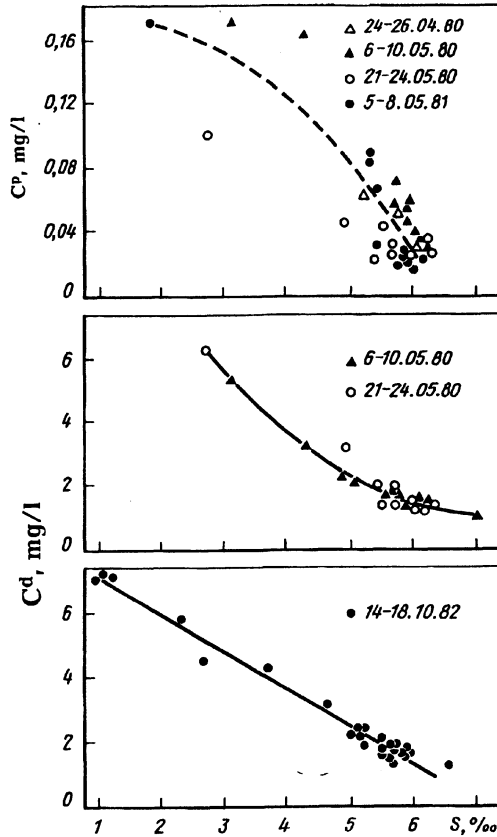


Fig. 66. The content of particulate and dissolved "coloured" substances in surficial waters of the Riga Bay plotted against salinity (Yurkovsky and Rugayne, 1986).

3.5.4. RELATION BETWEEN ORGANIC MATTER AND MICRO-ELEMENTS

To consider the peculiarities of suspended micro-elements behaviour and C^p in the area of mixing between river and sea waters we chose the section drawn from the Daugava river through the mixture zone to waters with salinity typical for the open part of the bay (Figure 67). The obtained results show that spatial distribution of C^p and micro-elements in studied waters is similar and has a complicated character (Figures 68–70). This is quite explainable if you take in view that the relative concentration of micro-elements in the suspension in the river–sea system is dependent on many factors: activity

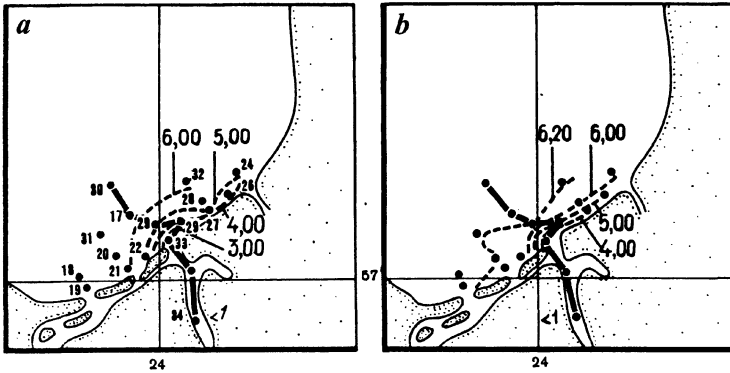


Fig. 67. Distribution of salinity (‰) in surficial (a) and near-bottom (b) waters of the southern part of the Riga Bay (Artemyev and Gorshkov, 1982).

of primary producers, presence of anthropogenic pollutions, physico-chemical regime of water medium, ability for interrelation with organic matter, etc.

Proceeding from hydrochemical and physico-chemical peculiarities of the water medium, it is useful to consider the spatial variety of concentration of C^p and micro-elements in surficial and bottom waters in three places of the section river-sea: river water-river mouth (initial stages of water mixture), area of sea and river water intermixture and sea water.

Relatively high concentrations of C^p at the early stage of intermixture of river and sea water in the surface suspension in the region of the Daugava river mouth may be bound up with anthropogenic pollutions, as well as with river colloid organic matter flocculation.

In the area of river and sea water intermixture, the concentration of C^p decreases quickly with an increase of salinity from 2.5 to 4.2‰, which may be associated with the process of desorption and C^p transformation into the dissolved form. With a further increase of salinity and motion to the boundary of the area of mixing of waters with sea water we observe a sharp increase of concentrations of C^p , suspended copper and zinc (Figures 68–70). In sea water their concentration is lower.

Thus, the area of intermixture of waters of the Daugava river and the Riga Bay are characterized by alternation of high and low concentrations of C^p and micro-elements in the suspensions which may be caused by both physico-chemical processes (flocculation, adsorption-desorption) and vital activity of primary producers.

As it has been shown in the sparse studies, flocculation of these or other micro-elements and organic matter, as a result of river and sea water mixture, may reach its peak at various salinities of water. So Martin and others (Martin *et al.*, 1971) suppose that flocculation of iron, manganese, cobalt and organic matter is maximum at 8‰. They also note that the influence of salinity on the adsorption of micro-elements from sea water is determined by the presence of organic matter of that or other composition.

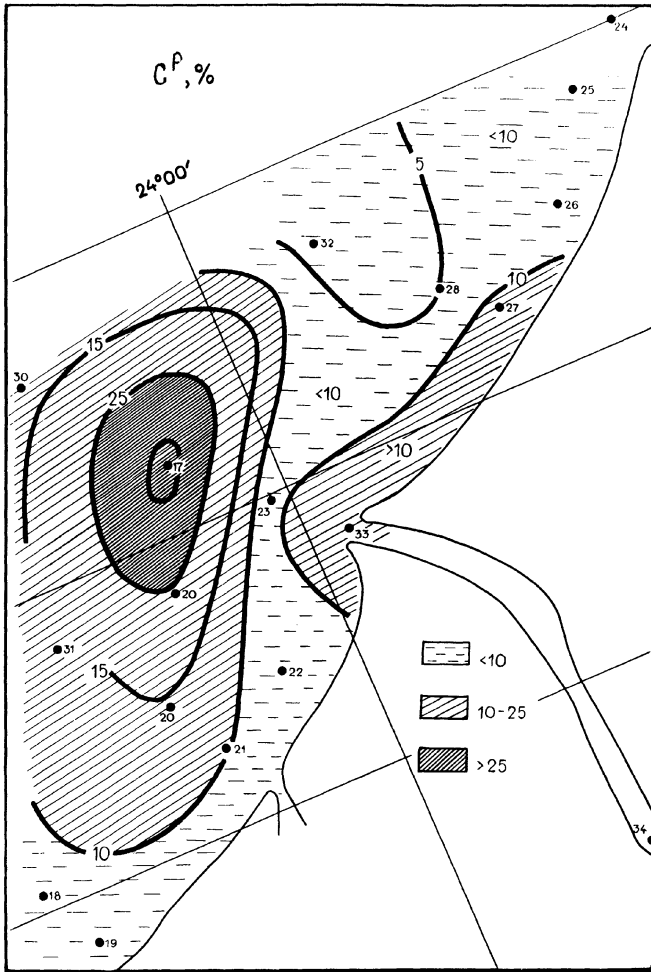


Fig. 68. Particulate organic carbon in the southern part of the Riga Bay (Artemyev and Gorshkov, 1982).

Alteration of charge sign on the surface of suspended particles (change of electrokinetic potential from negative to positive values) at which the process of adsorption is activated takes place at early stages of water mixture, at salinities of about 2‰ (Duinker *et al.*, 1974).

Within the period of our investigations of the behaviour of organic matter and microelements in the southern part of the Riga Bay in September 1977, we did not carry out

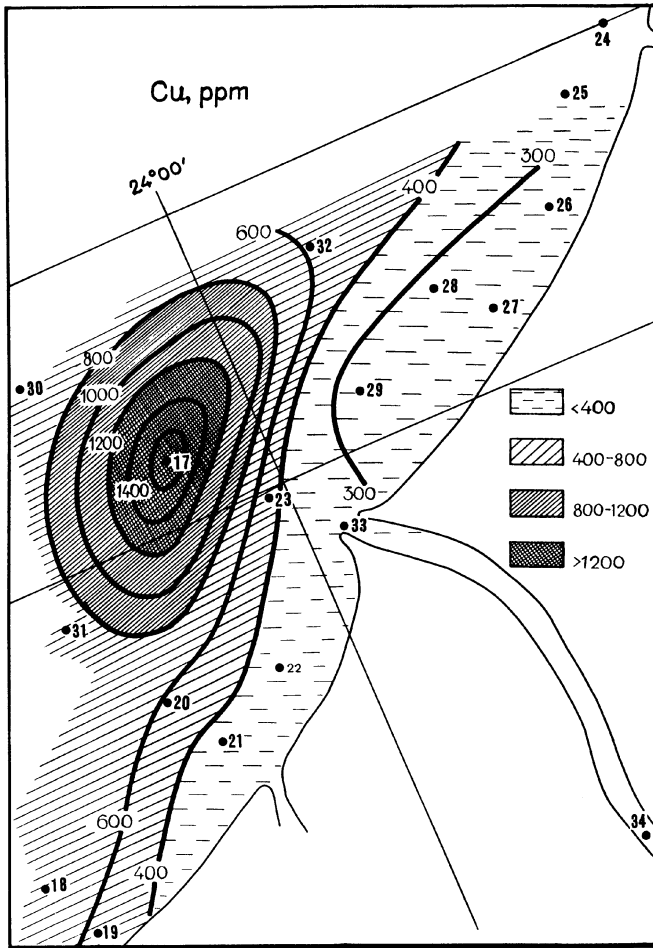


Fig. 69. Particulate Cu in the southern part of the Riga Bay (Artemyev and Gorshkov, 1982).

measurement of phytoplankton primary production value. But the data obtained earlier of seasonal measurements of biomass, phytoplankton production and their distribution in the southern part of the Riga Bay (Zute, 1974; Rudzroga, 1974, 1987) show that in September the values of primary production are very low; they were not changed practically within the boundaries of water area, studied by us, and consequently are not able to have a significant effect on the concentration and behaviour of organic matter and micro-elements. Thus, the main reasons for fluctuation of these components are the physico-chemical processes:

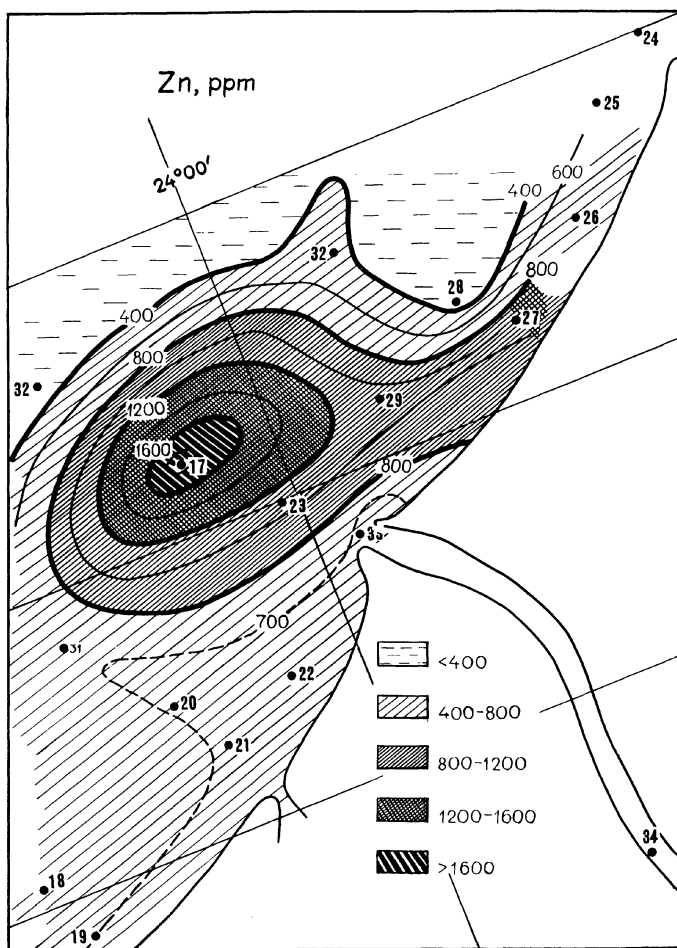


Fig. 70. Particulate Zn in the southern part of the Riga Bay (Artemyev and Gorshkov, 1982).

flocculation and adsorption-desorption, which may affect the behaviour of organic matter and micro-elements at various stages of water mixture. It also follows from Figures 68–70 that the behaviour of C^p , copper and zinc in surface waters of the Daugava river and the Riga Bay are similar. This proves their interrelation and migration in the form of organic matter–metal complexes or adsorptional complexes.

The analysis of behaviour of iron and organic matter forms in the southern part of the Riga Bay showed that in the initial stage of intermixture of the Daugava waters and sea

Table 49. Average content and forms of Fe, Zn and Cu (in $\mu\text{g/l}$) and C^{d} (in mg/l) in waters of the Riga Bay (Demina and Artemyev, 1984).

Water mass	Fe				Zn				Cu				C^{d}
	I	II	III	IV	I	II	III	IV	I	II	III	IV	
Surfacial ($d = 10 \text{ m}$, $n = 17$)	1.6	2.0	3.6	11.7 0.85	12.7	1.9	14.6	5.1	2.0	1.3	3.3	1.0	6.55
% of total dissolved form	44.6	55.6	-	-	87.0	13.0	-	-	60.6	39.4	-	-	453
% of total content	-	-	23.6	76.4	-	-	74.1	25.9	-	-	76.7	23.3	93.50
Deep and bottom ($d = 10 \text{ m}$, $n = 15$)	1.5	2.6	4.1	36.4 0.81	15.0	2.7	17.7	5.6 1015	3.3	1.0	4.3	0.6	5.50
% of total dissolved form	36.6	63.4	-	-	84.7	15.3	-	-	76.3	23.7	-	-	327
% of total content	-	-	10.1	89.9	-	-	76.0	24.0	-	-	87.7	12.3	95.00

Forms: I. inorganic dissolved; II. organic dissolved; III. total dissolved; IV. suspended (in nominator: for Fe - % dry weight, and for Zn and Cu - 10⁻⁴% dry weight); d = depth; n = number of samples.

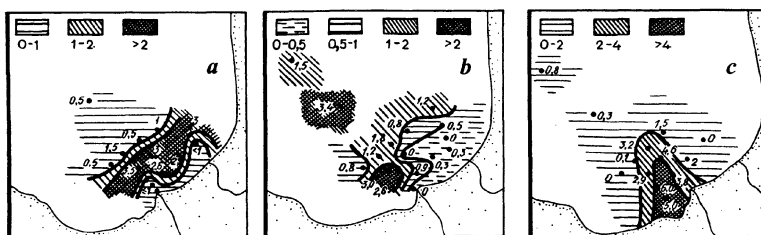


Fig. 71. Dissolved Fe (a), Cu (b), Zn (c) in surfacial waters of the southern part of the Riga Bay in July 1978 (mg/l, organic form) (Dyomina and Artemyev, 1984).

waters transition of iron from the dissolved into suspended form takes place as a result of flocculation (Demina and Artemyev, 1984). As is obvious from Table 49, the biggest part of iron in the solution is bound with organic compounds of evidently colloid form. During flocculation, iron is transformed into suspension which is deposited from surface waters and accumulated in bottom waters. It was also determined that higher content of both suspended iron and C^p and phytoplankton primary production (Figure 65) was found in the surface waters of the studied part of the Riga Bay water area, on the boundary of mixture of river waters with sea waters.

Thus, the concentration and the behaviour of suspended iron in the southern part of the Riga Bay is controlled primarily by the processes of primary production of organic matter by phytoplankton.

Distribution of the “organically dissolved” form of iron and copper in surface waters shows the same character as that of C^d (Figure 71): low concentrations are found near the Daugava mouth and high ones in the area of mixing of waters, at some distance from the river mouth, with high values of primary production (Figure 65). At the same time, the “organically dissolved” form of zinc is distributed in the opposite way: high concentrations are near the river mouth and there is a drop of concentration with an increase of the distance from it. Evidently, the river run-off is the only source for the “organically dissolved” form of zinc in the studied waters, whereas for iron and copper the main factor of organic complex formation is bound up with production of organic matter by phytoplankton in the area of mixing between river and sea waters.

3.5.5. CONCLUSIONS

1. The structure of water thickness in the southern part of the Riga Bay is characterized by a clear stratification and the presence of two types of water: surface, mainly riverine with high C^d content (8–12 mg/l) and subsurface, mainly sea water, with low concentrations of C^d (4–6 mg/l).

2. The dissolved form of organic matter (85–98%, average 94% of the sum of dissolved and particulate organic matter) prevails in the studied waters of the bay.

3. In the zone of transition from refreshed waters to sea waters (salinity 6–7‰) we found a noticeable increase of C^p content, which is principally bound up with the activation of the process of primary production of organic matter by phytoplankton. Another factor affecting the increase of C^p in these waters is the flocculation of dissolved organic matter, which is testified to by the decrease of C^d concentration.

4. The identical character of behaviour of particulate organic matter and a number of micro-elements (chromium, copper, zinc) in the studied waters depending on salinity testify to the transportation of these micro-elements in close connection with particulate organic matter.

5. Variation of concentration of particulate organic matter and micro-elements at the initial stage of waters intermixture is caused, mainly, by physico-chemical processes (adsorption-desorption, flocculation) and the primary production of organic matter is of minor importance here.

3.6. Seasonal Peculiarities of C^d and C^p Transportation on the River–Sea Section (Dvina Bay)

3.6.1. BASIC FEATURES OF THE HYDROLOGY OF THE SOUTHERN PART OF THE BAY

The lavish continental run-off into the White Sea averages 215 km³ and causes the permanent current, velocity which is equal to 0.3–0.7 knots. The value of this current is great for the dynamics of sea waters and for other elements of this hydrological regime. Continental run-off during all seasons affects the thermal and salinity regimes of the sea, especially in the region of neighbouring mouths of large rivers. The main part of this drainage is supplied into the White Sea in May–June (45%) and during the five winter months (December–April) when drainage is equal to 15%. The North Dvina river gives 48% of the total river drainage into the White Sea (Nadezhdin, 1966).

Normal thermal and salinity stratification accompanied by the decrease of temperature and increase of salinity with depth, is almost always kept in the Dvina Bay at relatively small depths and flat relief of bottom. Such schemes of salinity distribution are clearly revealed in the summer, autumn and especially in the winter (Figure 72).

The North Dvina river mouth includes the coast section of the river from Ust-Pinega to the coast shelf and the southern part of the Dvina Bay (Zotin and Mikhailov, 1965). The peculiarities of the hydrological regime of the North Dvina river mouth is mainly determined by the value and distribution of river run-off and by the tidal character of the sea. The upper boundary of the river mouth region goes near the Pinega river mouth (Figure 73) where tidal level variations are stopped. The sea boundary follows the slope of depths. The North Dvina river mouth area is subdivided into three parts: (1) river mouth section, from the Pinega river mouth to Arkhangelsk; (2) delta with the three main branches and numerous channels; and (3) river mouth shelf (Figures 72 and 73). The complicated hydrological regime of the river mouth region is formed as a result of the permanent interaction between river and sea waters.

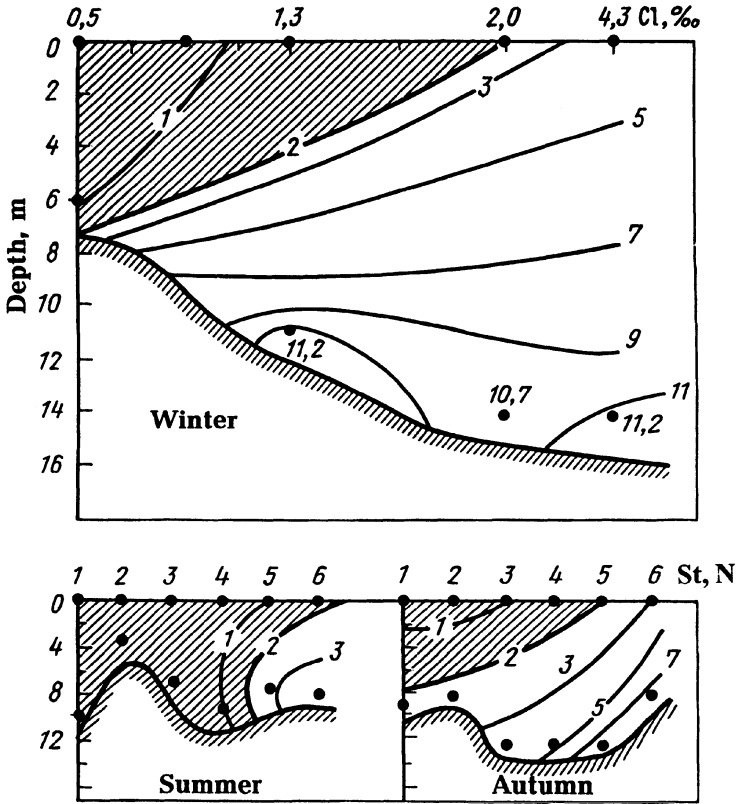


Fig. 72. Vertical distribution of chlorine content at the profile "North Dvina river mouth-sea" in different seasons (Artemyev *et al.*, 1984; Artemyev and Romankevich, 1988). (For location of stations, see Figure 8.)

The main features of the hydrological regime of the North Dvina river mouth region are as follows: periodical tidal-ebb tidal variations of the level which have a half-day character and the value of up to 1.5 m, spring flood, rise (1.5–2.0 m above the full water level) and lowering of level (0.5–1.0 m below the low water level). At the coast section of the river, variations of water level are clearly annual ones, two maxima and two minima being underlined. The first maximum is the spring flood at the end of April–May; the second maximum is autumnal in September–October, when run-off increases from autumn rains and piling up lifts the level. The minimum levels are in winter and in summer (February–March and August–beginning of September).

Distribution of salinity at the North Dvina river mouth shelf is characterized by the presence of a zone of considerable horizontal gradients (hydrological front) of salinity, being the boundary of two main water masses – river water and the water of the Dvina

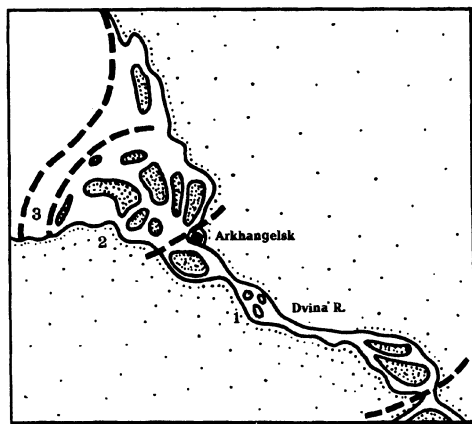


Fig. 73. The scheme of the North Dvina river mouth area (Zotin and Mikhailov, 1965). 1. Near-mouth region; 2. delta, 3. river-sea water mixing area.

Bay. The hydrological front is traced not only on the surface, but near the bottom too. The zone of maximum horizontal gradients of salinity lies at the slope of depth during the period of spring flood and is shifted towards the river, going along the line from Lebedin Island to the mouth of the Nikolsky branch during the other seasons (Artemyev *et al.*, 1984).

3.6.2. FACTORS DETERMINING C^d AND C^p BEHAVIOUR IN TIME AND SPACE

The seasonal character of the distribution of salinity, temperature, suspension and C^d and C^p in the area of mixture of waters of the North Dvina river and the Bay is shown in Figure 74. The temperature of the waters, as it should be expected, regularly increases from the winter to the summer season, from -1°C to $+18^\circ$. Salinity of surface and bottom waters during all seasons of the year, except for spring, increases in the direction towards the sea, from 0.0 to 4.3‰ in surface waters and from 0.5 to 10‰ in bottom ones. The most saline waters were found in the winter: 0.5–4.3‰, average 2.0‰ on the surface and about 10‰ near the bottom.

In spring, during the flood period, fresh waters propagate in particularly the whole thickness of waters. The value of salinity during the studied seasons correspond on the whole to the average multiyear values in the North Dvina river mouth area (Lupatchev and Makarova, 1984).

Differences of surface and bottom water salinity and the presence of clear stratification of the studied water thickness during all seasons, except the spring, testify to the different nature of water layers: surface ones are mainly river waters; bottom ones mainly sea waters. It also determines the differences of dissolved and particulate organic matter

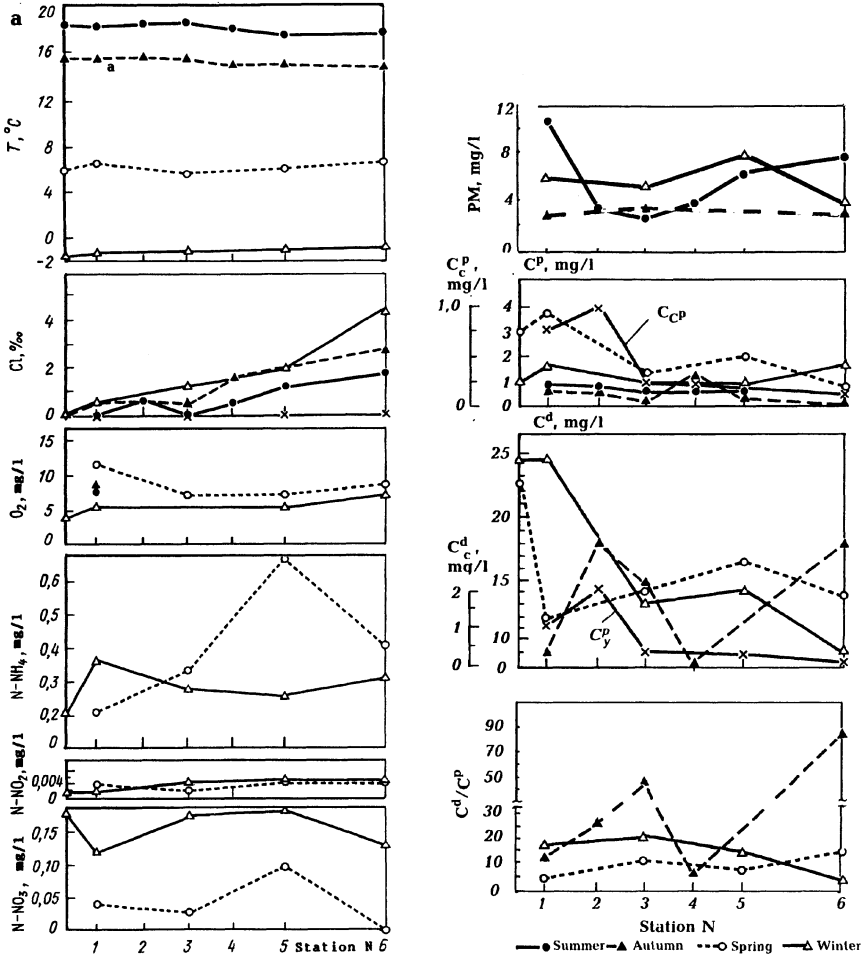


Fig. 74a. Seasonal peculiarities of the behaviour of hydrochemical components, particulate matter, C^d , C^p and carbohydrates at the profile "North Dvina river mouth-sea" (Artemyev and Romankevich, 1988). Surficial layer.

content in surface and bottom waters, their proportions in various points of section river-sea, hydrochemical and physico-chemical peculiarities of medium, etc.

Concentration of the suspension in studied waters varies from 1.8 to 10.9 mg/l averaging, for both surficial and bottom waters, 5.0 mg/l. In this case, no temporal or

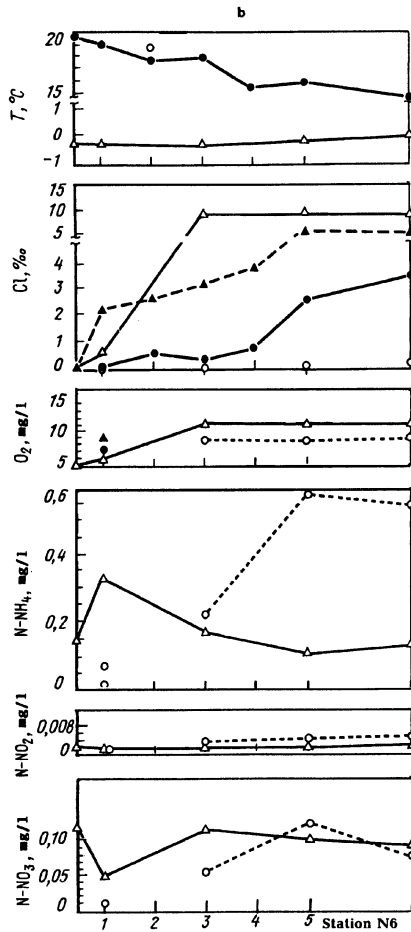


Fig. 74b. Near-bottom layer.

spatial differences are observed in the suspension concentration. Variations of suspension concentration in surface and bottom layers of water during the summer season on the river–sea section are bound up with the turbidity of the surface layer of bottom sediments as a result of mixing of water thickness by wind under the effect of turbulent processes in the bottom layer.

The share of organic matter in the studied suspension is equal to 10.9–96.1%, average 30.5% in surface waters and 39.1% in bottom ones, i.e. the main part of suspension consists, as a rule, of mineral particles. The maximum quantity of organic matter in

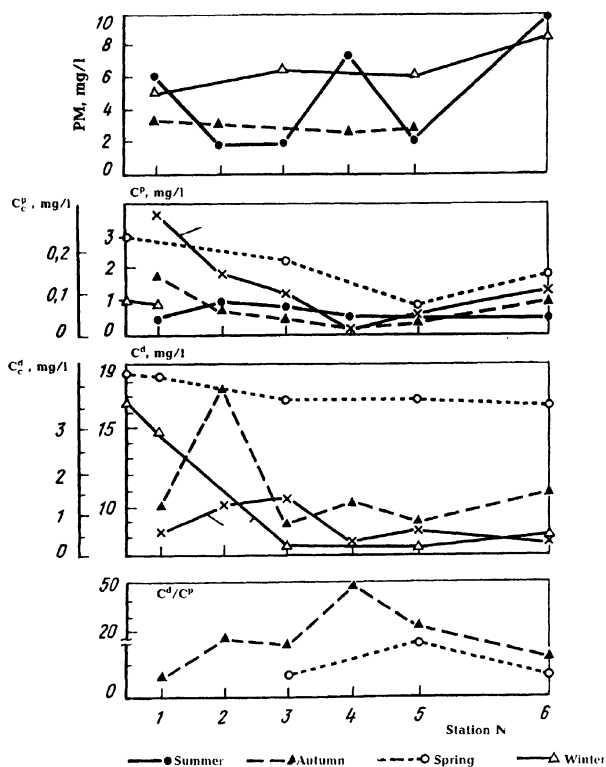


Fig. 74c. Near-bottom layer.

suspension, equal to 96.1%, was found in surface waters of the station of the section furthest from the sea, in winter.

The winter suspension is enriched with organic matter to the highest extent, compared with the suspension taken during the other seasons: 21.8–91.6%, average 46.8%.

In the organic matter of the area of mixture of the North Dvina river waters and waters of the Dvina Bay, the dissolved form prevails: 75.2–98.8%, average 91.4%. This is also indicated by the ratio of C^d and C^p at the section (Figure 74). The share of particulate organic matter is increased during the flood period, in spring, when it is equal to 5.7–24.8%, averaging 12.4% of the total organic matter.

The content of C^d and C^p in the studied waters varies respectively from 7.1 to 24.7 mg/l and from 0.2 to 3.8 mg/l, averaging 14.3 and 1.1 mg/l for surface waters and 11.6 and 1.0 mg/l for bottom waters. It is obvious from Figure 74 that the concentration of both C^d and C^p varies insignificantly, but it does vary with the increase of distance from the river mouth towards the sea, in the area of river and sea water intermixture. First of all,

attention should be paid to seasonal differences in C^d and C^p behaviour at the section river–sea. So in spring, for example, C^d concentration increases towards the sea and, on the contrary, C^p is decreased by more than three times. Since, in spring, the whole thickness in the studied region is occupied by fresh waters (Figure 74), variations of dissolved and particulate organic matter concentrations at the section river–sea cannot be bound up with the processes, typical for the regions of mixing between fresh and salt waters (flocculation, adsorption-desorption). The growth of dissolved organic matter in the direction river–sea may be bound up with the presence of anthropogenic pollutions in waters of the marine part of the section, and a particulate organic matter decrease with the deposition of suspended organic particles on the bottom.

The other processes are responsible for the behaviour of C^d and C^p in surface waters during the spring and autumn periods. Attention should be paid to the mutually opposite character of C^d and C^p behaviour in autumn at the early stages of mixture of waters in the medium part of the studied section. An increase of C^p content in these waters is followed by a decrease of C^d content, which is most often associated with flocculation of river dissolved organic matter, observed in water of similar salinity and in other areas of river and sea water intermixture studied by us. It should also be noted that the decrease in dissolved organic matter at the considered part of the section essentially exceeds the particulate organic matter growth. This is caused by the fact that only a small part of aggregates formed as a result of flocculation become a component of suspension in the surface layers of waters. Evidently, the largest aggregates are deposited on the bottom.

The mutually contrary character of C^d and C^p behaviour also caused by flocculation may be observed in winter on the far sea part of the section. Figure 75 generalizes the results of our studies of dissolved and particulate organic matter behaviour dependence upon the salinity on the section “North Dvina–Dvina Bay” for all seasons of the year. The noted peculiarities of C^d and C^p behaviour in the area of mixing between the North Dvina and the Dvina Bay waters are not isolated examples.

On the whole, variations of particulate organic matter concentrations in bottom, more salty waters of the studied section are poorly expressed. As for dissolved organic matter, attention shall be paid to stable high concentrations of C^d (about 17 mg/l) over the length of the whole section in spring. This is caused by intensive washing out of dissolved organic matter from soils by flood waters.

A sharp increase of C^d content in the beginning of the section in winter is bound up with the penetration of salt waters containing lower quantities of dissolved organic matter (compared with river waters) from the sea towards the river mouth. Therefore, and on the whole, concentration of C^d in the bottom waters on the section river–sea is lower in winter than that in surface waters. As it was already noted, any noticeable fluctuations in the behaviour of C^d and C^p in bottom waters bound up with physico-chemical processes typical for the water mixture area were not observed. In spring, fresh waters are spread in both bottom and surface layers; in autumn and winter, the salinity of waters in the bottom layer is, as a rule, higher than 10‰ which, as is obvious, does not create (or provide) the conditions required for the transformation of organic matter forms, namely its transition from the dissolved into the suspended state, and *vice versa*, under the action of physico-chemical processes (flocculation, adsorption-desorption).

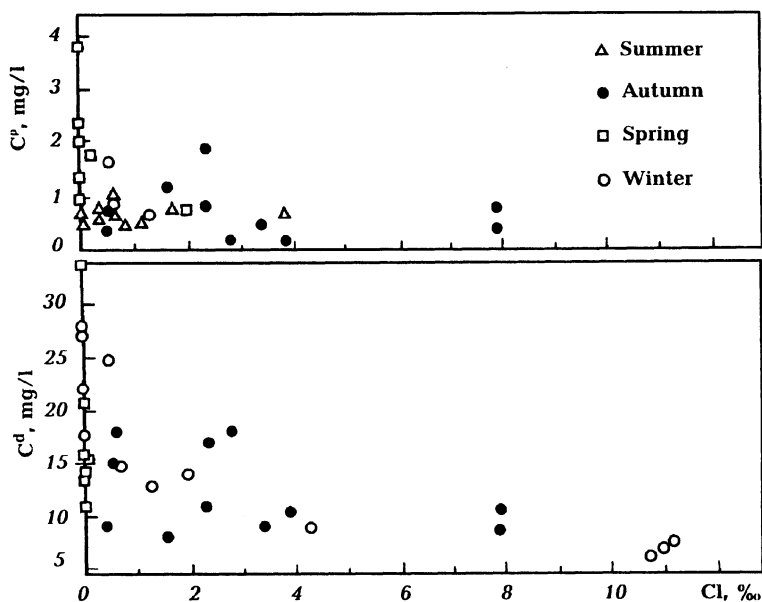


Fig. 75. C^d and C^p behaviour in the North Dvina river and sea waters mixing area in different seasons plotted against salinity (Artemyev and Lazareva, 1984; Artemyev and Romankevich, 1988).

The C^d/C^p ratio varies in the surficial layers from 3 to 90, and averages 23. In spring and winter, this values from 3 to 20. In autumn the ratio C^d/C^p increases sharply due to the decrease of the suspension concentration. In bottom waters, the ratio C^d/C^p varies from 5 to 52 and averages 18. As for surface waters, the highest values of C^d/C^p in bottom waters are typical for autumn.

Essential variations of C^d/C^p values on the section river–sea in both surface and in bottom (to a lesser extent) waters testify to the variations in the proportion of forms (dissolved and suspended) and composition of organic matter on the whole length of the section. An increase of C^d/C^p with an increase of off-shore distance is typical for both surface and bottom waters.

Since the proportion C^d/C^p for sea (oceanic) waters exceeds that for coastal waters, estuaries and near river–mouth areas of rivers, it may be considered as the index of the proportion of organic matter of continental and sea genesis for the river and sea waters intermixture area.

The analysis of particulate and dissolved carbohydrates (PC and DC) showed that these organic compounds compose a small part of organic matter (Figure 74). On average, the content of particulate carbohydrates in surface and bottom waters totals 0.06 and 0.10 mgC/l respectively (or 12.4 and 11.6% of C^p) and that of dissolved carbohydrates

equals 0.92 and 0.66 mgC/l (or 7.0 and 6.1% of C^d). When moving from the North Dvina river mouth towards the Dvina Bay, concentrations of particulate and dissolved carbohydrates increase, reaching more or less stable values by the early stages of mixing between fresh and salt waters. Thus, the non-carbohydrate components of organic matter take part in physico-chemical processes (flocculation, etc.) on the studied section river–sea, since neither particulate nor dissolved carbohydrates are subjected to any noticeable fluctuations during the process of transition from river waters to sea water.

3.6.3. CONCLUSIONS

The dissolved form noticeably predominates in the organic matter of the studied waters during all seasons; it averaged 91.4% of the sum of dissolved and particulate organic matter.

The largest quantity of organic matter in suspension, with an average of 46.8%, was found in winter, the lowest one in summer suspension, with average of 19.3%. The quantity and the quality of dissolved and particulate organic matter, peculiarities of its spatial distribution in the section river–sea are bound up with the supply of organic matter into water from the three sources: primary production of phytoplankton, with products of economic activity (for example residues of floating wood) and pollutions. The behaviour of dissolved and particulate organic matter at the studied section is a very complicated one and is characterized by alternation of maxima and minima over the entire river–sea section. In fresh waters (up to 1‰), as well as in waters with salinity exceeding 8‰, variations of organic matter concentrations are bound up with its supply from natural sources and pollutions. The physico-chemical processes (adsorption-desorption, flocculation) clearly revealed during all the seasons in 4–8‰ salinity waters, play an important role for the transformation of organic matter forms in waters of the intermixture area.

The ratio of C^d/C^p varies from 3 to 90 and averages 20, and may be considered as the index of the proportion of organic matter of continental and marine origin for the waters of the river and sea water mixing area.

The content of dissolved and suspended carbohydrates in the region of mixing between the waters of the North Dvina and the Dvina Bay averages 7.5% of C^d and 12% of C^p, i.e. the main part of the studied dissolved and particulate organic matter is represented by organic matter which are more resistant to decomposition.

3.7. Peculiarities of C^p Transportation in the Region of Intermixture of Waters of Mountain Rivers and Sea (Mzymta River–Black Sea)

The typical peculiarity of the regions of mixing between mountain rivers and sea waters is their small length and sharp transformation of all the parameters from “river” ones into “sea” ones. As is obvious from Figure 76, the zone of the maximum gradients of salinity is equal to just 0.5 km.

The distribution of suspension and C^p on the section “Mzymta river mouth–Black Sea” is characterized by the decrease of their concentrations in the direction river–sea

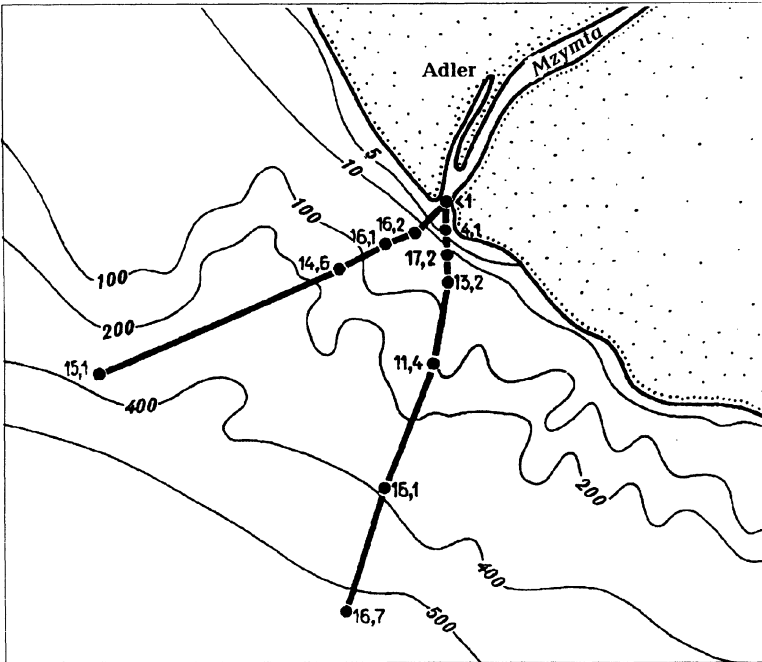


Fig. 76. Sampling stations at the profile "Mzymta river mouth-Black Sea" in May 1979.

(Figure 77). In the process of intermixture the concentration of C^p is decreased by a factor of 2.5–3, but organic matter content in the suspension composition increases.

The decrease of concentration of suspension and organic matter at the initial stages of water mixture is bound up with mechanical deposition of mainly large-sized particles. Delivery of particulate organic matter into the waters of the Mzymta river and sea water intermixture as a result of primary production processes is practically excluded due to the high turbidity of waters (more than 100 mg/l), especially near the river mouth, and due to the extremely low concentration of nutrient salts.

3.8. General Regularities for the Behaviour of Dissolved and Suspended Organic Substances in River and Sea Water Intermixture Regions (Comparative Analysis)

The results of the laboratory modelling of processes of intermixing of river and sea waters, and the data of natural observations in the regions of river and sea water intermixture, showed that the process of transformation of dissolved into particulate organic matter, and *vice versa*, takes place at all the stages of water intermixture (but most actively in waters

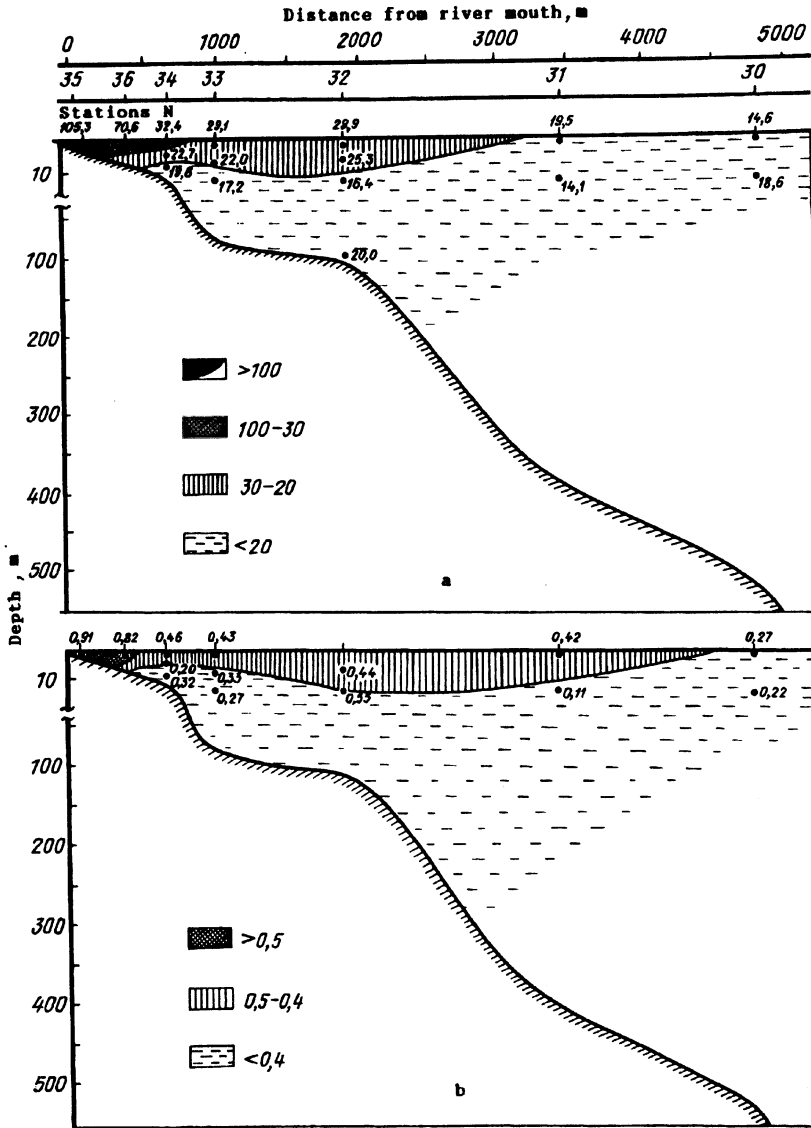


Fig. 77. Vertical distribution of particulate matter (a) and CP (b) at the profile "Mzymta river mouth-sea" in May 1979.

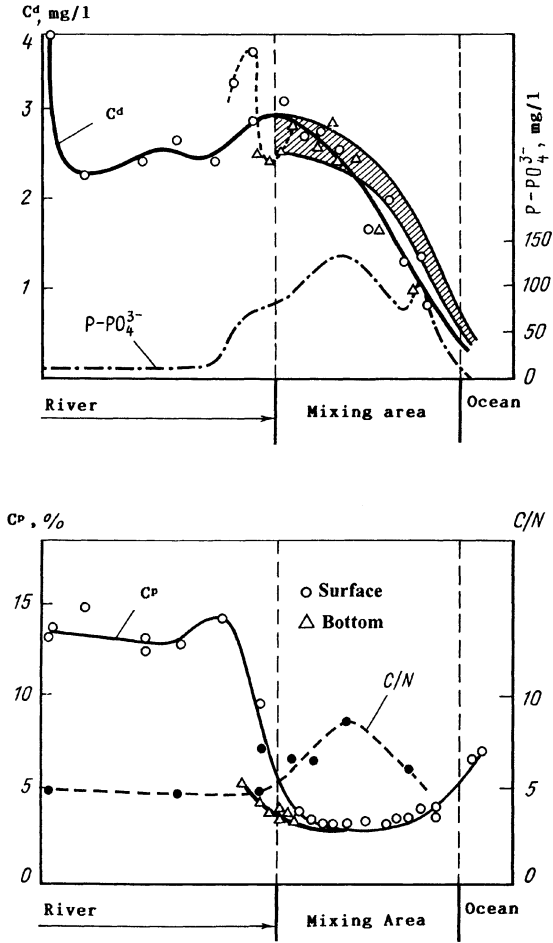


Fig. 78. C^d and C^p behaviour in the area of the Loire river and ocean waters mixing (Salot *et al.*, 1984).

with salinities of 5–10‰) as a result of flocculation and adsorption-desorption processes. The behaviour of C^d in the studied waters depending upon the salinity does not correspond to the simple dilution line, but is characterized by alternating high and low concentrations of dissolved and particulate organic matter.

The quantity and the quality of organic matter in the river and sea water mixing regions, especially spatial distribution, are bound up with the delivery of organic matter from

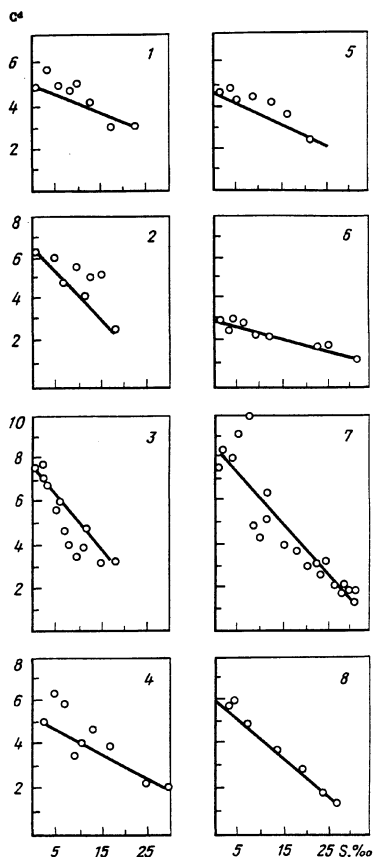


Fig. 79. C^d behaviour in estuaries (Fox, 1983). Estuaries: Murderkill (1, 9); Leipsic (2, 13); Mullica (1980) (3, 11); Broadkill (10, 1978) (4); St. Jones (5, 10); Delaware (6, 14); Mullica (1979) (7, 15); Broadkill (05, 1978) (8); Broadkill (12); Mispillian (16); 9–16 see Figure 80.

various sources (soils, plankton, phytobenthos, pollutions, etc.) and with hydrodynamic factors (direction and velocity of currents, peculiarities of water stratification).

The estimation of river organic matter “losses” in the case of mixture of river and sea waters was given in the example of the Amazon estuary by means of the developed model: for dissolved organic matter it is equal to 25%, for particulate organic matter it is 80%. These results correlate well with the data of Edmond *et al.* (1981), according to whom the quantity of C^p in the Amazon estuary is decreased by 60–70% compared with river particulate organic matter, which in the opinion of the authors is caused by partial mineralization of particulate organic matter in the tidal zone, or in the estuary at

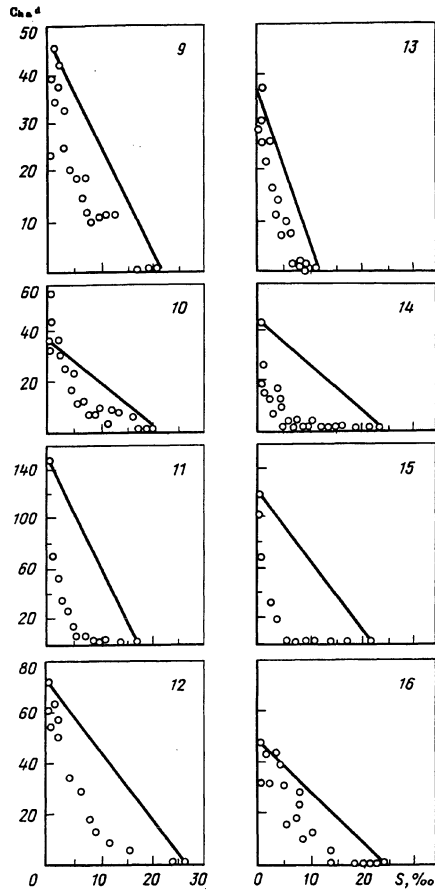


Fig. 80. Dissolved humic acids behaviour in estuaries (Fox, 1983).

low salinities, i.e. at the initial stages of water mixture. By the data of Eisma *et al.* (1985), only 25% or less of particulate organic matter delivered by rivers is supplied to the sea, and the largest part of river particulate organic matter is fractured and mineralized in estuaries. From the data of Degens and Ittekkot (1985), up to 70% of C^p may be destructed in the coastal sea medium.

Comparative consideration of the factors determining organic matter behaviour in the studied regions of river and sea waters intermixture showed that physico-chemical processes (flocculation, adsorption-desorption) are the first to be responsible for changes in the proportion of dissolved and particulate organic matter at the initial stages of water in-

termixture, with salinities of up to 10‰. The effect of the processes of primary production of organic matter by phytoplankton on the delivery of dissolved and particulate organic matter to estuaries is revealed only at a distance from the river mouth in waters accessible to the penetration of light. The distance between these waters and the river mouth is determined by several factors: river run-off value, concentration of suspension and the character of water circulation in the sea or ocean neighbouring the river mouth. So, in the Amazon estuary (where concentration of suspension in river mouth is 100–150 mg/l) high values of primary production of phytoplankton are observed at a distance of 150 km from the river mouth, in waters with salinity of 10–12‰, where suspension concentration is equal to 5–10 mg/l.

In the Temryuk, Taganrog and Riga Bays (where concentration of suspension in the mouths of the studied rivers is 40–60 mg/l) high values of primary production of phytoplankton are observed 5–7 km from the river mouths, in waters with salinity of 4–6‰ where suspension concentration is 10–30 mg/l.

Peculiarities, revealed by us, of C^d and C^p behaviour in estuaries and regions of intermixture of river and sea waters confirm the studies of foreign scientists. So the mutually contrary character of the behaviour of C^d and C^p in the region of the transition from river to oceanic waters was found in the estuary of the Loire river, see Figure 78 (Saliot *et al.*, 1984). The non-conservative behaviour of organic matter was observed in the majority of studied estuaries of the Atlantic coast of the U.S.A. (Figures 79 and 80; Fox, 1983), England (Hunter and Liss, 1982), in the estuaries of the Elba and Ems rivers (Michaelis *et al.*, 1986) and the Yang Tze and Yellow rivers (Cauwet and Mackenzie, 1993).

The areas of mixing of the North Dvina river and the Dvina Bay waters are characterized by suspension which is the richest in organic matter of all the studied regions: 46.8% in winter and 19.3% in summer. Content of organic matter in suspension in estuaries of moderate latitudes averages, as a rule, 9.4%.

The similar character of behaviour of C^p and a number of micro-elements (copper, nickel, zinc) in the studied regions of river and sea water intermixture with increase of salinity (Temryuk and Riga Bays) testifies to their interaction and transportation in the form of complexes organic matter–metal or sorption complexes.

Variation of dissolved and particulate organic matter composition in the regions of river and sea water intermixture is affected by phytoplankton, which in particular plays the main role in the delivery of dissolved carbohydrates into water.

Chapter 4

TRANSFORMATION OF PARTICULATE ORGANIC MATTER AND ORGANIC MATTER OF BOTTOM SEDIMENTS IN RIVER–SEA SYSTEM

Dissolved and particulate organic matter transported to the ocean with river run-off affect the distribution and composition of organic matter in sea sediments. Organic matter serves as the regulator of many biogeochemical processes in both the water column and in bottom sediments. These processes are bound up with the formation of many minerals, including a number of rare and non-ferrous metals. Therefore, the knowledge of the nature and regularities of the distribution of organic compounds in waters and sediments of the river–sea system is extremely important for the knowledge of sedimentation processes in the ocean.

4.1. Amazon River–Atlantic Ocean (Tropical Climatic Zone)

The studied organic compounds in the suspension and bottom sediments of the Amazon estuary include amino acids, humic acids and bitumoids (Artemyev and Lazareva, 1986; Artemyev and Danyushevskaya, 1988).

The content of amino acids in suspension of the Amazon estuary varies from 0.020 to 0.030% and averages 0.027%, converting into dry weight of suspension, and to 0.09% of organic matter. Compared with the river suspension, the content of amino acids in the Amazon estuary is lower.

As a natural result, the content of amino acids in the suspension decreases with an increase of distance from the river mouth towards the ocean (Table 25).

The proportion of amino acids groups varies in the direction river–ocean: the share of neutral amino acids is increased from 49.9% in river waters to 54.5% in the estuary waters, and the content of basic amino acids is decreased from 16.3 to 12.1%. The following acids prevail among the individual acids in the Amazon estuary (in decreasing order): glycine, glutamic acid and proline, and glutamic acid-glycine-asparagin acid in river waters.

Table 50. Organic carbon (C^P) and particulate carbohydrates (C_c^P) on the section "Amazon river–Atlantic Ocean" (Artemyev and Lazareva, 1986).

Station No.	S, ‰	C^P , mg/l	C_c^P in carbohydrate fraction, %				C_c^P , $\mu\text{g/l}$	C_c^P % of C^P	$C_c^P(3+4)/C_c^P$
			1	2	3	4			
1042	0.01	2.0	27.4	9.6	36.7	27.4	230	11.5	2.3
1043	0.02	1.4	20.3	22.5	15.0	42.1	133	9.5	2.8
1044-4	0.83	1.9	44.6	9.9	9.9	36.2	251	13.2	1.0
1044-8	1.26	2.0	12.6	17.3	30.7	39.3	127	6.3	5.5
1052	9.79	1.2	25.0	7.1	23.2	44.6	56	4.7	2.7
1050	10.66	0.7	56.5	25.3	10.1	8.2	269	38.4	0.3
1049	17.52	1.4	33.8	4.2	36.6	25.3	71	5.0	1.8
1047	22.18	1.1	37.0	14.8	18.5	29.6	54	4.9	1.3
1045	38.24	0.3	36.8	5.3	15.8	42.1	19	6.3	1.6
Average		1.3	32.7	12.9	21.5	32.5	134	11.0	2.1

Note: Fraction of carbohydrates: 1 = aqueous; 2 = alkaline, 3 = weak acid, 4 = strong acid.

The study of carbohydrates in the Amazon estuary showed (Table 50) that their concentration varies from 19 to 269 $\mu\text{g/l}$ and averages 134 $\mu\text{g/l}$. The share of particulate carbohydrates in particulate organic matter varies from 4.7 to 38.4%, average 11%. Aqueous, alkaline, weak acid and strong acid fractions in particulate carbohydrates composition are equal to 32.7, 12.9, 21.5, 32.5% respectively. Thus, about 50% of all particulate carbohydrates is represented by reactable compounds.

Comparative analysis of carbohydrate behaviour in suspension on the section "Amazon river–Atlantic Ocean" (Table 50) shows that river waters, waters of intermixture region and ocean waters differ noticeably by their composition of carbohydrates. The index of such differences may be the ratio of carbohydrates of acid fractions, most resistant to decomposition structure polysaccharides, to carbohydrates of aqueous fraction, to mainly reserve polysaccharides and oligosaccharides (Artemyev, 1976). As it is obvious from Table 50, this ratio for river waters averages 2.5, for intermixture areas 3.1 and for waters with salinity exceeding 17‰ it averages 1.6.

Thus, the least labile and reactive carbohydrates are particulate carbohydrates of river waters (mainly of soil origin). In ocean waters where the main source of organic matter is phytoplankton, particulate carbohydrates are more labile. In the estuary waters, as it is obvious, one may meet particulate carbohydrates which differ in their composition and degree of reactivity.

The most variable concentrations of particulate carbohydrates are in aqueous and acid (sum of weak and strong acid) fractions. So, within the borders of water intermixture we may separate two clear maxima of particulate carbohydrates content in the aqueous fraction, in waters with salinities of about 1‰ (station 1044-4) and about 11‰ (station 1050) where they are equal to 44.6 and 55.5% respectively. It is obvious from the given

data (Table 45, Figure 48) that the essential “losses” of dissolved organic matter take place just in these waters of the intermixture region as a result of the flocculation process and dissolved organic matter transition into the suspended form.

High contents of carbohydrates in the aqueous fraction of suspension at these stations testify that at least a part of organic matter transformed into the suspended form from the dissolved one in the composition of floccules is represented by reactive carbohydrates. The first maximum is followed by a sharp decrease of aqueous fraction content (Table 50), this being caused by the particulate organic matter desorption process taking place here, as a result of which the most labile compounds are the first to be transformed into dissolved form; those are carbohydrates of aqueous fraction (for example, water-soluble oligo- and polysaccharides). In water with high salinity (more than 17‰) of the studied section, the composition of particulate carbohydrates is stabilized, which is testified by the insignificantly varying (with increase of salinity) ratio of reactive (aqueous fraction) and decomposition resistant (acid fraction) carbohydrates. It may be only noted that with the decrease of distance to typically ocean waters the share of carbohydrates of strong acid fraction, which are most resistant to decomposition, increases.

According to the data of analysis of carbohydrates by gas-liquid chromatography, the following compositions of monosaccharides of aqueous and alkaline fraction of river suspension predominate (Table 50): rhamnose; arabinose; xylose; and ribose, which are respectively equal to 26.6; 24.3; 26.6; 19.8% and 28.9; 18.0; 16.2, 26.0% of the sum of monosaccharides.

Glucose and galactose were found in these fractions in trace quantities, but their content in the weak acid fraction is increased to 7.3% (glucose) and 3.3% (galactose). Application of gas-liquid chromatography for the analysis of particulate carbohydrates made it possible to determine the monosaccharide composition of those parts of particulate carbohydrates which, evidently, participate in the processes of flocculation during transportation of organic matter in the estuary waters.

Humic acids were not found in the Amazon estuary suspension and in river suspension (Table 31). Consequently, the process of transformation of organic matter towards the formation of geopolymers of humic acid type (humification) is not typical for river and estuary suspension, in contrast to pelagic processes of the ocean, where according to the data of Romankevich (1977) particulate organic matter composition includes humic acids with an average of 6.2%. In our opinion, this is bound up with various sources of particulate organic matter in the river–sea system (mostly terrigenous) and in the ocean pelagic (mainly planktonic) which may or may not be able to be transformed into geopolymers of humic acid type.

The typical peculiarity of particulate organic matter composition variation towards “the Amazon–estuary–ocean” is the decrease in the content of bitumoids (first of all of bitumoid A_{cl}), transformed, evidently, into “residual” organic matter or “complex” organic matter (Fichez *et al.*, 1993) or humines (Romankevich, 1977) resistant to chemical and biological fracture. Thus, the transformation of organic matter in the direction river–estuary–ocean is characterized by two interconnected processes: “debituminization–humification”.

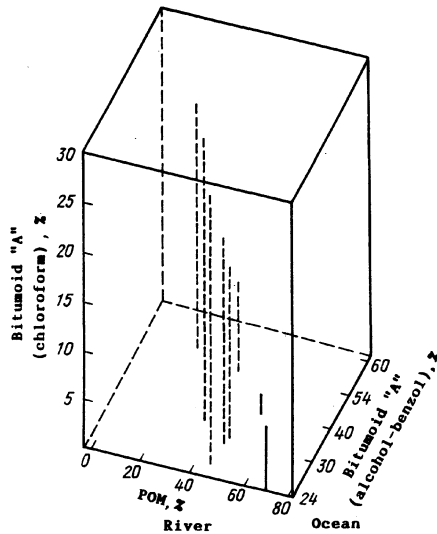


Fig. 81. Change of particulate organic matter composition in the Amazon river–ocean system.

The boundary of river run-off effect on the composition of organic matter in the system river–estuary–ocean may be set by a sharp change of organic matter composition in the direction river–sea (Figures 81 and 82).¹

The shelf in front of the Amazon river reaches a width of 300 km, narrowing noticeably northwards. Noticeable features of the shelf and continental slope are numerous canyons. The main canyon of the Amazon begins at the depth of 50 m and is traced to depths of 1.5 km (Demuth and Kumar, 1975). A part of the shelf and the slope are occupied by the Amazon debris cone (fan), which extends 650–700 km, reaching a depth of 4750 m.

The main part of the Amazon river “solid” run-off is accumulated on the shelf. Fine-grained muds occur in the immediate vicinity of the river mouth, up to the 60 m isobath, followed by the strip of sands. Deposition of muds near the river mouth is bound up with high rates of sedimentation of river deposits, exceeding 2 cm/year (Kuehl *et al.*, 1982).

The studied bottom sediments of the Amazon estuary are represented by mainly terrigenous pelite muds (Table 21) with insignificant amounts of amorphous silica and calcium carbonate (average 0.5 and 0.2% respectively). Content of C_{org} in these sediments is equal to 0.29–1.67%, averaging 0.47%, with nitrogen from traces up to 0.05%. The ratio C/N averages 11.8.

With an increase of the distance from the river mouth towards the ocean, the content of organic matter in terrigenous muds decreases from 5.3 to 0.9%.

¹The other possible criteria to distinguish organic matter inputs and origin are biomarkers (Lauveillard and Saliot, 1993).

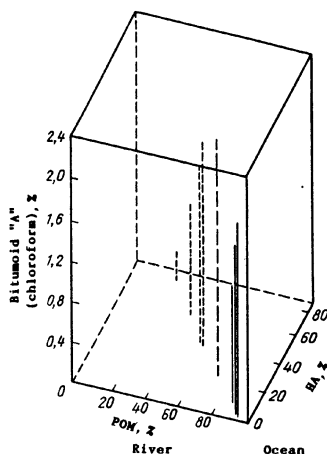


Fig. 82. Change of terrigenous muds organic matter composition in the Amazon river–ocean system.

Similar values of concentrations of C_{org} and nitrogen were found in the deltaic sediments of Arctic Alaska (Naidu, 1985). As it is obvious from Table 21, the value C/N decreases towards the river mouth, which is caused by the decrease of the quantity of terrigenous organic material and an increase of the share of “sea” organic matter in bottom sediments. Terrigenous organic matter is enriched with residues of higher plants with high content of lignin and cellulose, and therefore with a higher C/N ratio. In contrast to this, the sea biogenic residues are relatively enriched with nitrogen-containing compounds, such as proteins, pigments, etc. (Naidu, 1985).

Content of humic acids in terrigenous muds of the Amazon estuary is essentially lower compared with river muds (Tables 25 and 26) and averages 0.04%, converting into dry residue weight, and 8.3% of organic matter (in river muds it is equal to 2.39 and 47.7%, respectively).

Content of bitumoid A_{cl} and $A_{al,b}$ in the estuary muds remains approximately the same as in the river, and is equal in sum to 3.8% of organic matter (in river muds 3.7%).

Content of the least reactive and resistant to decomposition “residual” organic matter (humines) is considerably increased in the estuary muds, averaging 87.8% (in river muds 48.6%).

Thus, the predominating process in terrigenous muds in the direction river–estuary–ocean is dehumification–humination, i.e. the fracture of humic acids and the relative increase of the share of humines, which are stable to decomposition in this context. The boundary separating bottom sediments with river type organic matter from bottom sediments with ocean type organic matter (Figure 82) may be set by the variation of ratio of basic components (bitumoids, humic acids, “residual” organic matter) in the composition of organic matter of bottom sediments in the direction river–ocean.

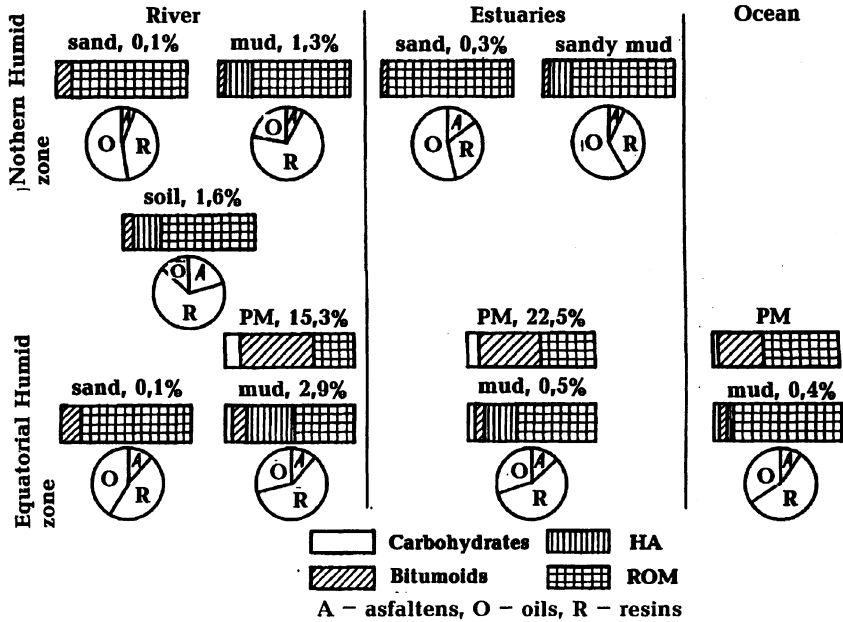


Fig. 83. Transformation of particulate matter and bottom sediments organic matter composition in the river-sea system.

The study of A_{cl} composition in terrigenous muds of the Amazon estuary showed its similarity with bitumoid A_{cl} in river muds in both northern humid and in equatorial humid zones, which testifies to their genetic similarity (Figures 83 and 84).

In the line "suspension-bottom sediments" we observe a sharp decrease of organic matter content (by approximately 40 times) which is bound up with its utilization by plankton, benthos and micro-organisms in the water column and on the boundary water-bottom.

The content of bitumoid $A_{cl+al,b}$ in the composition of organic matter of bottom sediments is essentially lower when compared with particulate matter, from 47.6% (suspension) to 3.8%, mainly at the expense of bitumoid A_{al-b} ; humic acids appear (terrigenous muds) and the content of "residual" organic matter is increased considerably. Thus, the typical process of organic matter composition transformation in the line "suspension-terrigenous muds" in the estuary, as in the river, are humification-debituminization.

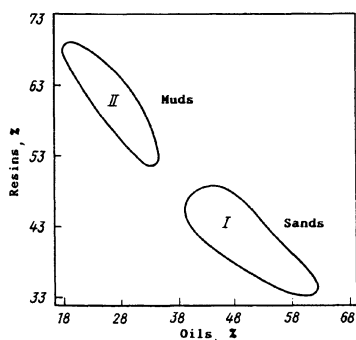


Fig. 84. The composition of chloroform bitumoid "A" in organic matter of terrigenous muds and sands in the river-sea system (Romankevich *et al.*, 1982; Danyushevskaya, 1984; Romankevich and Danyushevskaya, 1987; and the author).

4.2. North Dvina River-White Sea (Northern Climatic Zone)

The shores of the Dvina Bay, located in the eastern part of the White Sea are formed by residual rocks. The Dvina Bay was formed on the old skerries. The White Sea formation began here; the eastern boundary of this sea has existed for millions of years (Palenichko, 1968).

The southern part of the Dvina Bay is mainly characterized by large-sized detrital fractions (sandy, with gravel-pebble admixture). The North Dvina river run-off transports into the bay mainly fine pelite suspensions, as well as some quantities of sandy-aleurite material (Kalinenko *et al.*, 1976).

The delta and river-mouth regions of the White Sea are characterized by the diversity of colours of the granular components of sediments, with prevailing aleurite differences between the sediments. This complex is characterized by a sharply expressed patchy distribution of various granular types of sediments directly neighbouring each other.

Bottom sediments of the White Sea are characterized by C_{org} distribution zonality, bound up with hydrodynamics, depth and bottom relief, as well as by the relation of C_{org} distribution with river run-off deposits, primarily of the large rivers such as the North Dvina and the Onega rivers (Nevesky *et al.*, 1977). At the same time, the data on distribution of C_{org} in bottom sediments of the Dvina Bay, respectively in its river mouth part (southern), are practically absent.

As it is obvious from Table 18, the content of C_{org} in bottom sediments of the "sea" part of the section "North Dvina river mouth-Dvina Bay" in the river and sea water intermixture area is equal to 0.32-0.96%, averaging 0.59% (or 1.07% converting into organic matter), the content of nitrogen being equal to 0.006-0.029%, average 0.020%, and the ratio C/N varying from 16.5 to 53.3 and averages 34.3.

The typical process of transformation of organic matter composition of sands in the river-sea system is "debituminization", accompanied with an increase of the "residual"

organic matter share in organic matter composition. Absence of humic acids in organic matter of sand in the “North Dvina river–sea” system also indicates that humification of organic matter does not take place due to sharply oxidizing conditions, helping the destruction of labile organic matter, being a potential base for the formation of geopolymers of humic acid type.

Another peculiarity of organic matter of sands in the “North Dvina–sea” system is the similarity of composition of bitumoid A_{cl} in river and estuary sands, which differs essentially from composition of bitumoid A_{cl} of terrigenous muds (Figure 83). Thus, independently from various climatic conditions for the formation of bottom sediments organic matter, terrigenous sands in the river–sea system have the same bitumoid A_{cl} composition.

The distinctive peculiarity of terrigenous mud organic matter composition variation, as in the equatorial zone, in the direction “North Dvina–sea” is “dehumification”, and as a consequence of this there is an increase of the share of humines in organic matter composition. Consequently, the trend of transformation process for terrigenous mud organic matter composition in the river–sea system is “dehumification–humination”.

The composition of bitumoid A_{cl} in complexes with grains from North Dvina river bottom sediments (sandy muds with admixture of aleurite material) differs from the composition of bitumoid A_{cl} of river muds and estuary muds, and occupies an intermediate place between sands and muds.

Comparison between the distribution character for C^p and C_{org} of bottom sediments on the section “North Dvina river mouth–Dvina Bay” (Figure 85) gives a possibility to witness a number of peculiarities in their behaviour. C^p is characterized by a decrease in concentrations in the direction from the river mouth to the sea by both observational data during various seasons and by averaged data. Variations of C^p concentrations observed in river waters are related to the inhomogeneity of rivers particulate organic matter composition at various sections of the river mouth. Low concentrations of C_{org} (about 0.1%) are typical for river bottom sediments, medium-grained sands, and high concentrations of C_{org} (0.5–1.0%) for sediments in the river and sea water intermixture area, which are also mainly sands. The highest concentrations of C_{org} were marked in aleurites with admixtures of clay muds, which is bound up with their superior sorption ability, when compared with sands. Thus, we do not observe the uniformity in distribution of C^p and C_{org} in bottom sediments on the studied river–sea section. This is mainly bound up with the peculiarities of the considered region being the geochemical barrier. On the one side of the barrier, in river waters the content of C_{org} in bottom sediments is extremely low, despite high concentrations of C^p . This is caused by the fact that fine particles of suspension, which are enriched with organic matter to the greatest extent, have no favourable conditions for sedimentation due to the high velocity of the current. On the other side of the barrier, in waters of river and sea water admixture, the concentration of C^p is lower than in the river waters, but C_{org} content in bottom sediments (fine- and medium-grained sands) is higher than that in similarly composed river sediments (Table 18). This is associated to a considerable extent with more favourable hydrodynamic conditions for sedimentation of suspended particles, mainly due to a decrease of water current velocity.

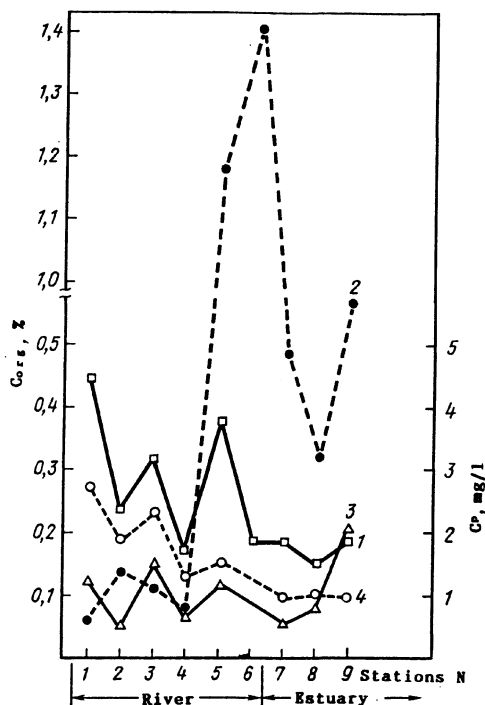


Fig. 85. The behaviour of C_p (1, 3, 4) and bottom sediments C_{org} (2) of the profile "North Dvina river mouth-sea" in different seasons. 1. Spring; 3. winter; 4. middle data (Artemyev *et al.*, 1984; Danyushevskaya *et al.*, 1990).

4.3. Peculiarities of Particulate Organic Matter Transformation on the Periphery of River-Ocean Water Mixing Area and Ocean Water (Mozambique Channel)

In February–June 1981 during the 32nd cruise of the research vessel "Akademik Kurchatov" we studied the peculiarities of organic matter composition transformation in water, suspension and bottom sediments on the periphery of river and ocean water mixing area in waters neighbouring the Limpopo (plankton, water, suspension, bottom sediments) and the Zambezi (suspension, bottom sediments) river mouths (Figures 86 and 87).

The studies were carried out in poorly refreshed waters with salinity of 30–35‰ which were propagated to the south-west from the Limpopo river mouth, under the effect of the Mozambique stream (Figure 88). The station nearest to the river mouth was located 3–5 km from the coast. It is obvious from Figure 88 that the Limpopo run-off effects the character of the distribution of all the studied parameters: suspension, plankton and

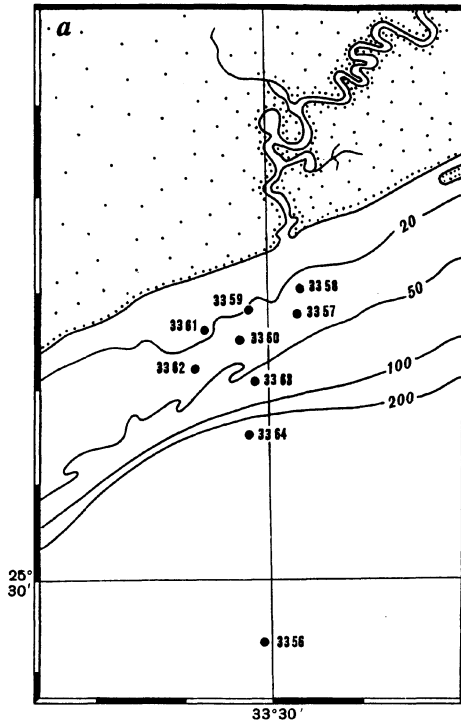


Fig. 86. Sampling stations at the profile "Limpopo river mouth-ocean" (May 1981).

organic matter. Their higher concentrations are near the zone of the refreshed waters and decrease towards the open ocean, reaching more or less stable values in waters with salinity of 35‰ and more, i.e. those which are not subjected to the influence of river run-off. The propagation of zones of high index concentrations towards the south-west is determined by the Mozambique Stream, and the decrease of concentrations with an increase of distance from the Limpopo river mouth is a result of both dilution of river waters with oceanic waters and the effect of flocculation processes (or adsorption-desorption) taking place on the boundary of refreshed and salt waters. The process of variation (decreasing) of all the studied components' concentrations towards the section "Limpopo river mouth-ocean" is accomplished with transition to ocean waters, and therefore the boundary of concentration stabilization is the 35‰ isohaline.

Concentration of suspension on the section "Limpopo river mouth-ocean" varies from 0.3 to 2 mg/l and is equal to 1.5–1.7 mg/l in the region of the Limpopo river mouth, and to 0.3–0.6 mg/l at the remote ocean stations (Figure 88). The suspension content in coastal

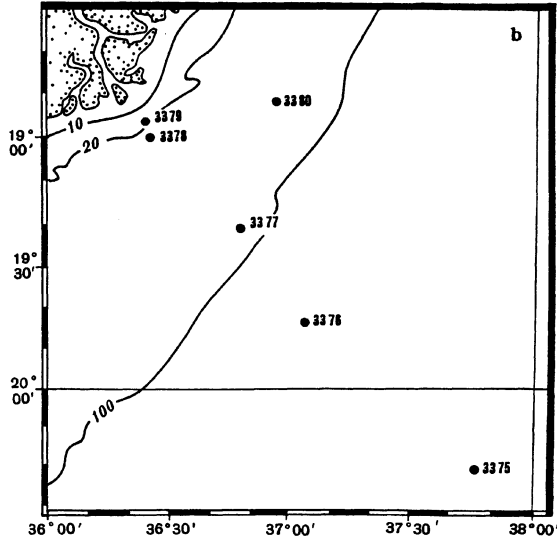


Fig. 87. Sampling stations at the profile "Zambezi river mouth-ocean" (May 1981).

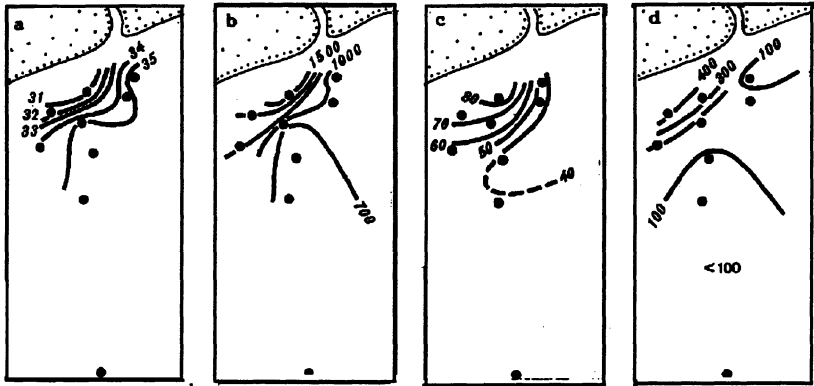


Fig. 88. Distribution of salinity (a), particulate matter, mg/l (b) plankton biomass, mg/m³ (c), CP, mg/l (d), in the Mozambique channel waters adjacent to the Limpopo river mouth (Artemyev, 1982).

waters does not essentially vary vertically, from the surface to the bottom (2 m from bottom) layer of water. In spite of the effect (although a minor one) of river run-off, plankton in the studied region are mainly oceanic, but for that at one station (3357) where the brackish

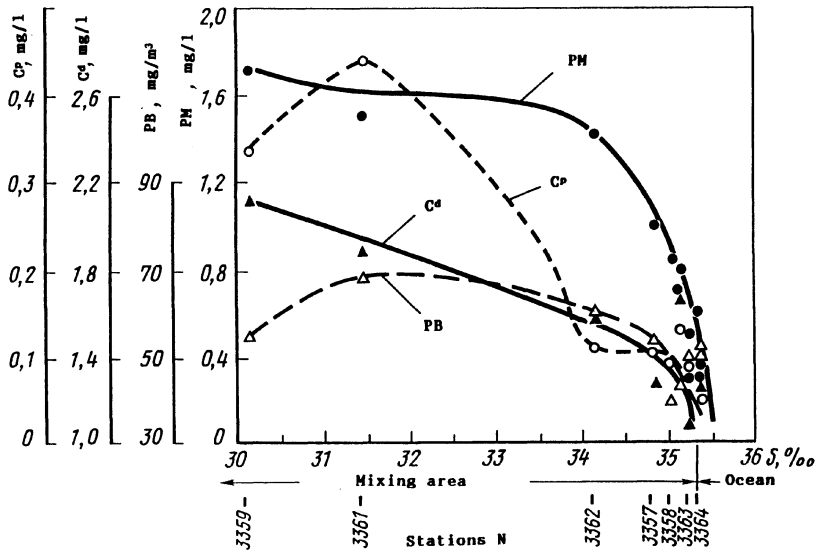


Fig. 89. Dependence of particulate matter, plankton biomass, C^d and C^p concentrations on salinity at the periphery of Limpopo river and ocean waters mixing area (Artemyev, 1982).

tolerant *Acartia* genus was found (Ponomareva, 1982). The biomass of plankton on the studied section is equal to 34–86 mg/m^3 , average 55 mg/m^3 , which is essentially lower than in the productive waters of the Indian Ocean. The character of the plankton biomass distribution on the section is similar to that for suspension (Figure 89) and explained by the proximity of its high concentrations to waters enriched with biogenous substances, delivered to coastal waters with river run-off.

Poorly refreshed waters on the studied section are characterized by high (compared with oceanic waters) concentrations of C^d . The source of C^d is river run-off and plankton. Content of C^d in the studied waters exceed C^p content by an order, and is equal to 1.2–2.4 mg/l , averaging 1.5 mg/l .

Content of C^p on the section "Limpopo river–ocean" varies from 0.014 to 0.443 mg/l and averages 0.12 mg/l . As it is obvious, the concentration of suspended organic material exceeds the biomass of plankton by several times, especially in coastal waters (Figure 88). The sources of particulate organic matter in the studied section are not only planktonic organisms, residues of their tissues, etc., but also the river run-off. Comparison of the character of distribution of the plankton biomass and C^p shows that terrigenous organic matter in the total quantity of particulate organic matter prevails noticeably in refreshed waters; in the direction of the "Limpopo river mouth–ocean" its content decreases, and the share of C^p in suspension varies from 30% in the Limpopo river mouth to 10–15% in the Mozambique Channel waters far from the river mouth. Content of C^p in the zone of

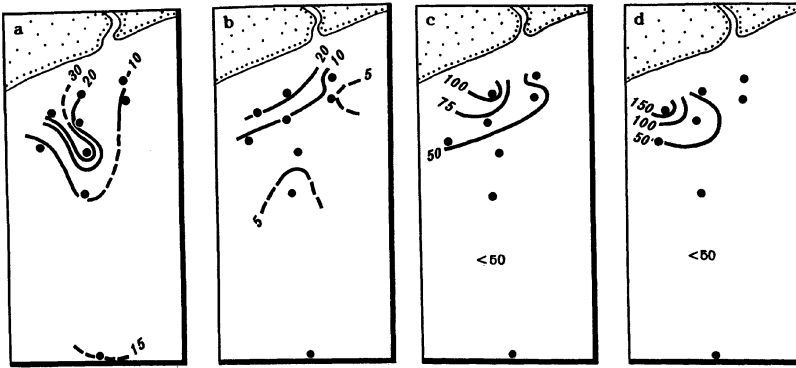


Fig. 90. Distribution of CP, % (a), carbohydrates, $\mu\text{gC/l}$ (b), lipids, $\mu\text{gC/l}$ (c), lignin, $\mu\text{gC/l}$ (d) in oceanic waters adjacent to Limpopo river waters (Artemyev, 1982).

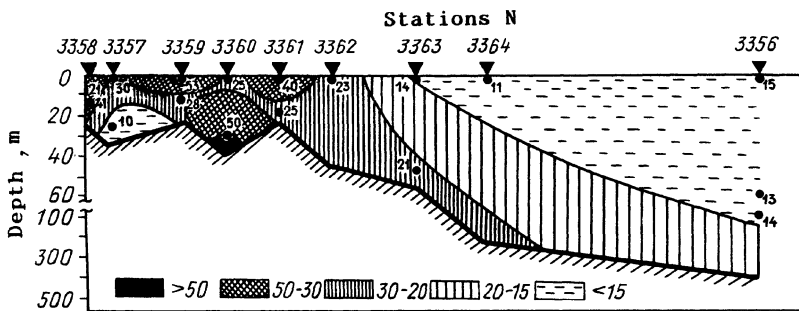


Fig. 91. Vertical distribution of particulate carbohydrates ($\mu\text{g/l}$) at the profile "Limpopo river mouth-ocean" (March-April 1981).

refreshed waters decreases vertically from the surface to the bottom by a factor of 1.5–2. Here we also observe the decrease of particulate organic matter in suspension composition, approximately by 30%. This is bound up not only with destruction of organic compounds during sedimentation, which is typical for open regions of the ocean, but also with the differences in genesis of particulate organic matter in surface and bottom water layers in the river-mouth regions. The source of particulate organic matter of surface water layers here are primarily river waters and plankton, and in the bottom waters the source is suspended particles, brought from other regions of the ocean.

As it was already noted, the main feature of distribution of individual components of particulate organic matter (carbohydrates, lipids, lignin) on the section "Limpopo river-ocean" is expressed by the decrease of their absolute concentrations when moving towards the ocean (Figures 90 and 91). The content of carbohydrates varies from 4 to 21 $\mu\text{g/l}$ and averages 10 $\mu\text{g/l}$. The content of particulate carbohydrates in bottom

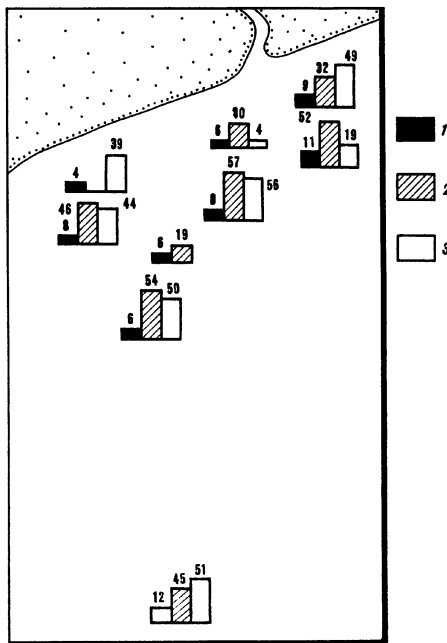


Fig. 92. Carbohydrates (1), lipids (2) and lignin (3) in the particulate organic matter (%) at the profile "Limpopo river mouth-ocean" (Artemyev, 1982).

layers, especially in refreshed waters is, as a rule, lower than that for surface waters. The content of carbohydrates of particulate organic matter composition varies from 3.6 to 42.8% and averages 12.8%. The content of carbohydrates of particulate organic matter composition in bottom water layers increases, as a rule, because of selective preservation of decompositionally resistant structural polysaccharides of the cellular walls of planktonic organisms in the composition of particulate organic matter (Artemyev, 1976). On the whole, it is obvious that carbohydrates equal an insignificant part of the total sum of organic matter.

In the studied samples of suspension, lipids are equal to 18–101 $\mu\text{g/l}$, average 45 $\mu\text{g/l}$. When moving away from the Limpopo river mouth to the ocean, their content in surface waters decreases from 100 to 20 mg/l (Figure 90). The content of lipids of particulate organic matter composition varies from 18.7 to 55.5% and averages 40.7%; consequently, lipids are one of the basic components of the studied suspension organic matter.

The content of lignin in surface suspension, and more precisely the content of one of the basic lignin components, paraoxybenzaldehyde, varies from 15 to 174 $\mu\text{g/l}$ and averaged 54 $\mu\text{g/l}$. In the direction of the ocean, the content of lignin in suspension decreases from 150 to 20–30 $\mu\text{g/l}$ (Figure 90). The share of lignin in particulate organic

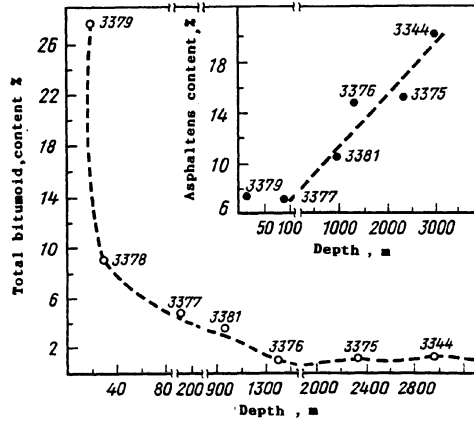


Fig. 93. Change of bitumoid content in organic matter of the surficial layer of bottom sediments at the profile "Zambezi river-ocean" (Danyushevskaya and Romankevich, 1987).

matter composition is equal to 4.4–55.8%, averaging 39.0%. When moving away from the Limpopo river mouth towards the ocean, the content of lignin of particulate organic matter composition increases (Figure 92). In the ocean regions located far from the continent, the main source of lignin in suspension and bottom sediments may be atmospheric dust, containing spores and pollen of ground plants (Bobileva, 1982).

The results of studying organic matter composition of bottom sediments on the sections "Zambezi river mouth-ocean" and "Limpopo river mouth-ocean" by Danyushevskaya *et al.* (1990) showed that the content of C_{org} in terrigenous pelite and aleurite-pelite muds was equal to 0.16–2.2%, biogenous amorphous silica was equal to 0.08–0.62%, nitrogen was equal to 0.04–0.16%, and the ratio C/N varied from 10 to 26.

Bottom sediments on the studied sections are characterized by bitumoid concentrations, close to the background one for the World Ocean (content of bitumoid A_{c1} averages 0.9% of organic matter). High bitumoid content is typical for the fine-grained sands of the Zambezi (Figure 93). In the upper layer of bottom sediments (sands) the bitumoid content decreases in the pelagic direction. The boundary for the sharp drop of bitumoid content is the upper part of the continental slope (Figure 93). This is, evidently, bound up with the fact that more conservative polymerized organic matter is accumulated in bottom sediments of deep water zones (Romankevich, 1977).

Humic acids are present in almost all samples of bottom sediments except for sands. Variations of content and composition of humic acids in pelite muds in the direction river-ocean are observed on the section of the "Limpopo river mouth-ocean" (Danyushevskaya and Romankevich, 1987). The average content of humic acid in the bottom sediments of the shelf is equal to 0.56%, converting into dry sediment, and 17.8% of organic matter. The deep water sediments contain about 10 times less humic acids (0.5% converting into

dry weight and 1.7% of organic matter) which is caused by polymerization of deep water organic matter and humic acids transformation into non-soluble organic matter, which is stable to decomposition (Danyushevskaya and Romankevich, 1987).

Concentration of lignin in the surface layer (0–5 m) of bottom sediments on the section “Limpopo river–ocean” varies from 0.4 to 1.8 mgC/l, or 7–9% of organic matter (Bobileva, 1982). High concentrations of lignin are typical for bottom sediments in the Limpopo river mouth region. Content of lignin in bottom sediments drops sharply toward the ocean (converting into dry weight), but at the same time its proportion in organic matter composition increases.

4.4. Conclusions

The river–sea system may be clearly subdivided into three groups by organic matter composition: river waters, estuary waters and ocean waters. In the direction river–ocean we observe in suspension the following: a decrease of content of most labile components (amino acids and particulate carbohydrates), a change of ratio of amino acids groups (increase of content of neutral amino acids and decrease of content of main amino acids) and of their individual composition, composition of particulate carbohydrates (increase of share of carbohydrate-like compounds most resistant to decomposition, and a decrease of content of bitumoids (first of all at the cost of bitumoid A_{cl}), transformed, evidently, into “residual” organic matter (humines) resistant to decomposition. Thus, the typical process of particulate organic matter transformation in the direction “sea–estuary–ocean” is the decrease of reactive compounds and the increase of a proportion of biologically resistant organic matter (humines).

The border of river run-off effect on the particulate organic matter composition in the river–sea system can be determined by a sharp change of organic matter composition, change of structure and concentrations of particulate organic matter components.

Absence of humic acids is typical for the estuary and river particulate organic matter; consequently, the process of particulate organic matter transformation towards the formation of geopolymers of humic acids type (humification) is not characteristic for particulate organic matter of the river–sea system.

The predominating process of organic matter transformation in terrigenous muds in the direction river–sea in both the equatorial humid zone and the northern humid zone is dehumification–humination.

Two types of bottom sediments, terrigenous sands and muds, are separated in the river–sea system, which testifies the existence of two types of bitumoid A_{cl} , the composition formation of which is not determined by the organic matter source, but by the sedimentation medium and by the bond with the mineral part of the sediment.

The typical process of organic matter composition transformation in the line “suspension–bottom sediments” in the estuary, as in the river, is humification–debituminization.

The typical process of transformation of organic matter composition of sands in the river–sea system is debituminization and the increase of the proportion of humines of organic matter composition. Organic matter of estuary sands, as that of river sands, are

characterized by the absence of humic acids, which testifies that humification of organic matter does not take place in coarse-grained bottom sediments, due to the quick fracture of relatively labile compounds which are able to be transformed into geopolymers of humic acids type.

The boundary separating bottom sediments with river forms of organic matter from sediments with oceanic forms of organic matter may be determined by the change of organic matter composition of bottom sediments.

The boundary of transition from river to sea (or ocean) forms of organic matter is clearly seen by the change of content of amino acids, humic acids, bitumoid A_{el} and $A_{al,ben}$ in organic matter of bottom sediments. The location of this boundary in relation to the distance from the river mouth is determined by the value of river run-off and the hydrodynamics of waters adjoining the river mouth, and therefore is different for each estuary or area of river and sea water intermixture.

Summary Conclusion

Consideration of the problems of the geochemistry of organic matter washed out by river run-off into the ocean and into the system "river–area of river and sea water mixing–sea" made it possible to obtain new data on the content and distribution of organic matter in rivers and areas of sea and river water mixing, as well as to determine the general regularities and peculiarities of organic matter in the river–sea system and its effect on the environment.

The main mass of organic matter is transported by rivers into seas and oceans in a dissolved form (60–90%). The analysis of data on the quantity of dissolved and particulate organic matter, transported by river run-off into seas and oceans, leads to the conclusion that distribution of river dissolved and particulate organic matter streams is dependent on climatic zonality. The greatest fluxes of dissolved and particulate organic matter are typical for rivers of the equatorial humid zone, where they are equal to 75.8 and 90.2%, respectively, of the total quantity of dissolved and particulate organic matter annually transported into seas and oceans by rivers of the world, or 0.204×10^9 t/year and 0.184×10^9 t/year, respectively. The climatic zonality is also revealed by the distribution of relative concentrations of C^d and C^p in world rivers.

High concentrations of C^d are typical for rivers of the northern humid zone, which is bound up with the delivery of organic matter, of mainly humic genesis, from soils of taiga-forest, forest-tundra and tundra zones. Relative increases of particulate organic matter proportions in river waters takes place in mountain rivers and it is bound up with a plentiful supply of suspended particles in river water. The highest concentrations of particulate organic matter are found in rivers of the equatorial humid zone with complex mountain-type relief of water accumulating basins (rivers of south-east Asia, etc.).

Seasonal variety of concentration and composition of river organic matter is bound up with climatic peculiarities of the region, which control the development of ground plants.

The highest concentrations of organic matter in river mouths of the northern and moderate humid zones are observed during the spring flood periods. In rivers of the

northern humid zone, high concentrations of C^P also occur in winter, due to the low rates of particulate organic matter destruction under conditions of low water temperature.

The distinctive peculiarity of dissolved and particulate organic matter distribution along river beds, which are not subjected to anthropogenous pollutions, is the absence of clearly expressed external concentrations of dissolved and organic matter. Just such a regularity was revealed in the main bed of the Amazon, where we measured concentrations of C^d and C^P at the extent of 2000 km from the place of confluence of Solimoiins and Negro rivers to the Amazon river mouth. The main part of river water dissolved organic matter (60–80%) is made up of decompositionally resistant geopolymers of humic acids type, the source of which is soil (Table 51). The content of labile components (amino acids, carbohydrates) in the majority of rivers of the world is equal to 30% (in total) of dissolved organic matter and 15% of particulate organic matter.

The process of humification in the river–sea system in the line “suspension–bottom sediments” only takes place in terrigenous muds. Humification of organic matter is not observed in suspension, or in terrigenous sands due to the rapid destruction of the labile compounds that are potentially able to form geopolymers of humic acids type under sharply oxidizing conditions (Figure 83).

The study of organic matter transformation processes in river waters and bottom sediments revealed a number of regularities. The distinctive feature of organic matter transformation on the line “suspension–bottom sediments” is debituminization, i.e. utilization of bitumoid components, especially prevailing in suspension, in the process of diagenesis on the surface of bottom sediments (Figure 83). In this case, bitumoids are transformed into insoluble complexes (humines) or sorptional complexes with humic acids (Romankevich, 1977). Absence of humic acids in the suspension testifies to the fact that humic acids are mainly formed in bottom sediments *in situ*.

Nevertheless, it is impossible to exclude a principal possibility of the delivery of soil humic acids to the surface of bottom sediments by the route: soils – river water – plankton – products of activity and destruction of plankton – bottom sediments. Under certain conditions, humic acids dissolved in water may be the source of food for water organisms (Spitzky *et al.*, 1991), and consequently get into the food chain and be buried in bottom sediments during the process of biosedimentation.

Comparison of the data on composition of organic matter of river terrigenous muds of the northern and equatorial humid zones, shows that the intensity of humification processes of organic matter in bottom sediments is determined by the climatic zone. The process of organic matter humification in river terrigenous muds of the northern humid zone occurs less activity than under conditions of tropical climates. In river terrigenous muds of the equatorial humid zone, conditions for organic matter humification are more favourable than that in respective granulometric type of sediments at northern latitudes due to the high temperature of the water (average 29°C over the whole year) and more active work of micro-organisms and bottom fauna on the transformation of organic matter in the surface layer of bottom sediments, leading to organic matter humification.

Independently from the climatic and circum-continental zonality of sedimentation in the river–sea system, we separated two types of organic matter, bound up with sands and terrigenous muds respectively. Organic matter of sands differs from organic matter of

Table 51. Transformation of organic matter in the river-sea system (Semenov, 1967, 1971; Romankevich, 1977; Smirnov *et al.*, 1978; Varshal *et al.*, 1979; Artemyev, 1981; Artemyev and Daryushvskaya, 1988; Seifert and Itekot, 1985; Itekot *et al.*, 1982a; Degens and Itekot, 1985; Ertel *et al.*, 1986).

Object of research	C _{org} content	% of Organic Matter						"Residual" organic matter
		Amino- acids	Carbo- hydrates	Humic substances	Bitumoids		A _{al.b.}	
					A _{cl}	A _{al.b.}		
RIVERS								
water	7 mg/l	4-5	10-20	60-80				
suspension	2 mg/l	10	15	n.d.	20	30	30	30
soils (Amazon basin)	2-4%	n.d.	n.d.	20-25	1-2	1-2	73	73
muds	1-3%	2-3	5-10	20-50	10	15	50-75	50-75
sands	0.1%	n.d.	n.d.	n.d.	5-10		80-90	80-90
REGIONS of								
water	3-13 mg/l	n.d.	10-25	n.d.	n.d.	n.d.	n.d.	n.d.
suspension	1 mg/l	0.2*	13	n.d.	2-10	25-50	40-70	40-70
river and	0.5%	2	n.d.	8	1-2	1-2	88	88
muds	0.5%	n.d.	n.d.	10	2-4	1-2	86	86
sea waters	0.5%	n.d.	n.d.	10	2-4	1-2		
SEAS								
water	1-2 mg/l	5-30	10-40					
suspension	0.1 mg/l	5-30	10-30	4-10		3-30	50-75	50-75
OCEANS**								
muds	0.5%	1-7	5-15	10	5	1	85-90	85-90

*"Free" amino acids.

** Romankevich, 1977.

n.d. = not determined.

Table 52. Composition of bitumoid A_{cl} (%) in bottom sediments of the river–sea system.

Object of research	Oils (I)	Resins (II)	Asphaltenes (III)	I:II:III
MUDS				
Amazon river	<u>18.3–30.2</u> 25.6	<u>61.8–69.3</u> 65.5	<u>8.1–12.7</u> 10.1	2:6:1
North Dvina	<u>20.4–23.1</u> 21.8	<u>60.7–67.9</u> 64.3	<u>10.1–11.0</u> 10.5	2:6:1
Amazon estuary	<u>27.8–41.6</u> 32.5	<u>47.7–59.6</u> 54.1	<u>4.8–12.2</u> 9.8	3:6:1
SANDS				
Amazon river	<u>39.9–52.0</u> 45.1	<u>40.9–43.4</u> 42.1	<u>5.3–16.0</u> 10.7	4:4:1
North Dvina	<u>41.6–62.9</u> 51.0	<u>33.7–52.7</u> 43.7	<u>2.5–6.0</u> 4.4	12:10:1
Dvinsky Bay	51.6	35.4	12.8	4:3:1

muds by the absence of humic acids, higher content of bitumoids and “residual” organic matter, as well as the composition of bitumoid A_{cl} (bitumoid A_{cl} of sands contains more oils, see Figures 83 and 84, and Table 52). The difference of composition of organic matter of terrigenous sands and muds and, in particular, of the composition of bitumoid A_{cl} , are connected with conditions of organic matter formation in the surface layer of bottom sediments, their relationship with the mineral part of sediments, as the “medium of inhabitation” and of micro-accumulations of organic matter, supplied to bottom sediments or with a suspension or formed *in situ* with participation of bottom-dwelling fauna and micro-organisms.

It is known that processes of sorption of organic matter by clay minerals in terrigenous muds help to preserve organic matter against micro-biological attack in the early stages of diagenesis. In sands, particles of organic matter are not bound with the mineral part of sediments as in clay muds, and are, therefore, subjected to mechanical destruction and biodegradation.

Being supplied to the sea or ocean medium with river run-off, dissolved and particulate organic matter are subjected to complex transformation under the effect of physico-chemical and biogeochemical processes in the area of river and sea water intermixture. The data of natural observations in the river estuaries of various climatic zones of the Earth, as well as the results of experiments on mixing filtered river and ocean waters showed that the process of dissolved and particulate organic matter transformation occurs under the action of mainly physico-chemical processes (flocculation, adsorption-desorption) at all stages of water intermixture. This process goes on most intensively in waters with a salinity of 5–10‰. Performed calculations, statistical processing of the obtained data

showed that C^d and C^p behaviour in the area of river and sea water intermixture does not, as a rule, correspond to the line of simple dilution and has a “non-conservative” character as a result of dissolved organic matter transition into suspended form and *vice versa*, into the dissolved form, at various stages of river and sea water intermixture.

Estimation of river organic matter losses during the mixing between river and ocean waters is given by means of our model on the example of the Amazon estuary: for dissolved organic matter 75%; for particulate organic matter 80%. If it is assumed that such values of losses are, on the whole, typical for river and sea water intermixture areas we can infer that every year 153×10^6 tons of river C^d and 37×10^6 tons of river C^p are delivered to the ocean pelagic zone and 51×10^6 tons of C^d and 147×10^6 tons of C^p respectively remain in the river water and sea water mixing area.

The behaviour of organic matter and a number of micro-elements (copper, zinc, nickel, chromium) in river and sea water mixing areas have a similar intercombined character, dependent on the salinity of the waters, which testifies to their migration in the river–sea system in the form of complex compounds “organic matter–metal”.

If physico-chemical properties determine the behaviour of dissolved and particulate organic matter in the case of the mixing of fresh and salt water, and are associated with variation of water salinity, the biogeochemical processes predetermine the transformation of organic matter going in two directions “river–estuary” and “suspension–bottom sediments”.

The basic trend of particulate organic matter composition transformation in the direction river–ocean is “humination” or decrease of concentration of the most reactive, labile compounds (amino acids, carbohydrates), content of bitumoids (primarily at the cost of bitumoids A_{cl}) and increase of chemically and biologically resistant organic matter.

The dominating process of organic matter transformation in terrigenous muds in the direction river–sea, in both the northern humid zone, and in the equatorial humid zone, is “dehumification–humination”, and in sands it is “debituminization–humination”.

The higher humic acids content in terrigenous muds of the Amazon estuary, in comparison with the North Dvina estuary, testifies that most active humification processes are characterized by terrigenous muds of equatorial humid zone.

The characteristic process for the line “suspension–bottom sediments” (terrigenous muds) in estuaries and also in rivers, is “debituminization–humification”.

The boundary of river run-off effect of organic matter composition in the river–sea system, separating the medium with river and ocean types of organic matter, may be determined by variation of the ratio of particulate organic matter components and organic matter of bottom sediments in the direction “river–estuary–ocean”. This makes it possible to forecast the remoteness of propagation of the main mass of organic matter, including pollutions, in seas and oceans that has the main practical value, and is very important for solving a number of economical problems (Figures 82 and 84).

As it is known, the main regularity of C_{org} distribution in oceanic sediments is the circum-continental localization of concentrations of C_{org} (Romankevich, 1977). It is expressed by the proximity of high content of C_{org} to periphery zones of oceans, to sediments of bays, lagoons, etc. Especially large masses of C_{org} are accumulated in zones of sedimentary material run-off by rivers of South and South-East Asia and West

Africa (more than $200 \text{ g/m}^2/1000 \text{ years}$ (Romankevich and Bobyleva, 1990)) for which largest streams of river dissolved and particulate organic matter are typical. The maximum reserves of oil in delta bottom sediments were found here, at tropical latitudes (Geodekyan *et al.*, 1988).

Thus, we may state that the regional peculiarities of river organic matter accumulation in river mouth areas of seas and oceans, typical for the geological past, also remain at present.

It is known that very favourable conditions for accumulation and relatively fast deposition of muds enriched with organic matter and the formation of various forms of sand bodies exist in river-mouth regions of seas and oceans.

Bottom sediments most favourable for oil formation are accumulated under conditions specific to bays and deltas. These bottom sediments were called "delta-estuary" (Veber *et al.*, 1960). All the required prerequisites for the subsequent generation, accumulation and preservation of oil and gas are created here. Thick layers of terrigenous rocks with good reservoir properties and enriched with organic matter are accumulated in the river-sea zone.

Numerous investigations prove the regular relationship of the largest oil fields with avandelta deposits of paleorivers. The river valleys of many modern and paleorivers coincide in their main features (Volga, Don, Dnieper, Ob, Orinoko, Missouri, Mississippi, Ganges, Brakmaputra, etc.).

An exclusive role of delta areas of palaeorivers in oil-and-gas accumulation is confirmed by the following data: the productivity of delta deposits was revealed in more than 40 oil-and-gas bearing basins of the world, and about 1500 hydrocarbons accumulations were discovered among these deposits. Collectors (reservoirs) of deltaic origin in basins of passive peripheries of continents contain more than 10^{10} tons of oil and almost $7 \times 10^{12} \text{ m}^3$ of gas. For example, in basins located in the zone of transition from the Phillipine Arc to the continent of Asia, deltaic sediments become the main oil-and-gas-containing formations: they contain 9×10^8 tons of oil and $1.1 \times 10^{12} \text{ m}^3$ of gas (Geodekyan *et al.*, 1988).

Investigation of modern biogeochemical processes in the river-sea system expands our understanding of processes for organic matter transformation in paleorivers mouths. Only as a result of studying physico-geographical, geochemical and biological processes going on in modern river mouths is it possible to explain the reasons for high productivity of deposits in these areas, then subjected to deepening to an optimal depth, corresponding to the main stage of oil-and-gas formation (Markovsky, 1981).

Thus, the study of specific features of organic matter behaviour in the river and sea water intermixture area and biogeochemical processes in the river-sea system is closely bound up with problems of oil-and-gas formation. The modern estuaries and river mouth sections of rivers are the natural polygons, the study of which will help our better understanding of conditions for formation of oil fields in the distant parts.

Works on the geochemistry and biogeochemistry of organic matter in the river-sea system are also of doubtless practical interest in connection with the extremely unfavourable ecological situations which exist in mouths of many of the largest rivers on the territory of some countries.

The most important targets of subsequent investigations concerning geochemistry of organic matter in the river–sea system are:

1. Organization and carrying out of systematical (seasonal, annual) biogeochemical investigations in river mouth areas and estuaries of large rivers with the application of up-to-date methods of study and equipment.
2. Study of the migration mechanisms of organic matter, transported with river runoff in the line “water–suspension–bottom sediments” with the emphasis on studies revealing the places of river organic matter burial in the bottom sediments of estuaries.
3. The working out of recommendations for the rational management and development of mineral and biological resources in river mouths and the regions of neighbouring seas.

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