

Chapter 2

Hydrological Processes

Water regime, flow rate in rivers, external and internal processes of water exchange in reservoirs are important physical parameters determining water quality. Changing such elements of water regime as water level, flow rate, water distribution in a river, accounts for considerable variations in the chemical composition of water masses.

The chemical composition of natural waters is the result of a number of physical, physicochemical and biological processes, whose boundary parameters are determined by physical and geographical conditions. The transport of reaction products by solid and gaseous components is provided by water as a major energy carrier [54].

Effects of global factors such as solar energy and gravity account for the continuity of the water cycle between the atmosphere, lithosphere and hydrosphere, the individual phases of which differ significantly in their energy potential.

The kinetic energy of a rainfall is generated due to the friction of drops and reaches on an average $30\text{--}40\text{ J/m}^2\text{ mm}$ or $1.8\text{ J/m}^2\text{ s}$ [49]. The total energy is defined as a product of falling raindrops speed (cm/s) and a layer of precipitation (mm). With rain intensity of 25 and 50 mm/h the hourly release of energy amounts to $6.7 \times 10^3\text{ J}$ and $1.7 \times 10^9\text{ J}$ per hectare respectively [35]. The impact of drops on the ground results in the release of energy which causes destruction and displacement of soil and is partly dissipated as heat.

The energy of a stream flow is generated owing to river discharge and elevation difference. This accounts for high variation of these indicator values for individual rivers and their sections. Unconfined flows (slope run-offs) have little energy potential, but during rain or snowmelt they cover almost the entire catchment area. In natural conditions, water flow energy is spent to overcome friction forces between the particles of water and water and the bottom, and is externally manifested as soil erosion, riverbed erosion and transport of solid materials.

The interaction of water flow with the underlying surface in the “water—solid phase” system, in addition to mechanical erosion, results in the dissolution of salts in the soil and leaching of minerals owing to a very pronounced tendency of ions in

a solid phase to pass into solutions, which in terms of thermodynamics is the most likely process. The driving force behind the formation of solutions is the system's wont to reduce free energy. The exceptional solubility of water is accounted for a high value of its dipole moment ($\mu = 1.86$ D) and dielectric permeability. It is common knowledge that the intensity of inter-atomic and inter-molecular interaction on the surface of the substances submerged in the water decreases 80-fold [99]. Water molecules are concentrated around the electronic charge carriers of a solid phase, attracting to them by an oppositely charged dipole end and forming a hydration zone. The thermal energy of water molecules causes demolition of a crystal lattice and opening of chemical bonds in soil minerals, and the detached molecules start moving throughout the volume of an ambient solution due to diffusion process. In the case a mineral has excess loose molecules on its surface, the diffusion process will slow down. Ingress of new portions of water or its stirring will facilitate the withdrawal of molecules from the surface and dissolution process will continue.

Interactions in heterogeneous systems ("water-solid phase", "water-air") can be illustrated by using a conceptual approach of the systems theory. The continuous water cycle is based on the thermodynamic openness of water bodies allowing for an exchange of matter and energy with the environment. The latter accounts for an out-of-balance condition of the system, and all processes occurring in it become irreversible. As a result, the system experiences persistent concentration gradients. Volumes of fresh atmospheric moisture continuously withdraw reaction products from the interface between the phases, with chemical reactions producing more soluble forms.

Apart from dissolving and leaching, an open system can feature ion exchange, sorption and other processes, the combined effect of which would determine mass-transfer of agents in a river basin system.

2.1 Transport of Substances Within a River Basin

The issue of quantification of chemical elements circulating in ecosystems was first highlighted in the fundamental works of Polynov [72, 73] and Perelman [71]. According to Perelman [71], the driving force of migration of substances is caused by two types of factors: external and internal. The first are determined by landscape and climatic conditions, and the latter ones are inherent to highly specific types of watershed. The migration flows between different components of ecosystems serve as sort of channels of linkage, and their quantitative characteristics are determined by the parameters of carrier's phase and migrant's phase [20].

The boundaries of drainage basins of chemical elements runoff coincide with the boundaries of river basins, and its yield would qualitatively characterize the basic expenditure balance of chemical elements in a river basin, the amount of soil and rock erosion, the process of weathering, karst, terrain salinization.

The basics of the study of hydrochemical runoffs of river basins was laid down by O.O. Alekin, which subsequently was developed by numerous scholars in their works, dedicated to basins of different physiographic zones [1, 2, 33, 53, 69, 74, 112].

The runoff rate of specific chemical components for a certain period of time (day, decade, month, season) is estimated as follows:

$$R = W \cdot C,$$

where R is the runoff of a specific component (g, kg, t, kt); W —volume of water runoff, m^3 ; C —component concentration in 1 m^3 of water.

Figures per annum are calculated by summation of respective components (daily, per ten days, monthly, seasonal).

The above formula shows that the runoff rate of any component from the surface catchment depends on factors W and C and all changes in hydrochemical runoff patterns will be determined by these variables.

Alekin O.O. found out that the highest chemical concentrations in runoffs are characteristic of basins, in which at high rates of water runoff the concentrations of substances are not minimal [1]. Thus, the rate of ion runoff in the rivers of the Far North, despite high flow rates, is low due to good washing of soil in the water-logged area. A significant amount of salts is accumulated in the soil of river basins in the steppe zone and semi-deserts, but the loss of moisture through evaporation hinders the realization of water flow function of dissolving and transporting substances.

As per the rivers of Ukraine, consider the case studies of Danube and Siversky Donets basins. An average runoff of the Danube has been 203 km^3 (with variation range of $132\text{--}262 \text{ km}^3/\text{year}$) for many years, and mineralization near the city of Reni has been 390 mg/L .

Compared to the Danube, the water of the Siversky Donets River contains much more dissolved salts $\sim 1133 \text{ mg/L}$, although an average annual volume of the Siversky Donets runoff is more than 90 times lower $\sim 4.26 \text{ km}^3$ [27]. A calculation of ion flow for both these rivers, made for the period 1989–2001, showed that the figure obtained for the Siversky Donets was much smaller compared to the Danube (~ 17 -fold), respectively 4.5 million t/year and 78.7 million t/year (Fig. 2.1). This fact is accounted for high volume of water runoff in the Danube River.

For both, the Danube and the Siversky Donets, there is a close relationship between the water flow and the discharge of dissolved salts (Fig. 2.2). The correlation coefficient for the said two indicators is: for the Siversky Donets 0.96 , and for the Danube -0.87 (the figures were defined based on the Student distribution, $p = 0.05$; $r > 0.57$).

The dependence between the discharge of chemical components and water flow is also typical for other water components, as illustrated by the case study of humic substances (Fig. 2.3). Coherence of these parameters implies a decisive role of water flow in the discharge of humic substances from the surface of drainage-area.

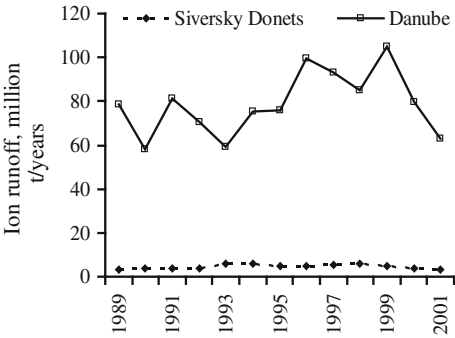


Fig. 2.1 Ion runoff in the Danube and Siversky Donets rivers (in Ukraine), 1989–2001 [67]

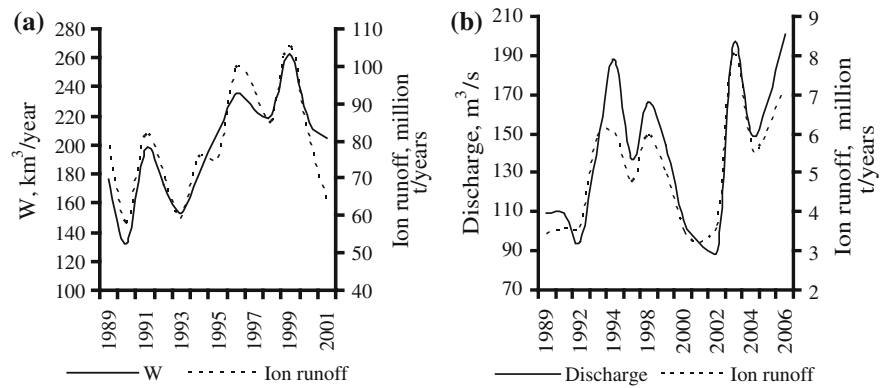
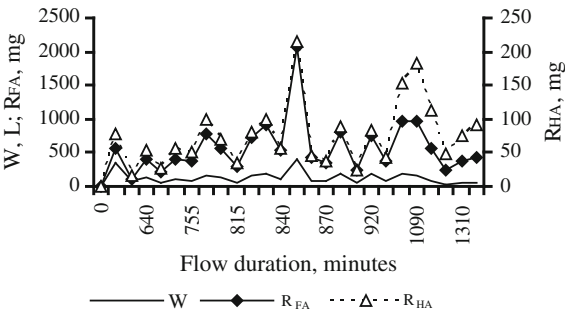


Fig. 2.2 Long-term dynamics of **a** ion and water runoff (W) in the Danube, city of Reni **b** water discharge and ion runoff in the Siversky Donets, Kruzhylivka village [67]

Fig. 2.3 Dynamics of water runoff and leaching of humic acids (HA) and fulvic acids (FA) from the surface of the experimental runoff plot, 22 February 2008 [64]



The coefficients of pair correlation between the value of W and carry-over of humic and fulvic acids reach 0.7 and 0.8 respectively ($p = 0.05$; $r > 0.43$).

The research of chemical components runoff in the rivers of Ukraine was conducted by various scholars [51, 69, 74, 111, 112], including the authors [33, 65], and the results show significant variability of the investigated parameter values. This is primarily due to fluctuations in the water level of rivers and the influence of local lithological and hydro-geological characteristics.

The aforecited sustains the need of analyzing the impact of hydrological processes quantitative adjectives on the formation of water quality.

Among the various hydrological factors, their three key groups are discussed below: volume of water runoff, hydrodynamic processes, hydrophysical parameters of water masses and bottom sediments.

An effective role of hydrological processes in the formation of water quality makes it possible to consider them as an aquatic ecosystems control factor allowing for the development of mathematical systems to forecast water quality. Changing water regime elements such as external and internal water exchange, water level, flow velocity etc., one can achieve a shift in the balance of self-cleaning—self-pollution processes, thereby changing chemical composition of the water. The methodology and techniques to control aquatic ecosystems by changing the regime of surface waters in Ukraine, that were practiced on many water bodies of the Danube, Southern Bug and Dnipro basins, are detailed in [56–59, 61, 88–92].

Using artificial water exchange (“blowdown”) in the cooling ponds of thermal and nuclear power plants, whereby the total dissolved solids are being reduced, is a bright illustration of using hydrological processes to regulate chemical composition of water.

2.2 Effects of Water Runoff on the Chemical Composition of Water Bodies

The impact of some hydrological parameters on the chemical composition of surface water should be considered versus the hydrological regime of water bodies, which are divided into streams and reservoirs.

Streams are characterized by permanent or temporary water movement in a channel in the direction of its general inclination. These can be rivers, canals, streams, and others. Ponds are stagnant or slow runoff water masses that accumulate in depressions of natural or artificial origin.

2.2.1 Watercourses

Water runoff of rivers is determined by the conditions of their nourishment, whose major source is atmospheric precipitation. Graphic illustration of water runoff is shown in Fig. 2.4.

Depending on general conditions of the catchment, and especially the properties of soils, atmospheric precipitates, after having reached the earth's surface, run off it or seep deeper. Part of the water is evaporated. In the course of the runoff several genetically distinct categories of water are formed, whose metamorphization degree differs essentially. P.P. Voronkov divides them into surface-slope water, soil-surface (water of micro-moat network), subsoil and groundwater [107, 108].

Given full moisture capacity of the soil, its deep freezing or high intensity rainfall, the water quickly flows down the slope, forming a surface runoff (surface-slope and soil-surface waters). With its formation an intense increase of water discharge is observed, correlating with the rising limb of the runoff hydrograph. The income of surface water occurs relatively quickly and is observed during intensive snow melting and heavy rains.

The forming of the underground component of river recharge essentially depends on the filtration properties of soil material. Water seepage into the soil has a great bearing on the water content of the soil, the intensity of surface runoff and groundwater replenishment [10, 85]. Fine, long and continuous rains create the most favourable conditions for infiltration of water. Ground water that feed rivers

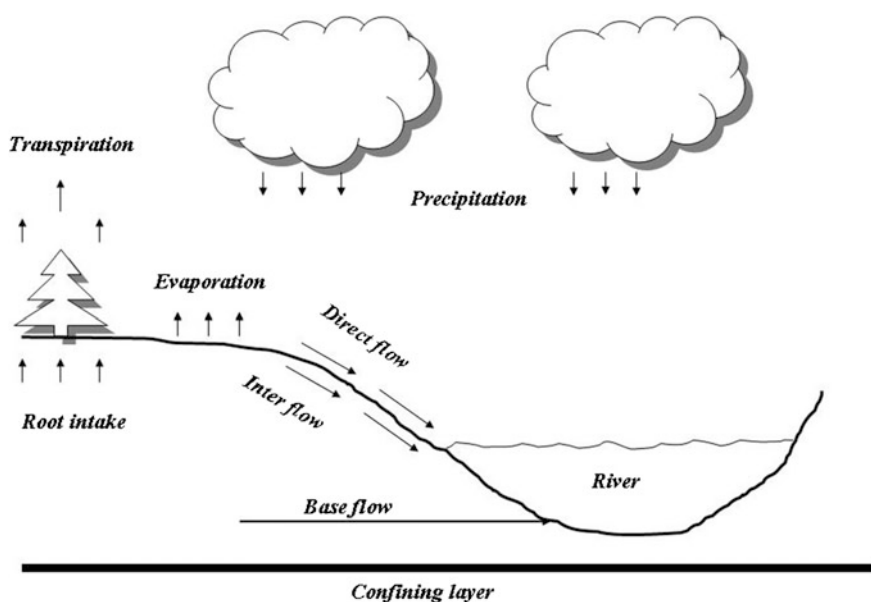


Fig. 2.4 Scheme illustrating water runoff phenomenon

are usually divided into two main categories: subsurface water of aeration zone and groundwater. Water-holding horizon of the former rests in the soil column, and its water table is permanently or periodically located in the soil. During the periods of increased moistening the soil column features a groundwater movement down the slope, the formed runoff is called subsoil runoff (according to Voronkov classification, subsurface and ground waters [108]). The said subtype of a runoff represents the bottom portion a recession limb of the hydrograph, playing the role of a seasonal water flow regulator [23].

All free-flow (or with local pressure) ground waters located below the soil column, belong to the category of groundwater and determine a permanent deep-soil water supply. They have steady flow rates throughout the year and are classified as average as per the smallest monthly discharges for some years.

Classification of runoff as surface or underground primarily depends on the amount and regime of the rainfall, type and properties of the soil, topography of the watershed. According to S.M. Bogolyubov, who drew a distinction between surface and ground water flow depending on the size of watershed and depth of a channel, the surface flow of rivers with deep incision is less than 40–50 %, that of the underground flow –50 to 60 %, increasing in the areas with permeable soils to 70–80 % [85].

Therefore, given the unpolluted river basins, chemicals can enter the channel directly with precipitation, be washed out from the soil and rocks with surface and subsurface runoff, as well as with groundwater. Voronkov P.P. has introduced an important concept that the hydrochemical conditions of a local runoff reflect the change of waters of various origin in the channel network, that is a change of one source by another [108].

Therefore, to establish patterns of forming the chemical compositions of rivers it is important to divide runoff into genetic components and quantify the content of individual ingredients in different types of flow.

Precipitation. The atmosphere receives water during evaporation from the land and ocean. Sea breezes enrich precipitates with sodium and chlorine ions, and terrigenous dust—with calcium ions. Mineralization of uncontaminated rainfall in most cases does not exceed 100 mg/L, in Ukraine this figure varies within 30–50 mg/L. Regardless of the physiographic zone, the anion component of precipitation in the plain part of Ukraine is dominated by sulphate ions, and among the cations magnesium is dominant. When moving from the forest zone to steppe zone there is a slight increase in ion number due to added ions Ca^{2+} , HCO_3^- , Cl^- . Apart from Salts, precipitates contain significant amounts of dissolved gases (nitrogen, oxygen, carbon dioxide) and hydroxides of inactive elements: aluminum, vanadium, titanium, and sometimes of iron. In the forest zone precipitation is formed in an oxidizing environment, which accounts for a significant concentration of oxygen in it, and has acidic reaction ($Eh = 530$ mV, $pH = 5.2$). The inorganic nitrogen compounds are predominated by nitrates. This is due to oxidation of nitrogen under the influence of solar radiation and electric discharges. Precipitation in the steppe zone also has acidic medium and oxidizing conditions ($Eh = 500$ mV, $pH = 5.5$).

Table 2.1 The values of atmospheric components in total average runoff in Ukraine, Ktons [22]

Physiographic zones	Ca^{2+}	Mg^{2+}	$Na^{+} + K^{+}$	HCO_3^{-}	SO_4^{2-}	Cl^{-}	Σ_I
Mixed forests	30.8	35.3	49.0	90	212	42.9	460
Wooded steppe	72.0	60.0	82.0	204	429	91.0	938
Steppe	35.0	27.0	35.0	66.0	18.7	49.0	399
Subcarpathia	16.5	15.1	18.8	32.3	102	18.7	203
Mount. and Volcan. Carpathians	42.2	38.3	47.7	82.1	260	47.7	518
Transcarpathian Plain	2.7	2.5	3.1	5.3	16.6	3.1	33.3
Crimean Mountain Plain	10.8	7.3	9.5	29.0	30.3	11.6	98.6
Total for Ukraine	213	186	245	508	1236	264	2650

The nitrogen compounds are dominated by ammonium and nitrites and nitrates are present in trace amounts. Rainfall waters in the steppe zone have high oxidative capacity ($Eh = 500$ mV) and compared with the previous zones they have significantly higher pH that range from 5.6 to 5.9. Growing hydrogen value in the rainfall water is accounted for the atmosphere being dust-filled with mineral aerosols, elevated concentrations of calcium, long rainless periods. The compounds of $N_{\text{miner.}}$ are dominated by ammonium ions, the average concentrations of which are 2–3 times higher than the corresponding values of the forest and steppe zones. The latter is due to severe eolian erosion of arable land, which area reaches 70–75 % of the total zone area.

An average value of the atmospheric component in total ionic runoff of rivers in Ukraine is 2.65 million tons (10 %). The contribution of precipitation to the formation of ionic runoff varies from 3 % in the steppe zone to 23 % within the Crimean Mountains. The affect of rainfall on runoff of individual ions within different geographical zones is shown in Table 2.1.

Waters of surface and subsurface runoff Migration of precipitates over the surface of a catchment results in the metamorphization of their chemical composition due to contact with the underlying substrate (soil mantle, rocks) [110]. Due to the difficulty of identifying different river source elements, the chemical composition of subsoil water runoff remains so far little known.

Soils enrich water with salts, organic matter, gases. Vernadsky V.I. in his works [103–105] stated that about 90 % of surface water salts come from the soils. The substances coming from the soil are determined by the material composition of its solid phase [110]. The main contribution is made by the process of dissolution of soluble salts, in which case the dependence of the concentrations of respective components on soil moisture has a linear form. The concentrations of elements that are part of low-solubility compounds are maintained at a level that depends on the product of solubility of relevant substances.

The interaction of precipitates with soils is often accompanied by changes in the water composition due to adsorption and ion exchange. Basic principles of these processes are formulated in the fundamental work of K.K. Gedroits, who proposed the theory of cation-exchange capacity of the soil and first formulated the concept of its absorbing complex [19].

The oxidation of organic matter of the soil by precipitation oxygen results in the emission of carbon dioxide, which is the source of formation of hydrocarbon ions. Biogenic substances, the bulk of which is made of silicon compounds (40–60 %), also enter water from the soil. Organic matter of the soil, mostly humic acids, is also dissolved in the water.

Rocks are a leading factor in the mineralization of natural waters. The main soluble minerals that affect the chemical composition of natural waters are halite (NaCl), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$).

The predominance of bicarbonate-calcium waters in nature is accounted for the widespread of limestone, whose solubility dramatically increases in the presence of CO_2 in the water.

The concentration of substances in interstitial water reflects a dynamic balance that is established between the solid and liquid phase. This balance can easily be distorted due to the formation of water flow in favour of the dissolution of soluble compounds present in the solid phase.

The waters of surface runoff quickly flow down the catchment surface, not being able to achieve balance with the solid phase and saturate the solution with soil components. Another important factor that affects the chemical composition of water runoff is the degree of soil leaching by the time of achieving full water-holding capacity. In the areas where rainfall exceeds evaporation, soil layer is well washed and depleted of mineral components. In areas of low moisture (rain < evaporation) a significant amount of salts accumulates in the soil layer due to their income from the zone of capillary rise. The relative contents of individual elements in different types of soils are given in Table 2.2.

In Ukraine, the majority of rivers are fed by melting snow, resulting in a sharp rise of water levels in the spring and the development of floodplains. During this period it is mainly surface runoff that enters the channel causing drastic changes in the concentrations of dissolved solids, the manifestation of which depends on the physical and geographical location of a watershed. Let us illustrate the above said by several examples.

During the spring flood there is a significant increase in water discharge due to the income of low-mineralized snowmelt, which results in the dilution of channel water and reduced concentrations of main ions (Fig. 2.5).

The degree of water dilution largely depends on the intensity of the snowmelt, that is on general hydrometeorological conditions prevailing during this period. A certain role is played by the late fall weather. Heavy rains add to washing out the soil, and a rainless fall would feature slight accumulation of salts in the ground, which are later washed away by a flood.

During flooding periods an inverse relationship between the water flow and the concentrations of major ions and salinity of water is observed. Thus, for the Desna

Table 2.2 Average elemental composition (%) of different types of soil in Ukraine [62]

Soils	O	H	C		N	P	S	Si	Al	Fe	Ti	Mn	Ca	Mg	K	Na
			Humus	Carbonates												
Peat	36.86	5.33	53.33	None	1.900	0.200	0.240	1.00	0.12	0.50	–	0.05	1.20	0.13	0.30	0.07
Podzol																
Loamy	49.60	0.06	0.66	0	0.080	0.054	0.031	34.86	6.33	3.02	0.28	0.20	0.78	0.72	2.04	1.28
Sandy-loam	50.66	0.05	0.67	0	0.066	0.022	0.020	39.57	4.31	1.16	–	–	0.58	0.70	1.81	0.90
Sandy	52.20	0.04	0.64	0	0.060	0.022	0.026	43.77	1.72	0.55	–	0.06	0.28	0.09	0.33	0.16
Gley-podzol	49.10	0.08	1.12	0	–	0.105	0.056	33.85	6.98	3.11	–	0.20	0.80	0.60	2.50	1.43
Humic-gley	49.10	0.08	1.17	0	–	–	–	33.02	7.39	3.12	–	0.09	1.15	0.81	2.64	1.41
Grey forest	49.27	0.09	1.25	0.04	0.115	0.044	0.076	33.45	6.67	3.80	0.45	0.06	1.24	1.02	1.60	0.76
Humus-carbonate	50.12	0.08	1.21	0.93	–	0.100	0.056	30.14	6.80	3.15	–	0.11	3.60	1.83	1.18	0.75
Misc. black soils	48.74	0.16	2.20	0.38	0.200	0.071	0.156	34.71	6.86	3.59	0.46	0.08	2.36	0.95	1.36	0.65
Black soils																
Leached	49.9	0.17	2.36	0.10	–	0.061	0.018	31.94	6.84	3.79	0.52	0.08	1.22	–	0.82	1.38
Typical	48.0	0.22	3.09	0.30	–	0.100	0.136	31.28	7.09	3.71	0.36	0.16	2.00	–	0.97	1.71
Normal	49.3	0.15	2.05	0.48	–	0.070	0.168	31.32	6.88	3.69	0.47	0.05	2.47	–	1.00	1.32

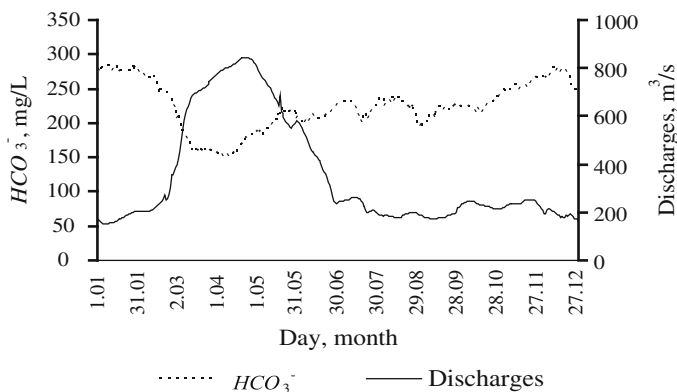
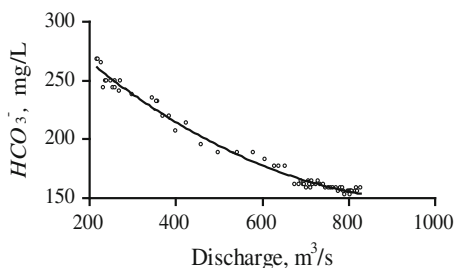


Fig. 2.5 Annual dynamics of hydrocarbon ions content and water discharge in the Desna River near outlet station (Litky village), 1995 [67]

Fig. 2.6 The relationship between water flow (Q) and content of HCO_3^- at the stage of high water levels during floods (the Desna River near outlet station, Litky village) [67]



River concentration dependence of HCO_3^- from Q is approximated by the equation (Fig. 2.6):

$$HCO_3^- = 0.0002 \cdot Q^2 - 0.3623 \cdot Q + 330.81 (R^2 = 0.98) \quad (\text{Fig. 2.6}).$$

Over a long period, the water discharge in the Desna River at a high flood stage has been increasing 3.8 times and the content of hydrocarbon ions decreasing 1.8 times. The main ions mode in the basin of the Siversky Donets River differs significantly from the mode in the Desna River. The upper portion of the Siversky Donets Basin is located in the wooded steppe zone, and as per the hydrochemical regime, according to the classification of A.A. Alekin, belongs to the rivers of Eastern European type [27]. An inverse relationship is observed between the water flow and concentrations of main ions. Water chemistry in the middle and lower stretches of the river, located in the steppe zone, differ significantly from the upper one. As shown in Fig. 2.7, an increased water discharge in the monitoring section near the city of Lysychansk results in the increase of its salinity.

At the beginning of a flood, when water levels rise and sloped surface runoff is formed, a short-term phase of dilution of channel water with low-mineralized meltwater sets in. After thawing of the soil the surface waters feature a sharp

Fig. 2.7 The relationship between discharge and salinity of water in the Siversky Donets River, city of Lysychansk, 1999 [67]

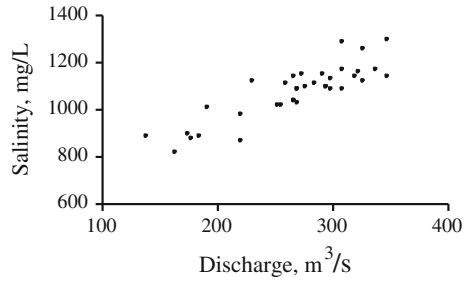
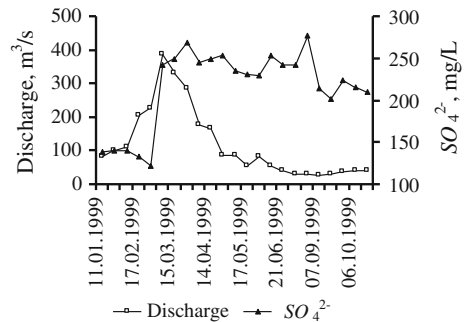


Fig. 2.8 Annual dynamics of water flow and concentration of sulfate ions in the Siversky Donets River, city of Lysychansk, 1999 [67]



increase of sulphate ions. For instance, over a period of two weeks in 1999 the content of SO_4^{2-} in the water has doubled—from 123 to 242 mg/L (Fig. 2.8).

Another situation occurs in the rivers, which flow in karst areas. For example, we consider fluctuations in water salinity in the Black River, whose basin is located in the Crimea in the area of limestone karst. The Black River is characterized by low water flow not exceeding several m^3/s and has an average water mineralization 350 mg/L. However, during the period 1997–1999 prevailing weather conditions led to a sharp increase in discharge up to 100–350 m^3/s . As a result, an additional amount of hydrocarbon ions was leached from the surface of the catchment, and water salinity reached 1200–1400 mg/L. Due to the chemical composition the river water was reclassified from freshwater to brackish water (Fig. 2.9).

The increase of flow rate during seasonal flood also causes income of other chemical components whose content in soil is high, notably organic matter, nutrients. We have conducted field studies in simulating the phenomenon of runoff on an experimental plot (Bohuslav city, experimental base of the Ukrainian Hydrometeorological Institute). The results showed growth of humic acids (HA) and fulvic acids (FA) concentrations in water in the rising limb of the runoff hydrograph (Fig. 2.10).

By using a method of dividing flow hydrograph into genetic components, we found out that 6.2–41.8 % of HA and 27.1–79.0 % of FA entered the Prypiat River basin with surface runoff. The fluctuations in the relative share of humic substances in surface runoff depend on a change of water content (Fig. 2.11).

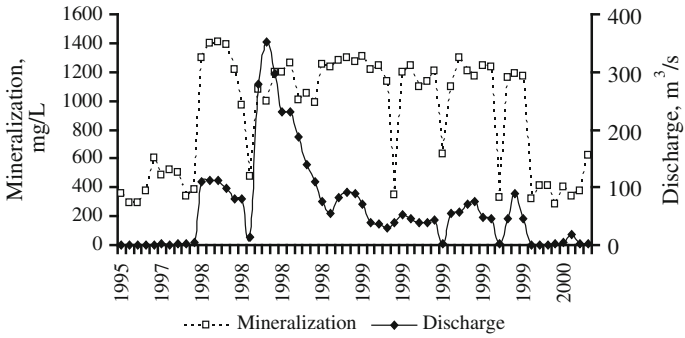


Fig. 2.9 Dynamics of water mineralization and discharge in the Black River (Crimea), during the period of 1995–2000

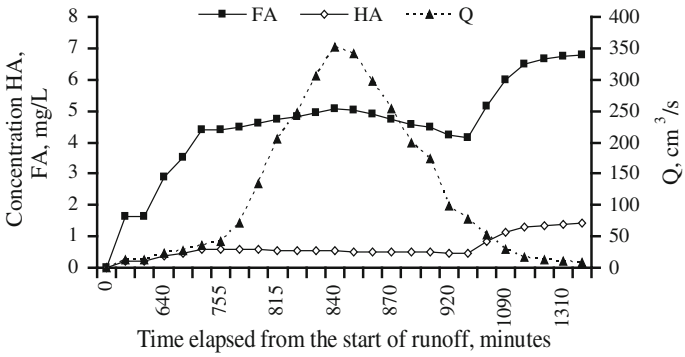


Fig. 2.10 Dynamics of humic and fulvic acid concentrations at various stages of generation of water runoff (according to the experimental simulation) [64]

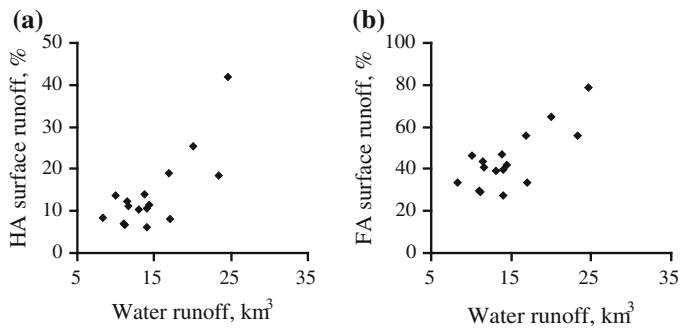


Fig. 2.11 Dependence of relative share of surface runoff on water content **a** HA and **b** FA [65]

Table 2.3 Surface ion runoff in the rivers of the lowland part of Ukraine, Ktons/year [69]

Physiographic zones	Ca^{2+}	Mg^{2+}	$Na^+ + K^+$	HCO_3^- in the form of CO_3^{2-}	SO_4^{2-}	Cl^-	Σ_i
Forest	432	55	66	569	191	81.1	1393
Wooded steppe	935	231	565	1462	1032	660	4885
Steppe	1111	231	1410	998	3228	1876	8855
Ukrainian lowland in general	2479	516	2041	3029	4451	2617	15133

Table 2.4 The relative share of individual ions in the formation of slope-surface ion runoff in various physiographic zones of Ukraine, % [69]

Physiographic zones	Ca^{2+}	Mg^{2+}	$Na^+ + K^+$	HCO_3^- in the form of CO_3^{2-}	SO_4^{2-}	Cl^-	Σ_i
Forest	31	4	4	41	14	6	100
Wooded steppe	19	5	12	30	21	13	100
Steppe	13	3	16	11	36	21	100

Research of melting runoff on slopes showed that the chemical composition of runoff water largely depends not only on the type of soil, but also on land use patterns (forest, meadows, fallow, crops) [8].

The estimated values of surface (slope-surface in the author's interpretation) ion runoff for plain terrain of Ukraine are presented in [69] (Table 2.3).

In general, a determinate increase in total volume and a change in ionic composition of surface ionic runoff are observed when moving from the forest to the steppe zone, while indicators of water flow in this direction are decreasing. Forest zone runoff is characterized by bicarbonate-calcium composition due to ions leaching from the geological substrate. As per the steppe zone, the leading role in forming the ion flow is also played by Ca^{2+} and HCO_3^- ions, although the role of chloride, sulfate and sodium ions is growing significantly (Table 2.4).

A transformation of ionic composition in surface runoff from calcium hydrocarbonate to sodium-sulphate-chloride is observed in the steppe zone. The increase in surface ionic runoff is accounted for the leaching of soluble salts from the soil and rocks. The rocks and soils in the zone of insufficient moisture are predominated by updrafts of moisture due to evaporation of groundwater in the capillary layer. Under these conditions, large amount of salts of continental origin is accumulated as a whole during an active water and salt exchange due to evaporation. With that, the sediments are mainly formed by calcium and sodium sulphates.

With the formation of subsurface runoff the period of contact between solid and liquid phase increases due to slow moving of water masses down the watershed slope. The maximum flow rate of these waters in the channel network coincides

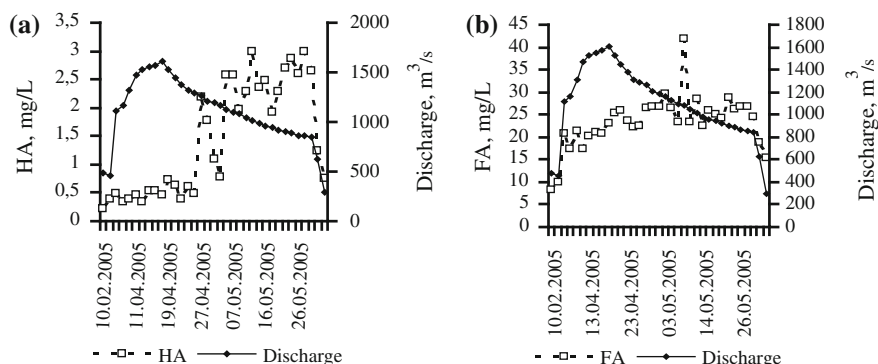


Fig. 2.12 Dynamics of the change of water flow and concentrations of **a** humic and **b** fulvic acids in the Prypiat River, city of Chernobyl, during the flood in 2005 [64]

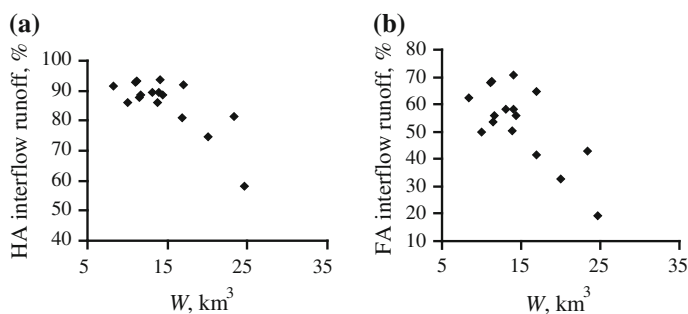


Fig. 2.13 Dependence of relative portion of interflow runoff of **a** humic and **b** fulvic acids in the basin of the Prypiat River on water content [64]

with the end of a flood. The increase of a groundwater share in water supply of a river is characterized by the beginning of a significant increase in the concentrations of chemical components and changes in the chemical composition of water, compared with the reference flood period. For humic substances it is clearly demonstrated in Fig. 2.12, which shows flood behaviour at the outlet of the Prypiat River, and in Fig. 2.13, reflecting the dynamics of water flow and concentrations of humic substances in the experimental runoff section.

Studies of the composition of lysimetric waters in the sod-podzolic soils [99] showed that ions of NO_3^- and partly of iron and aluminum are carried out predominantly by a vertical infiltration flow. While silicon, magnesium, calcium, bicarbonate ions and organic substances migrate with horizontal subsurface runoff.

According to calculations that we made for the basin of the Prypiat River, 21.4–81.2 thousand tons of humic acids and 101.5–387.4 thousand tons of fulvic acids are contributed to the channel of the river with subsurface runoff.

Although in absolute terms the volume of subsurface runoff is the smallest (1.19–4.56 %), it carries out the bulk of organic acids of humic origin (86 % of HA and 53 % of FA). Ground waters in the basin of the Prypiat River are not too deep, and during high water season may even come to the surface. Hence, the subsurface water comes in contact with the upper layers of soil with a maximum content of humic substances. Eluviation of HS with subsurface runoff depends on its volume, but with increasing of water content an overall tendency to decreased share of this type of HS runoff can be observed (see Fig. 2.13).

It was determined that subsurface waters also played a dominant role in the removal of cesium—137 with the Prypiat River water in the aftermath of the Chernobyl accident [21].

The role of subsurface waters, despite their relatively small share in the hydrosphere, is extremely important in the process the material cycle. This is accounted for their location on the boundary between the atmosphere and part of the lithosphere. According to [102], subsurface waters are the most active agent in the transformation of surface waters.

Groundwater During a flood the income of deep groundwater in the channel network is Low-flow period lasts on average for 9 months (including the summer and winter time). The rivers of the Polissya and forest-steppe feature the lowest water discharge in August and September, and in the steppe zone—in June and July [79].

The distribution of ground waters in Ukraine is determined by geological structure and history of the various geological formations. There are seven major hydro-geological areas that are identified in Ukraine:

1. *Hydro-geological region of the Ukrainian Craton (UC)*, featuring mainly fissure waters confined in not very thick layer of fractured rocks. Aquifers of Quaternary deposits have been identified within the region; pre-Quaternary deposits (Paleocene, Cretaceous and Jurassic in crystalline basement) and fractured zone of Precambrian crystalline rocks. The diversity of chemical composition of UC ground waters is accounted for the conditions of their formation. Before the waters, that infiltrate vertically, reach the surface of fractured crystalline rocks, they pass through the thickness of surface sediments, then through Quaternary rock covering the region. Precipitates undergo transformation of their chemical composition in the sedimentary rocks due to the processes of exchange absorption, leaching of cations and dissolution of salts. The waters of the aquifers of Quaternary deposits have calcium hydrocarbonate composition in the northwestern part, which has rich sand deposits. In the Central part they have sulphate hydrocarbonate composition, and chloride hydrocarbonate composition—in the southern and south-western parts due to the concentration by evaporation. The aquifer in Kharkiv and Buchach deposits in the northeast contains calcium hydrocarbonate waters, which are transformed into sulfate-bicarbonate calcium-sodium waters with mineralization increasing from 0.1–0.5 to 1.3 g/L. In the Kryvorizhzhya area mineralization is 2.0–4.0 g/L.

The waters of fractured formations in the northwestern part of the region have calcium bicarbonate composition with mineralization 0.5 g/L. The waters of the central region are characterized by the presence of sulfate ions and sodium with increased mineralization up to 0.5–1.0 g/L. An adjacent zone with production of sodium sulfate water with mineralization of 1.3 g/L borders in the south. The dominant anions here are chloride and sulfate, among cations—sodium.

2. *The Dnipro-Donetsk artesian basin*, which in terms of its geological structure is associated with the homonymous depression. The chemical composition of aquifers that lie above the local base levels of erosion, is determined by physiographic factors, among which the major one is leaching of rocks. There are three groundwater zones with characteristic chemical composition that can be identified in the cross-section of sedimentary rocks [29]:
 - fresh calcium bicarbonate waters that were formed as a result of significant moistening. They embrace aquifers of Quaternary, Neogene and Mezhygiryia-Obukhiv deposits in the central part of the basin, and within the north-eastern and western sides of the basin—older sediments (Cretaceous, Jurassic, and others.);
 - bicarbonate-sodium-chloride and chloride-sodium-bicarbonate waters are abundant in the central part of the basin in the Buchach-Kaniv sediments, and further to the southwest—in the Cretaceous and Jurassic sediments;
 - saline and salt waters (1–5 g/L) embrace the lowest tier of the central part starting from the Cenomanian-Albian sediments. This zoning is disturbed within salt domes in the side parts of the basin.
 - One of the main features of the basin's vertical groundwater zoning is the absence of sulphate waters.

The most massive zone of fresh water (300–800 m) was developed in the marginal parts of the basin (Kharkiv, Poltava). In the central trough the basin of fresh water has thickness of 200–400 m.

3. *The Volyn-Podillya artesian basin*, located in the northwestern part of Ukraine. Mainly fissure waters are abundant in this basin confined to terrigenous-volcanic rock unit of wide stratigraphic range. Hydrochemical zoning reflects the complex history of basin sedimentation, which was accompanied by multiple alternating of marine and continental regimes and led to the accumulation of two main types of waters—sedimentation and infiltration waters [80]. Different hydrochemical zones are formed within the basin when moving from east to west, depending on the degree of washing of the massive material. There is only one zone of fresh calcium hydrocarbonate waters in the eastern and northern parts covering the entire thickness of rocks until the crystalline basement. Normal zoning as for platform conditions is established in the central part, westward from the city of Rivne longitude: hydrocarbonate, sulfate and chloride water zones. There are only two zones in the western part—hydrocarbon and chloride waters. In the western and central parts of the basin the fresh water zone

extends no deeper than 100 m. The deeper parts of Lviv depression contain highly mineralized sodium chloride waters.

4. *The Black Sea artesian basin.* The aquifers in the Black Sea area are associated with sediments of Cretaceous, Paleogene, Neogene and Quaternary age. The chemical composition of groundwater is characterized by water mineralization variability and extensive development of brackish and salt water, which is due to the Black Sea territory being under the sea level in Pre-Neogene time. The chemical composition of groundwater depends largely on permeability of the upper part of sedimentary rocks and landscape. Basically, the depth of a zone of intense water exchange increases from north to south from 50 to 250 m [80].

Magnesium-calcium hydrocarbonate waters with mineralization of up to 0.5–0.6 g/L prevail mainly in the northeast. Fresh water is missing in the areas of continental salinity—in the Syvash Plain area and Kerch Peninsula. Bicarbonate-chloride and sodium bicarbonate-chloride and magnesium waters with mineralization of up to 5.3 g/L are abundant in the southwest.

Paleogene, Cretaceous and Jurassic sediments contain sodium chloride salt water with mineralization from 5–10 to 35–40 g/L.

5. *Donetsk folded hydro-geological region*, which includes small basins of edge waters and block type formation the Donetsk Ridge. Determinate variations of chemical composition of water can be observed from top downward within individual blocks that represent separate hydro-geological bodies: bicarbonate, sulphate-bicarbonate, sulphate, chloride and sulphate-chloride waters with simultaneous increase in mineralization. The thickness of weakly mineralized waters zone in the open Donbas is 300–800 m, while in the south it decreases to 50–100 m [29]. A similar pattern of water composition change depending on depth is observed at the junction of the Donbas and Azov Sea area crystalline basin. Geodynamic stresses sometimes cause discharges of sodium chloride deep waters into near-surface horizons.

There is an increase in groundwater salinity in the Donetsk region due to the mass closure of mines with the use of the “wet” method of lay-up.

6. *The Carpathian folded hydro-geological region*, which includes the Carpathian artesian basin, folded Carpathian Mountains and the Transcarpathian artesian basin.

The area of folded Carpathians came out from below sea level in the early Miocene. Since then, the conditions have been in place for displacement of marine waters and their dilution with precipitation. Good leaching of water-bearing material and intense water exchange create conditions for the formation low-mineralized waters. Their thickness ranges from 100 to 500 m. Sodium chloride waters with high mineral content are encountered at a depth of 500–600 m, regardless of age [29].

Fresh waters in the Carpathians are found only in the Quaternary sediments. The deeper Paleogene and Cretaceous sediments carry abundant sodium chloride brines with high salinity.

Transcarpathian Quaternary sediments carry well-developed fresh waters with salinity lower than 1 g/L of calcium bicarbonate and calcium-magnesium. Their salt composition is determined by the processes of dissolution and leaching of the water-bearing material.

7. *The folded hydro-geological region of the Crimean Mountains.* The basins of fracture-karst and fissure waters in the mountainous Crimea are confined to tectonic structures and have strata-block nature. Upper Jurassic deposits are characterized by significant karstification. As per chemical composition, karst waters are the best on the Crimean Peninsula. These are calcium bicarbonate, magnesium-calcium, and less abundant hydrocarbonate-chloride waters with mineralization up to 1 g/L [80].

Statistically assessed chemical composition of ground waters of Quaternary and Pre-Quaternary sediments in Ukraine are presented in [70] (Figs. 2.14 and 2.15).

The dominance of ground waters during low water seasons accounts for stable characteristics of the chemical composition of surface water. The values of water discharge and concentrations of dissolved ions during these periods vary within small amplitude, as demonstrated by the case studies of the rivers of different geographical zones (Figs. 2.5, 2.8, 2.16 and 2.17).

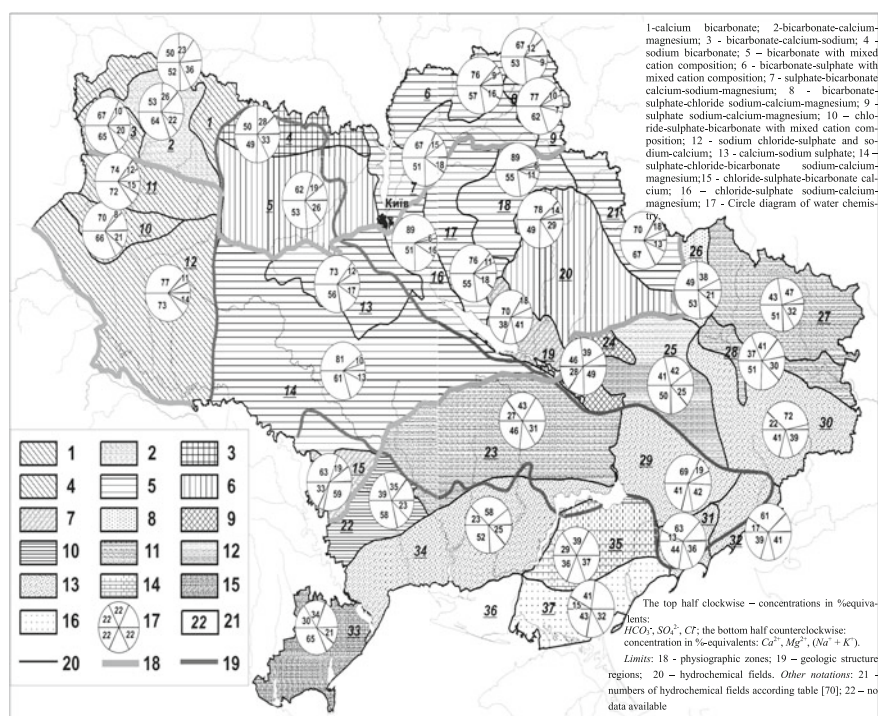


Fig. 2.14 Chemical composition of groundwater in Quaternary sediments [70]

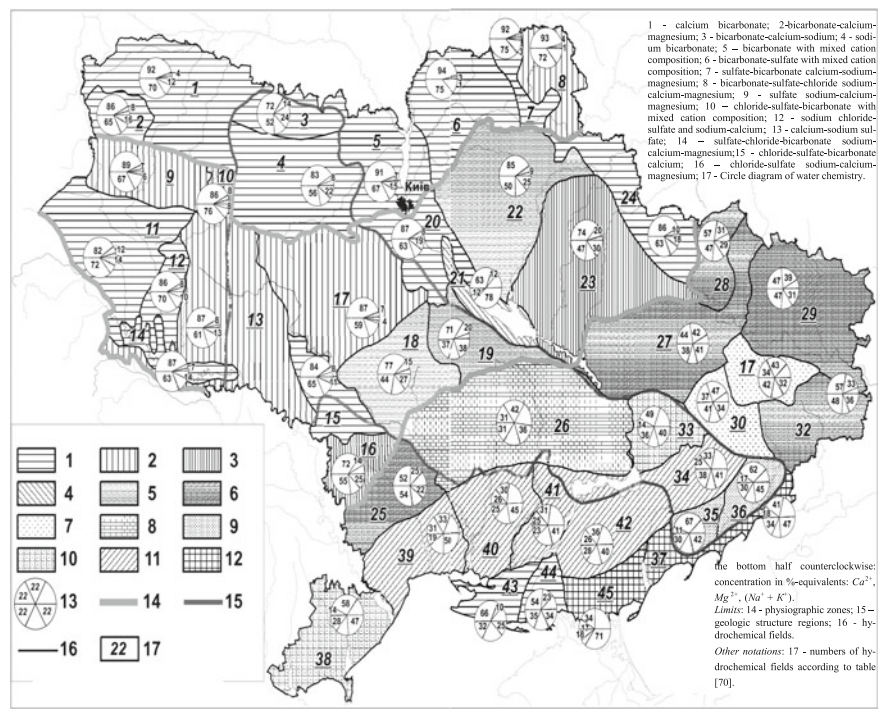


Fig. 2.15 Chemical composition of groundwater in Pre-Quaternary sediments [70]

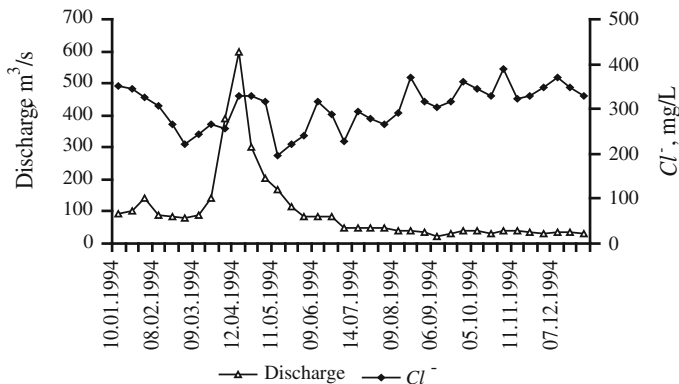


Fig. 2.16 Annual dynamics of water discharge and chloride ion content in the Siversky Donets River, the city of Lysychansk, 1994 [67]

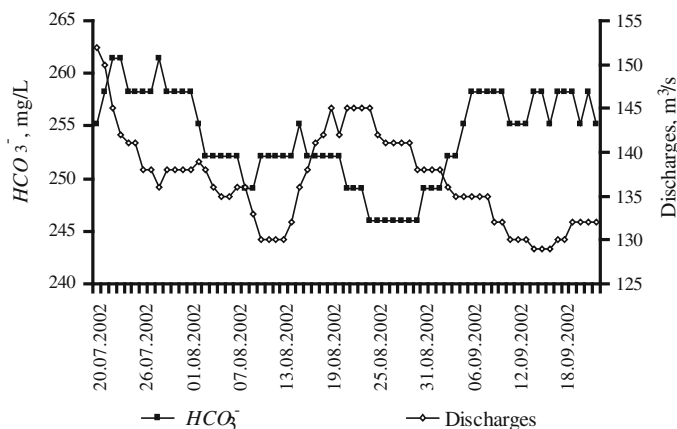


Fig. 2.17 The dynamics of hydrocarbon ions and water discharge during the summer-autumn low water (case study of the Desna River, vil. Litky, 2002) [67]

The distribution of main ions (except HCO_3^-) and mineralization of water are characterized during low water by a gradual increase in concentration from when moving from the northwest to the southeast [79].

Thus, the hydro-chemical regime of dissolved components is determined by the prevalence of one of the sources of river nourishment during a certain hydrological phase. In the case of contaminated wastewater discharge the volume of natural water flow of the river is crucial. Self-cleaning of the river will be determined in the first place by the physical process of sewage dilution. The most difficult environmental conditions are typical for locations where significant amounts of wastewater are discharged into rivers with low volume of runoff. In the context of Ukraine, it is most evident in the Poltva River, which is the most polluted water body in Ukraine. The river takes a large amount of waste water from the city of Lviv. The Lopany River downstream from the city of Kharkiv and the Ustya River downstream from the city of Rivne also face environmental challenges.

2.2.2 Reservoirs

The formation of the chemical composition of water in reservoirs is significantly influenced by water exchange, which can be external or internal.

External water exchange is accounted for the change of water balance parameters that determine the inflow and runoff of water and chemical components in it.

The content of dissolved substances in water depends on the ratio of incoming and outgoing components of water and material, quantitative assessment of which is based on the water balance:

$$(I_p + I_t + I_u + I_d + P) - (R_p + R_w + R_s + E) = A. \quad (2.1)$$

The incoming components include inflows from of the main river (I_p) and tributaries (I_t), underground inflow (I_u), precipitation (P) falling on the water surface and all kinds of wastewater discharge (I_d). The outgoing components includes runoff from the principal river (R_p), all kinds of water intake (R_w), seepage (R_s) and evaporation (E) from water surface. The difference between incoming and outgoing components is accumulation (A).

For most reservoirs the dominant role in water balance equation is played by inflow and runoff from the main river and in some cases by inflow from the tributaries and withdrawal of water [12, 45]. The role of precipitation depends on the water surface area and its geographical location (in the direction from north to south the role of precipitation decreases). These same parameters determine evaporation, whose discharge increases in the direction mentioned above. Groundwater inflow does not exceed 1 %, and seepage is <1 %.

As per Dnipro cascade reservoirs the main components of the water balance are surface inflow and runoff. Thus, for the upper Kyiv reservoir, which is formed mainly by the waters of the upper Dnipro and the Prypiat rivers, the income part of the water balance is 33.1 km³. The discharge balance corresponds to runoff through the dam of the Kyiv hydroelectric station. For the next, Kaniv reservoir, 75 % of inflow is provided by the discharge of the Kyiv hydroelectric station, other 10 km³ of water are added by the Desna River [90, 93]. In the downstream reservoirs about 94 % of runoff is provided by the inflow from the upper reservoirs. The Kremenchug and Kakhovka reservoirs lose 0.5 and 0.7 km³/year respectively due to evaporation. For the Kakhovka reservoir, which is the end reservoir of the cascade, substantial losses may be accounted for the filtration through waterworks.

External water exchange of a water body plays an important role in the formation of the chemical composition of the water. To characterize it, rate of replacement (R_r) is used to show how many times the volume of water flowing through a reservoir for a base period ($W_{\text{inflow, runoff}}$) exceeds the volume contained in it (V).

$$R_r = W_{\text{inflow, runoff}} / V$$

Flushing period (t), showing a time period during which inflowing water completely replaces the water stored in the reservoir, is also used as a characteristic of water exchange. The values of R_r and t for Dnipro reservoirs are presented in Table 2.5.

The process of replacing the “old” water in low-flow water reservoirs by river inflow is gradual, and the mixing front can be of complex nature [97]. The mixing of water masses is greatly impacted by wind turbulence.

Table 2.5 External water exchange in Dnipro reservoirs in the years with different water content [90]

Reservoir	Volume (total), km ³	Water content rate					
		High		Medium		Low	
		R _r , year ⁻¹	t, 24 h	R _r , year ⁻¹	t, 24 h	R _r , year ⁻¹	t, 24 h
Kyiv	3.73	15.6	23	10.1	36	6.70	54
Kaniv	2.62	23.1	16	18.2	20	12.80	28
Kremenchug	13.51	6.14	59	4.3	85	2.41	151
Dniprodzerzhynsk	2.45	32.7	11	20.2	18	13.50	27
Dnipro (Zaporizhzhya)	3.30	24.9	15	15.8	23	8.90	41
Kakhovka	18.21	4.66	78	2.8	130	1.63	224

To predict the concentrations of individual components the notion of a rate of water replacement (B) is introduced, which is calculated by the equation [37].

$$B = 1 - \left(\frac{V_0}{V_k} \right)^{1 + \frac{W_{\text{runoff}} \cdot V_e}{1 - V_0 \cdot V_e}}, \quad (2.2)$$

where V_0 , V_k are the volumes of the reservoir at the beginning and the end of the base period, m³; W_{runoff} —runoff for the same period, m³.

When taking into consideration turbulent mixing, the rate of water replacement is denoted as B' and determined by the following equation [89, 90]:

$$B' = 0.5 \cdot V^{-1} (V + Q_{bp} \cdot t - 14 \cdot b \cdot h \cdot \sqrt{t}), \quad (2.3)$$

where Q_{bp} is the average for the base period volume of water entering a reservoir, m³/s; V —volume of the reservoir, m³; t —base period, s; b —the average width of the reservoir, m; h —the average depth of the reservoir, m.

The monthly values of B' rate of the Dnipro reservoirs, calculated by formula (2.3), are shown in Fig. 2.18.

The calculation of water salinity level with the use of the rate of water replacement was conducted [6] according to the following formula (2.4):

$$C_k = C_0 + \left(C_{in} \frac{W_{in}}{W_{in} + W_{prec} - W_{evap}} - C_0 \right) : B \quad (2.4)$$

where C_0 and C_k are the average water salinity levels at the beginning and the end of the base period, mg/L; C_{in} —salinity of water that entered the reservoir, mg/L; W_{in} and W_{pr} are the volumes of water received during the base period with inflow and precipitation, m³; W_{evap} —the volume of water evaporated from the water surface, m³. It is obvious, that Eq. (2.4) reflects the impact of hydrological factors on concentrations of all dissolved substances, and not only on water salinity. However, it should be noted that concentrations of biogenic elements, organic

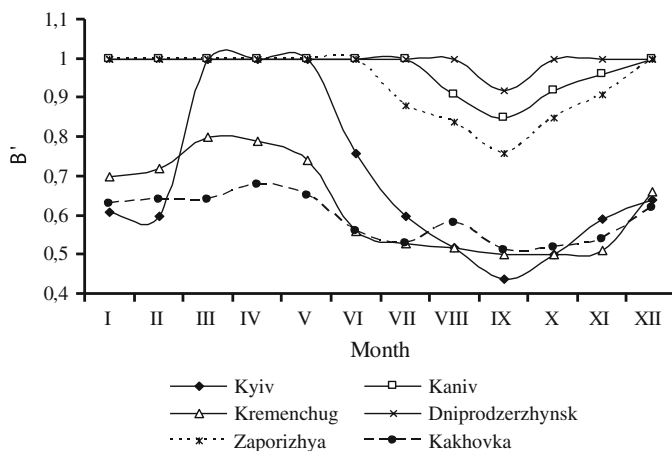


Fig. 2.18 Water replacement rates in the Dnipro reservoirs [14, 90]

compounds and trace elements, in particular metal ions, are also influenced to a great extent by physical, chemical and biological processes that are discussed in Sects. 2.3 and 2.4.

The intensity of water replacement process in reservoirs is closely linked with their trophicity [12, 106]. In the context of flooded water bodies in the Dnipro mouth it is demonstrated [93, 97] that lakes with intensive water exchange feature scarce species and population of phytoplankton. The amount of algae dramatically increases in lakes with slow water exchange, and those lakes where daily water replacement does not exceed 0.25 % show signs of dystrophization.

Znamensky paper [114] studies in detail the system of the Volga reservoirs and shows the dependence of their water salinity levels on water exchange. Due to different chronology in the occurrence of extreme values of water salinity in the Volga and Kama rivers, two minima and maxima are observed in the annual values of corresponding indicators in the Samara, Saratov and Volga reservoirs. The paper also shows that water exchange has greater impact on water salinity of lake-alike reservoirs compared to narrow channel reservoirs.

The processes of external water exchange determine water inflow and runoff as well as chemical components carried by it, causing indicator differentiation in different parts of a reservoir. We take as an example the cascade of Dnipro reservoirs, particularly its upper reservoir—Kyiv, whose water mass is formed mainly by merging the upper Dnipro River and its main tributary the Prypiat. These rivers differ significantly in their chemical composition, especially in the content of organic substances, the bulk of which are natural components of humus origin—humic (HA) and fulvic acids (FA). The waters of the upper Dnipro contain on average 0.73 mg/L of HA and 18.6 mg/L of FA, while in the Prypiat these values are almost twice as high and are respectively ~ 2.0 mg/L and 32.0 mg/L. These differences persist in further migration of water masses through the reservoir. Using HA and FA contents as indicators of migration of water masses, it was found

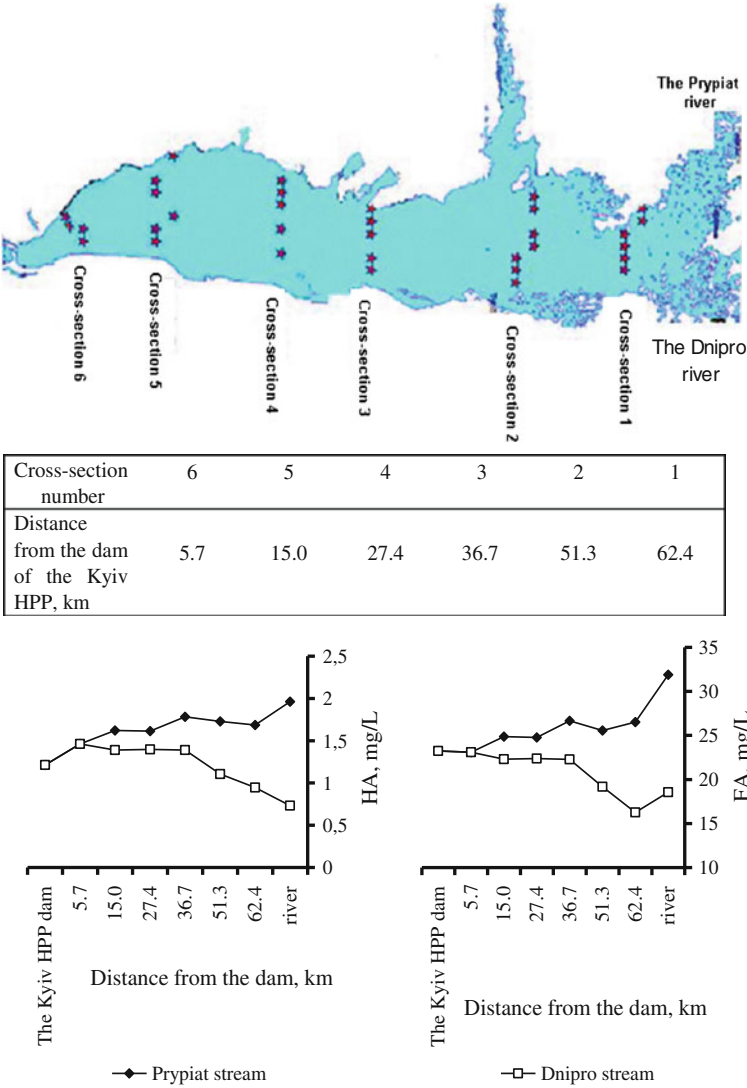


Fig. 2.19 Changing of HA and FA content along the Kyiv reservoir during summer low water, 1999 [64]

out that the two genetically different water masses of the Prypiat and the Dniro move, starting from entering the reservoir and up to the control section near the village of Sukholuchchya, virtually without mixing. The water masses partially mix downstream of the mentioned control section and get completely mixed only at the lower reached of the reservoir (section №6) at the control section near the village of Stari Petrivtsi (Fig. 2.19).

Apart from water exchange, altering of the water balance in a reservoir may occur due to an increase of its other component—evaporation. The impact of this process is most significant in man-made cooling ponds, the main feature of which is a significant heat load associated with the operation of an energy facility. Consider this phenomenon using the example of the Zaporizhia NPP cooling pond (ZNPP CP). Its water temperature was 7–16 °C higher than the corresponding natural parameters, which caused increased evaporation, water loss being compensated by recharge from the Kakhovka reservoir.

At the initial stage of ZNPP operation (1984) chemical composition and quality of water in the cooling pond had the same characteristics as in the Kakhovka water reservoir. During the period from 1996 to 2000 a large number of dissolved substances accumulated in ZNPP CP as a result of distorted water balance and high thermal load. During the period 1984–1993 total mineralization of the water increased more than 2.5 times, and at the end of 1993 reached almost 1000 mg/L, while increasing of salinity in the Kakhovka reservoir was not actually registered.

The process of evaporation leads to concentration, which leads to increased water salinity and content of individual ions, in the first place HCO_3^- , CO_3^{2-} , Ca^{2+} , and then consecutively SO_4 , Cl^- , Na^+ . Further increase in water mineralization leads to withdrawal from the solution phase of slightly soluble compounds in the following sequence: carbonates—sulphates—chlorides [15]. The least soluble CaCO_3 is the first to be withdrawn from the solution phase. Further salt deposition sequence will be determined in accordance with the principle of chemical separation depending on water chemistry. This principle [15] reads as follows: whenever a binary salt is precipitated in the process of evaporation and an effective ratio of two salt ions differs from the mixing ratio of these ions in solution, further evaporation will lead to higher content of the ion, which is available in the solution at a higher relative concentration, and to reduced content of the ion, which is available in a lower relative concentration. That is, one of the ions, which is part of the precipitated salt, will grow in number, and the concentration of the other will decrease.

Based on this principle one can consider two most likely scenarios of transformation of salt composition in water.

The first type is a sequence of CaCO_3 – CaSO_4 – NaCl . It will occur, when after the precipitation of CaCO_3 the following correlation will be in place in the water:

$$\text{Ca}^{2+} \text{ (mM/L)} > \text{HCO}_3^- + \text{CO}_3^{2-} \text{ (mM/L)},$$

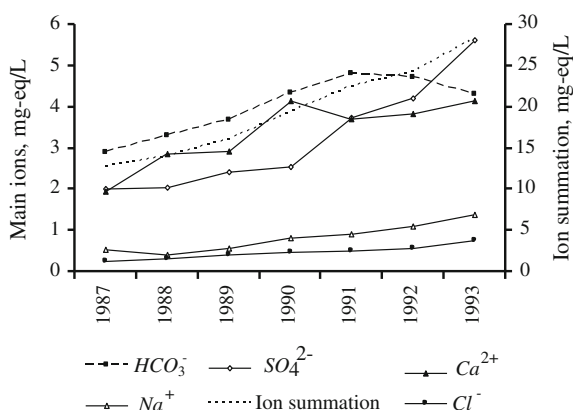
or in the form of balance of charges

$$2\text{m}_{\text{Ca}^{2+}} > \text{m}_{\text{HCO}_3^-} + 2\text{m}_{\text{CO}_3^{2-}},$$

The above relation indicates a chemical separation equilibrium point [15]. If this relation does not hold in a solution, the concentration of calcium or alkali ions will increase during evaporation.

Given the relation $\text{Ca}^{2+} \text{ (mM/L)} > \text{HCO}_3^- + \text{CO}_3^{2-} \text{ (mM/L)}$, calcium will start accumulating in water and it will precipitate not only as CaCO_3 , but also as CaSO_4 .

Fig. 2.20 Dynamics of main ions content and water salinity in the cooling pond of the Zaporizhzhya NPP during its operation in non-blowdown regime (1987–1993) [67]



Otherwise, if after precipitation the concentration of $CaCO_3$ will be lower than the alkalinity of water, carbonate ions will accumulate in the water and the precipitation will occur in the sequence $CaCO_3$ – Na_2CO_3 – $NaCl$. That is, sodium carbonate salinization will occur.

During the period 1984–1992 the salinity of water and contents of Na^+ and Cl^- soluble ions in ZNPP CP showed a steady increase (Fig. 2.20).

Thereby, the total amount of ions changed more than twofold—from 12.7 to 28.3 mg-eq/L. In 1989 there was a decrease of Ca^{2+} ions, however, given that relation $Ca^{2+} > HCO_3^- + CO_3^{2-}$ still was holding, this ion continued to accumulate in the water, and in 1990 its contents reached 4.15 mg-eq/L. Under these conditions $CaSO_4$ started to be removed, which led to corresponding reduction of sulphate ions. As relation $m_{Ca^{2+}} > m_{SO_4^{2-}}$ was in place, calcium started to accumulate in the solution again, up to 4.15 mg-eq/L. This cycle repeated again over the next three years. This allowed us conclude that under the given margins of water salinity fluctuation, calcium content will not rise above 4.15 mg-eq/L, i.e. the condition of calcium-carbonate equilibrium will cause its withdrawal from the aquatic environment. This condition will be observed until relation $m_{Ca^{2+}} > m_{SO_4^{2-}}$, will hold.

If the right part of the latter relation will prevail over the left one, calcium will be excluded at all from the system, and sulphate and magnesium ions will start accumulating in the water.

2.3 Hydrodynamic Processes

Water masses are an environment where substances and energy circulate within the hydrologic system, and which gives rise to the development of biological objects. On this premise, the chemical composition of water, apart of quantitative parameters of water runoff, will significantly be affected by the process of fluid motion to facilitate the levelling of concentrations. As per conservative substances, the role of hydrophysical factor is decisive. The movement of liquid is determined by the type of

water body and its hydraulic characteristics. The types of water bodies were discussed above, and the most important hydraulic characteristics include water discharge and its average flow velocity. There are two main flow regimes of fluid that are recognized in hydrodynamics: laminar and turbulent. Laminar regime can be observed in slow currents and is characterized by drift of fluid in layers along the general flow. Turbulent regime features pulsating and chaotic movement which causes mixing of fluid. This results in levelling of the concentrations of substances in water bodies.

2.3.1 Watercourses

Watercourses are free-flow turbulent flows with uneven movement of water under the force of gravity. Mathematically, this movement can be described by a well-known Navier-Stokes equation [36, 87]. To solve practical problems in the case of open channels, its simplified version—Saint-Venant equation is often used. The latter represents a set of two combined equations: equation of continuity (2.5) and equation of dynamic balance (2.6).

$$\frac{\partial h}{\partial t} + \frac{1}{b} \frac{\partial Q}{\partial x} = 0 \quad (2.5)$$

$$\frac{1}{g} \frac{\partial v}{\partial t} + \frac{v}{g} \frac{\partial v}{\partial x} + \frac{\partial h}{\partial x} = J - \frac{Q^2}{K^2} \quad (2.6)$$

for postulated initial conditions:

$$Q(x, 0) = Q_0(x), h(x, 0) = h_0(x)$$

and boundary conditions:

$$Q(0, t) = Q_1(x), h(0, t) = h_1(t),$$

$$Q(l, t) = Q_2(x), h(l, t) = h_2(t),$$

where t is the time, $0 \leq t \leq T$, $T = \text{const}$; x —the spatial coordinate in the direction of motion, $0 \leq x \leq l$, $(0, l)$ —boundaries of a river stretch without tributaries; J —the inclination of a bed; G —the acceleration by gravity; b —the width of the channel; $K(h)$ —channel discharge characteristics; $h(x, t)$ —the depth of the channel; $v(x, t)$ —the average water flow velocity in the channel cross section at point x and time t ; $Q(x, t)$ —the water flow rate through the cross section.

To describe the transfer of substances the hydrodynamic component is supplemented by a diffusion-convection equation:

$$\frac{\partial C}{\partial t} + V_x \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} \quad (2.7)$$

where C is the concentration of a substance; V_x —the average flow rate; D —the coefficient of turbidity diffusion.

To determine the latter is one of the most difficult tasks, because it depends on many factors specific to a particular water object [90].

Turbulent diffusion causes mixing of water masses, resulting in dilution of contaminated waters with clean waters and progressive levelling of concentrations of substances downstream.

Under natural conditions, mixing of water masses is due to the confluence of tributaries with different chemical composition. The Prypiat River is the most striking example. Its left-bank tributaries are fed mainly by wetlands, which leads to the enrichment of river waters with organic substances and their high color. Mineralization of such tributaries is low. Right-bank tributaries, whose watershed is formed in Ukraine, by contrast, have groundwater inflow. This accounts for minor content of organic substances in the water masses and their higher mineralization. Consecutive confluence of tributaries with the main channel causes heterogeneity of water composition in cross-section. A similar phenomenon is observed in the Desna River after its confluence with its tributary the Seim River. The phenomenon of heterogeneity of chemical composition across the width of a river is also observed in the Volga River after the confluence with the Oka River [1]. In general, heterogeneity of chemical composition in a cross-section is a local phenomenon, and the chemical composition of water in a principal river is balanced due to turbulent mixing.

Heterogeneity of chemical composition in river depth is actually not observed, due to the turbulent flow and mixing of water masses.

Heterogeneity of chemical composition is most pronounced along watercourses, particularly large ones, which cross several geographical zones with different conditions of forming the water constitution.

Hydrodynamic factor in rivers plays a much greater role in assessing the impact of waste water discharges. Dilution of contaminated water in the main stream depends on flow velocity, water runoff and roughness of the channel. A number of methodological approaches are used for assessing quantitative dilution of waste waters.

The method developed by Karaushev [30, 31], is based on the turbulent diffusion equation and provides a picture of spatial distribution of concentrations of substances within the entire estimated area regardless of the types of water bodies. According to his approach, the turbulent diffusion equation is written in the form of finite differences, when differentials ∂c , ∂x and ∂z are replaced by finite increments Δs , Δh and Δz . The entire computational domain of a flow is fit into an analysis grid with coordinates x , y , z . Along X -axis of such elements k is plotted, along Z -axis— m . Each element is assigned index number correlating with an axis. An increase of the index by a unit means transition from one sector to another. Altered concentrations in each sector are assigned similar indices. Calculation for each sector is performed by the following equation [31]:

$$\frac{\Delta_x C}{\Delta x} = \frac{D_{cp}}{V_{cp}} \left(\frac{\Delta_y^2 C}{\Delta_y^2} + \frac{\Delta_z^2 C}{\Delta_z^2} \right) \quad (2.8)$$

where C is the concentration of pollutants, g/L; V_{av} —the average flow rate, m/s; D_{av} —the average turbulent diffusion coefficient, m²/s; x, y, z —the coordinates of analysis grid.

For a plane with coordinates x, y concentrations of pollutants are calculated by the equation:

$$C_{k+1,m} = 0.5(C_{k,m-1} + C_{k,m+1}) \quad (2.9)$$

A disadvantage of the above method is the neglect of river's tortuosity.

One of widely used simplified methods for calculating the mixing of waste waters with river water flow is the Rodziller-Frolov formula, which is used under condition that ($0.0025 \leq q_{ww}/Q \leq 0.1$). This formula allows for determining concentrations of substances in the most polluted streams at a given distance from the release of wastewater without specifying the size, shape and location of the jet [77]:

$$C_{max} = C_{bg} + C_{ww} - C_{bg}/n, \quad (2.10)$$

where C_{max} is the maximum concentration of a substance in a contaminated stream, g/m³; C_{bg} —the concentration of a substance in cross-section above the waste water release site (background concentration), g/m³; C_{ww} —concentrations of substances in wastewater, g/m³; n —reciprocal dilution of waste water at a given distance from the release site.

Reciprocal dilution of waste water is calculated by the formula:

$$n = \frac{\gamma \cdot Q + q_{ww}}{q_{ww}}, \quad (2.11)$$

where Q is the water runoff in a river; m³/s; q_{ww} —wastewater discharge, m³/s; γ —mixing ratio, which is calculated by the formula:

$$\gamma = \frac{1 - e^{-\alpha \sqrt[3]{L}}}{1 + \frac{Q}{q} e^{-\alpha \sqrt[3]{L}}}, \quad (2.12)$$

where L is the distance along the midstream from the waste water release site to a control section, m; α —coefficient that depends on the hydraulic flow conditions:

$$\alpha = \xi \cdot \phi \cdot \sqrt[3]{\frac{D_c}{q_{ww}}}, \quad (2.13)$$

where ξ is the coefficient that depends on the location of the waste water release site, $\xi = 1$ for near-shore release, $\xi = 1.5$ for midstream release; φ —coefficient of watercourse tortuosity (the ratio of a distance between the control sections along the mead-stream to the distance along a straight line); D_c —coefficient of turbidity diffusion.

$$D = \frac{V_{av} \cdot H_{av} \cdot g}{2 m c} \quad (2.14)$$

where V_{av} is the average flow rate, m^3/s ; N_{av} —average depth, m; g —gravity acceleration = 9.81 m/s^2 ; m —the Boussinesq's coefficient, $m \approx 24$; s —the Chezy factor, which is determined by using the table. If $10 < p < 60 \text{ m} = 0.7c + 6$, at $s \geq 60 \text{ m} = 48 = \text{const}$; m has dimension m/s^2 . This coefficient describes the intensity of turbulent exchange of water masses and has maximum values at weak exchange and minimal values at vigorous exchange.

Given measured energy gradients (I) c is defined as:

$$c = \frac{V_{av}}{\sqrt{RI}} \quad (2.15)$$

where V_{av} is the average flow rate, m/s ; $R = F \cdot \chi$ —hydraulic radius of the flow, m; F —discharge area, χ —wetted perimeter.

In the absence of data on energy gradient c is estimated by the N.N. Pavlovsky formula:

$$c = \frac{1}{n_r} \cdot R^y \quad (2.16)$$

where n_r is the roughness of channel; y —index which is function of n_r and R . Value of n_r varies from 0.02 to 0.06 depending on the character of bed.

$$R < 1\text{m } y = 1, 5\sqrt{n_r} \quad R > 1\text{m } y = 1, 3\sqrt{n_r}$$

For wide rivers it can be assumed that $R = H$, in other words the hydraulic radius is equal to an average river depth H . In this case $\chi = B$, where B is the width of a river.

For lowland rivers turbidity diffusion coefficient can be calculated by the simplified M.V. Potapov formula:

$$D = \frac{v_{av} \cdot H_{av}}{200} \quad (2.17)$$

where V_{av} is the average water flow velocity in the stretch between the background and monitoring sections, m/s ; H_{av} is the average depth of the watercourse in the area of interest, m.

In addition, many express methods to calculate dilution have been developed, in particular the Bestsennaya methodology [5], that of approximating functions [47], that of Tallinn Polytechnic Institute [68, 86], that of Ural Research Institute of Water Management [75], VodGEO [77].

2.3.2 Reservoirs

The movement of water masses in reservoirs without changing their total volume under the influence of meteorological factors (temperature, wind), of waterworks and others determine internal water exchange. The volume of water masses involved in the internal water exchange in a narrow channel is commensurable with bypassing volumes, and in large lakes may far exceed them [114].

The movement of water masses with internal water exchange may occur in vertically and laterally and lead to balancing of concentrations of dissolved substances, turbidity and color of water and other indicators among different reservoir areas or their depths.

Convective mixing of water masses occurs as a result of seasonal homeothermy, when the temperature of maximum water density ($\sim 4^\circ\text{C}$) is setting in essentially through the entire depth of the reservoir. During this period, water masses are easily intermixed by wind. Further warming (cooling) through a reservoir results in stratification, and convective mixing stops. However, in the case of small lakes, homeothermy can be observed throughout the whole ice-free season [25].

Turbulent mixing caused by wind-wave processes is much more powerful factor influencing the chemical composition of water in reservoirs. A simplified equation of substances transport due to turbidity diffusion (2.8) is given in Sect. 2.3.1. One of its required input parameters is an turbidity diffusion coefficient. Practical hydrodynamic calculations considerable difficulties [17, 18, 26, 76, 90]. Its value depends essentially on the density of water and thermal stratification of reservoirs, which vertically and laterally can vary by several orders of magnitude. Formula (2.18) and the A. Karaushev formula (2.19) appeared to be the most appropriate for determining an turbidity diffusion coefficient for shallow water reservoirs in Ukraine [90, 91, 98]:

$$A_z = \frac{\gamma_h}{4\rho a_0} wh \quad (2.18)$$

where A_z is the vertical turbulent exchange coefficient; γ_h —the parameter of air friction; w —wind module; h —depth of a reservoir; ρ —density of water; a_0 —wind factor, the recommended value of which is 0.0125.

$$A_z = \frac{gh\bar{v}}{C(0.7C + 6)} \quad (2.19)$$

where A_z is the vertical turbulent exchange coefficient; C —the Chezy factor; h —the depth, m; \bar{v} —the average flow velocity, m/s.

Horizontal turbulent diffusion coefficient is determined through experimental investigations by the formula (2.20):

$$K_L = \frac{r_{\max}^2}{4t_{\max}} \quad (2.20)$$

where K_L is the horizontal turbulent diffusion coefficient; r —spot radius at its maximum size, m; t —time to reach a maximum size of the spot, s.

The analysis of the experimental data obtained [90] in the conditions of Ukraine justifies the use for calculations of L. Richardson's four-thirds power equation. According to this law, the change in turbidity viscosity of water during the horizontal diffusion depends on the distance between objects in the water, which are in turbulent motion, raised to 4/3 power [25]. The resulting value can be used in Eq. (2.8) as turbidity diffusion coefficient.

Studies [90, 94] show that an average intensity wind causes complete mixing of water masses in shallow waters only. Wind at velocity of 10 m/s mixes a water column up to the bottom in 70–75 % of basins of the Dnipro cascade except deeper Kremenchug and Kakhovka reservoirs. In the latter case wind mixes only for 32–54 % of the area.

Along with the mixing factors, currents are also a determining factor in the redistribution of substances in water reservoirs. The latter may occur for various reasons. In running-water lakes and reservoirs a significant role is played by discharge currents, a prerequisite for which is inclination of water surface. Typically, discharge currents occur in small upper (river) parts of reservoirs where there are no suitable conditions for producing other types of flows. The regime of discharge currents in reservoirs is almost completely determined by the operation of waterworks. Discharge currents play a dominant role in the cascade of Dnipro reservoirs and in the Dniester reservoir itself. Their flow rates in a year of average water content vary within 1.5–7.0 cm/s and 3.2 m/s, respectively [14, 24].

Wind currents occur in large lake-alike areas of reservoirs and closed lakes that can engage not only surface layers, but also layers up to 1/3 of the depth of water. Deeper waters feature generation of reverse flows. The velocity of wind currents in Dnipro cascade reservoirs reaches 0.4–7 % of overwater wind speed [14]. The mechanism of wind currents is quite complex and is directly related to the wobbling and wave motion of water masses.

An important role in water exchange of lakes and reservoirs is played by near shore currents which provide flushing of shallow waters. A research of this water exchange in reservoirs of Ukraine has shown that the ratio of currents in general shoal water exchange is 65–85 %. Phytoplankton follows the near shore currents and settles down in shoal waters, thus improving their oxygen regime and reducing eutrophication.

In general, currents of the same type appear in reservoirs quite rarely, and the combination of different by origin movements of water masses produces a complex picture of general circulation in a reservoir.

Well developed mathematical tools have been obtained recently for estimation of reservoir internal circulation. A series of one-, two- and three-dimensional system mathematical models are used for numerical calculations. Two-dimensional models obtained by averaging finite equations of depth hydrodynamics are considered to be most appropriate for large reservoirs [18, 26, 76]. A hydrodynamic model for calculating wind circulation at a variable value of the vertical turbulent exchange coefficient, developed by Felzenbaum [16], is a typical model of this kind. The tasks of estimating transport of substances with a high degree of reliability are solved by using a numerical method for full flows, adapted for small depths [90].

Water level is an important factor of functioning of reservoir ecosystems. There are sharp fluctuations in water levels in the upper parts of the Dnipro cascade reservoirs, which are characterized by variable backwater. Water levels in the lower, lake-alike parts with steady backwater depend on the mode of reservoir operation. The change in the level regime of Dnipro cascade reservoirs results in the deterioration of water quality in the reservoirs themselves and especially in the estuarine section of the river [41]. It causes increased water salinity, deteriorating oxygen conditions with the appearance of anaerobic zones, increase of biogenic substances, organic matter and heavy metals in the water.

Water surface disturbance is another factor of water turbulence. Generation of large waves is most likely in the Kremenchug and Kakhovka reservoirs due to the large size of their surface areas. In addition, the former features coincidence of biggest fetch legislation and the prevailing direction of strong winds, as well as an increased depth along the fetch.

2.3.3 Regulated Flows

The impact of flowage on the hydrochemical regime is convincingly demonstrated by changes of quantitative characteristics of chemical composition of water bodies after their regulation. Reservoirs are built to solve a set of economic tasks, but their creation may backfire with a number of multidirectional ecological consequences.

A number of general issues relating to the impact of hydrological factors on the formation of water quality and ecology of water bodies are considered in the works Avakyan [4], Voropayev [109], Kriventsov [37], Butorin [9], Timchenko [90] and many others, on the basis of which a conclusion was made about the change of the type of matter and energy cycle in reservoirs from transit to closed one. The functioning of ecosystems of Dnipro and Volga cascade reservoirs received most attention in the works [13, 14, 28, 34, 52, 100, 112, 114].

Creation of a reservoir results in the change of hydraulic conditions, reduction of the intensity of water exchange, flow velocity and enhancing the role of endogenic processes, as well as affects regimes of all groups of substances. The reservoirs face

a dramatic decline of the rate of flow and turbulent mixing of water. Thus, the flow rate in the Dnipro River before the regulation ranged within 0.6–0.8 m/s, and after it decreased to 0.3–0.02 m/s. Stagnant zones were formed due to reduced water exchange. Slackened water currents led to increasing the role of accumulative processes that can be estimated approximately by an empirical equation [14]:

$$A = 99.6 - 2.32 V, \quad (2.21)$$

where A is the accumulative capacity of reservoirs; V —average speed of runoff currents cm/s.

Precipitation of suspended solids of mineral and organic origin in the areas with active sedimentation processes promotes withdrawal with them of many ingredients from an aqueous solution. Under specific physicochemical conditions of the water environment, transformation and redistribution of dissolved elements occur from top downward with following deposition of sediments. Long-term research of Dnipro cascade reservoirs prompted a conclusion about their significant role as a powerful ecosystem biogeochemical barrier that was most evident during the Chernobyl disaster in 1986.

Salinity of the lower reaches of the Dnipro during the existence of the Dnipro cascade reservoirs has significantly increased, which is due to discharges of water from the Kakhovka reservoir. There appeared suitable conditions for penetration of sea waters in the lower reaches of the Dnipro. Seasonal and perennial dynamics of water mineralization in some reservoirs is determined by their specific hydrological characteristics and location in the cascade. Generally speaking, main ions and water salinity values feature a decline in the amplitude of annual fluctuations of their content due to increasing their minimum and decreasing their maximum values. Unlike rivers, the reservoirs have heterogeneous content of all components across the water area and depth.

Deterioration of reservoir water chemistry at the first time after their filling was related to active inflow of biogenic substances and organic matter from the flooded reservoir bed, which caused outbreaks of phytoplankton “blooms”. After the stabilization of reservoir regime (10–15 years) endogenic processes have started to play a major role.

The Dnipro reservoirs belong to high productive water bodies that stand out for the accumulation of a significant amount of autochthonous organic substance. Circulation of organic matter is the basis of any functioning water system. Dynamics of easily oxidized substances reflect the ratio of production-destruction processes and describe tropho-saprobic status of aquatic ecosystems. Studies carried out in the lower reaches of the Dnipro have shown that all variables of the organic substance balance equation depend on the water regime [57, 58, 61]. The balance of production-destruction processes in the tail-pond of the Kakhovka HPP is observed at discharge 470 m³/s.

2.4 Hydro-Physical Parameters

Among a number of hydro-physical parameters temperature, transparency, turbidity and formation of ice cover have the greatest impact on the chemical composition of the water.

2.4.1 *Effect of Hydro-Physical Factors on Dissolved Oxygen Concentrations in Water*

Dissolved oxygen in water is among the most important physicochemical parameters that determine water quality due to intensification of purification, physico-chemical transformation and hydro-biological cycle of substances. Its concentration in water is determined by the ratio of differently directed physicochemical, hydro-biological and hydro-physical processes that occur in an aqueous environment and in the interface of “water-atmosphere” phases (Fig. 2.21). This section examines the role of hydro-physical factors. Biological and chemical processes are described in the following sections.

Natural water bodies continuously interact with the air as a result of exchange in the interface “water-atmosphere” due to the difference in partial pressure in liquid and gas phases. The balance between them is maintained by a continuous

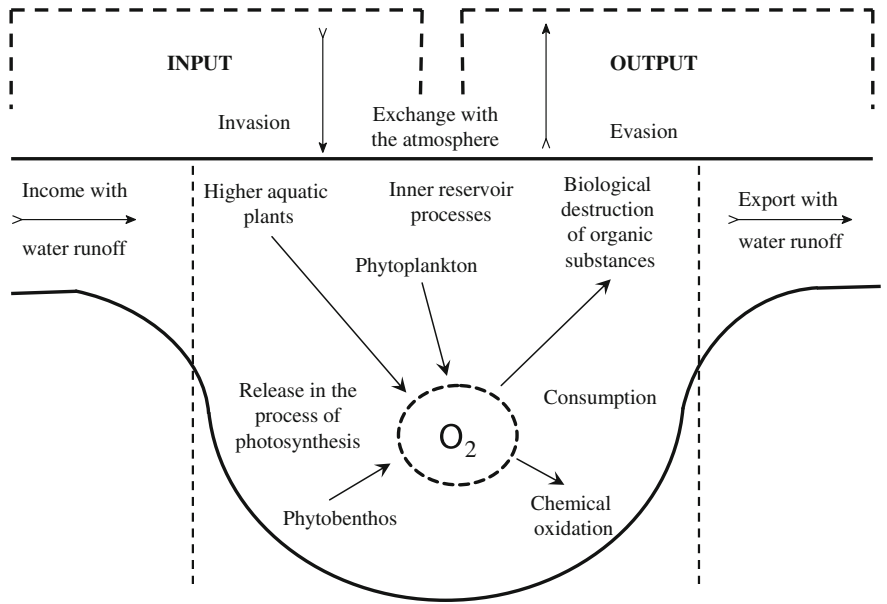


Fig. 2.21 Diagram of dissolved oxygen circulation in aquatic ecosystems [78]

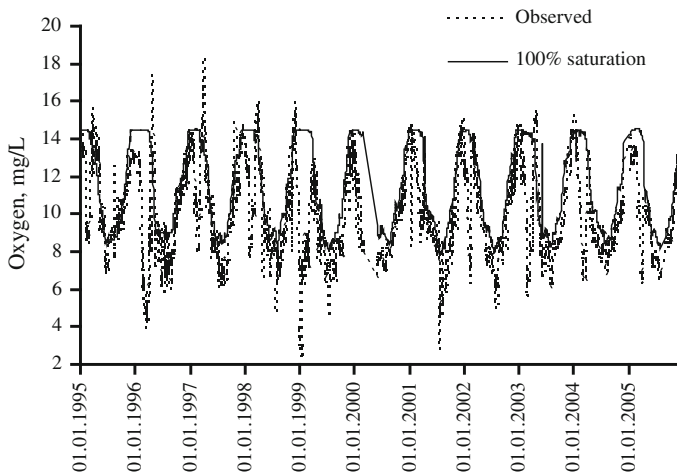


Fig. 2.22 Long-term (1995–2005) dynamics of dissolved oxygen concentrations in the Kyiv reservoir, vill. Novopetrivtsi, compared to 100 % saturation concentration

redistribution of oxygen. In case of excess partial pressure of oxygen in the surface layer of water compared with the near-water layer of the atmosphere, its emission in the atmosphere occurs (evasion), and at a lower pressure, by contrast, its ingress from the atmosphere occurs (invasion). Experimental work [81], conducted in the lower reaches of the Dnipro, showed that under regulated runoff ingress of oxygen from the atmosphere dominates as a whole in the course of a year. In quantitative terms, it is $102 \text{ g/m}^2 \text{ year}$.

Ingress of gas from the atmosphere is limited by its solubility, which corresponds to the concentration of dissolved oxygen (C_s), balanced with the partial pressure of gas in the air. The value of the saturation concentration (C_s) depends on the water temperature and can be obtained from special tables designed for pressure of 1 atm. [50], or defined by the following empirical formula:

$$C_s = 14.62 - 0.4042 - T + 0.00842 - T^2 - 0.00009 - T^3 [7], \quad (2.22)$$

where T is the water temperature, $^{\circ}\text{C}$. Figure 2.22 shows a long-term history of dissolved oxygen concentrations in the Kyiv reservoir compared to the run of a curve of 100 % saturation. As can be seen, the water in the Kyiv reservoir is undersaturated with dissolved oxygen for most of the year from September to December.

It has been proved by numerous theoretical and experimental studies that the ingress of oxygen from the atmosphere (reaeration) is determined by molecular diffusion process at an interface of the air and liquid phases. This process can be described by the equation:

$$\frac{dC}{dt} = K_2(C_s - C) \text{ or } \frac{dC}{dt} = aK_L(C_s - C) \quad (2.23)$$

where C and C_s are the real concentration and oxygen saturation concentration, respectively; K_L —mass transfer coefficient; K_2 —reaeration coefficient; t —time; a —the ratio of the free surface area of water to its volume.

K_L and K_2 are the coefficients characterizing the rate of transfer of oxygen through the water surface. K_L , as follows from formula (2.23), describes oxygen flow rate, provided that $C_s - C = 1$.

Theoretical substantiation for determining a mass transfer coefficient was preceded by experimental studies performed on different types of water bodies. These methods include the use of special plastic domes, installed on water surface [11]. Mass transfer coefficient is determined by the change in the oxygen content in the air contained under the dome. As per small watercourses, there was developed an upset equilibrium method [115]. The method involves creation of an artificial shortage of oxygen in a river stretch by adding sodium sulfite or nitrogen gas and the subsequent direct determination of intake rate of oxygen from the atmosphere. However, when using this method errors can reach significant values. Radioisotope method is also used to determine the oxygen mass transfer coefficient [101]. Despite its accuracy, a limiting factor is the need to add radioactive substances in the flow.

From the beginning of experimental work an important question was raised about the role of natural convection and turbulence in gas exchange between the atmosphere and water. First there was suggested a film theory, according to which the surface of liquid is covered by a film, diffusion through which controls the process of gas absorption by the liquid. The thickness of the film (δ) depends on the hydrodynamic and aerodynamic conditions in the contacting phases. Over time, there appeared a surface renewal theory which substantiated continuous replacement of fluid surface layers by deeper layers. Thereby, the thickness of the diffusion layer decreased with increasing stream turbulence [7].

To determine turbulent flow reaeration coefficient (K_2) numerous theoretical approaches have been offered, each of them having certain limitations. The most common formula is (2.24):

$$K_2 = 3.68 \sqrt{\frac{V}{h^3}} \quad (2.24)$$

where K_2 is the reaeration coefficient, $1/24 \text{ h}$; V —flow rate, m/s ; h —depth of flow, meters.

Dependence of the reaeration coefficient on temperature is calculated by formula (2.25).

$$K_2(T) = K_2(20^\circ\text{C}) \cdot 1.04^{T-20} \quad (2.25)$$

Typically, the value of reaeration coefficient ($1/24 \text{ h}$) lies in the range 0.1–2.0.

The formula shows that the waters of rivers that flow down from mountain slopes and have significant flow rate will always be enriched with oxygen.

For water reservoirs a significant role in the gas exchange between the atmosphere and water masses is played by convection transport associated with the formation on the surface of the liquid phase of so-called cold film. This indicates that the reservoirs without currents are more sensitive to pollution. Low reaeration rate in them against the background of intense oxygen consumption can cause a summer fish kill.

Based on the results of the work performed, it was concluded that in the reservoirs where turbulence is generated mainly by wind, gas exchange between the atmosphere and water can be estimated with sufficient accuracy on the basis of the film model and formula $KL = D/\delta$, where D is the coefficient of molecular diffusion; δ —thickness of diffusion layer [7].

Experimental study of gas exchange in the lower Dnipro reaches has shown that water with high oxygen saturation (130–140 %) arrives from the upper reservoirs during spring floods [81, 113]. However, turbulent mixing causes an active return of oxygen to the atmosphere, which reaches 200 mg/m² day. Rise in the temperature of water intensifies processes of oxidation of organic matter and oxygen flows change their direction for the opposite. During summer low water the process of oxygen consumption from the atmosphere is prevailing and reaches 1200–2700 mg/m² day. Oxygen exchange in autumn is determined primarily by hydro-physical factors, among which an important role is played by hydroelectric complex operation [41].

The dependence of oxygen regime of water bodies on hydro-physical factors was used in [59, 60, 92, 95, 96, 98] to develop a methodology for regulation of oxygen content by intensifying water exchange, which was practically applied in river stretches of the Dnipro cascade reservoirs.

Ice cover is an important factor in the formation of dissolved oxygen regime. Under the conditions of complete freezing oxygen deficiency often occurs in water reservoirs. The analysis of variations of air temperature, water temperature and dissolved oxygen concentrations during freezing periods of 1995–2005 showed that O_2 concentration rapidly decreased on a third–fifth day after the formation of ice cover, in some cases up to 10.8 mg/L, while in 2006—up to 2 mg/L (Fig. 2.23).

Fig. 2.23 The content of dissolved oxygen in the near-dam section of the Kyiv reservoir during the freezing periods in 1995–2006

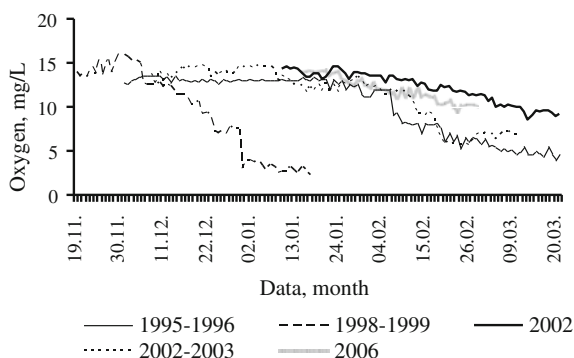


Fig. 2.24 The dynamics of the dissolved oxygen content and water color in the near-dam water of the Kyiv reservoir during the freeze-up of 1998–1999

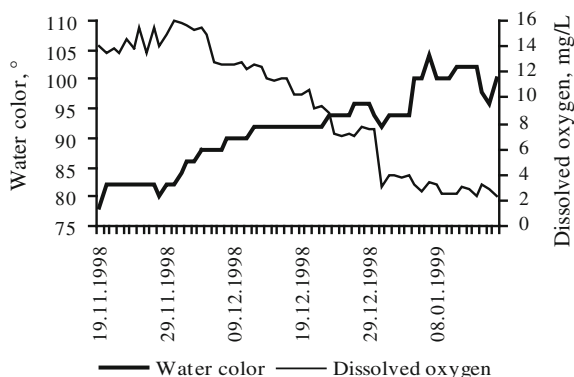
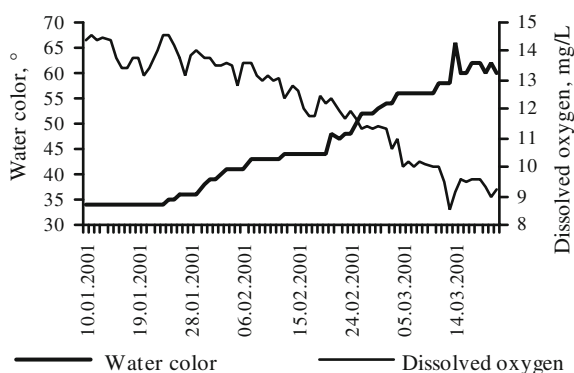


Fig. 2.25 The dynamics of the dissolved oxygen content and water color in the near-dam water of the Kyiv reservoir during the freeze-up of 2001



During this period, oxygen is actively utilized for the oxygenation of organic matter, while its production during photosynthesis is slowed down. The ice layer acts as a screen that prevents attaining balance with the atmosphere. A quantitative estimate of dissolved oxygen balance in the Kyiv reservoir, accomplished in [60], showed that its input is formed mainly by atmospheric invasion, while photosynthetic activity was suppressed. Oxygen consumption ranging within 0.07–0.25 mg O_2 /L day was associated with biological processes (decomposition of organic matter, nitrification, oxygenation of methane and other compounds), consumption by benthic sediments –0.022 to 0.035 mg O_2 /L day, chemical oxygenation of manganese ~0.3–0.8 mg O_2 /L day.

An increased amount of humic substances that come with the Prypiat River waters is registered in the upper Dnipro cascade reservoirs. A tendency of altering the concentration of dissolved oxygen in these reservoirs during freeze-up shows its close relationship with color of water which indirectly characterizes humus content (Figs. 2.24 and 2.25).

The occurrence of acute shortage of dissolved oxygen in the Prypiat in those winters that followed wet summers and autumns, is also mentioned in the monograph [3]. The authors associated the reduction of oxygen concentrations with higher intake of organic matter.

The use of oxygen for oxygenation of humic substances is an issue for discussion, as they belong to biochemically stable compounds. However, the results of experimental work suggest otherwise. Thus, Skopintsev and Bikbulatova have shown that about 15 % of humic substances decompose within 545 days [84]. It was revealed in [42, 43] that mixing of humic substances with water that was in contact with sediments, resulted in the reduction of oxygen content virtually to zero. The data cited by Orlov in [63] indicate that photochemical degradation of humus has an oxygenating mechanism involving free radicals.

The photochemical oxygenation leads to destroying of the least stable double bonds of aliphatic chains, which play the role of a bridge between the more persistent components of molecules.

This view is also supported by the information about oxygen content in the Prypiat arm of the Kyiv reservoir, being always smaller compared to the left bank of the reservoir, which receives water from the upper Dnipro. The results of our field observations indicate that, depending on the conditions at the beginning of freeze-up, oxygen consumption in the Kyiv reservoir was 0.1–0.2 mg O_2 /L day at oxygenation parameter = 8.6 mg O/L and color of water up to 40°. With oxygenation parameter increasing to 15 mg O/L and color of water to 90°, oxygen loss increased to 0.3 mg/L day [67].

2.4.2 Turbidity

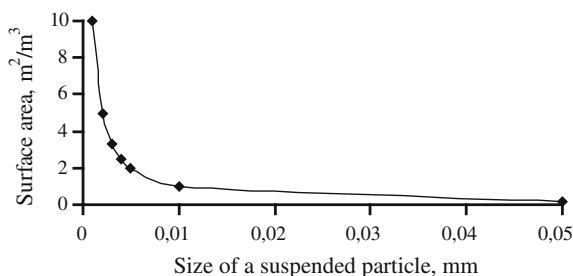
In natural conditions, water flow energy is spent on transport of solid materials causing the formation of suspensions, which determine the turbidity of water. Suspended solids include particles of both mineral and organic origin.

The transfer of suspended particles in water is determined by the hydraulic regime of water flow, on which depends its lift, and by size and specific weight of the particles themselves.

The presence of suspended solids plays a significant role in creating self-purification ability of aquatic ecosystems. Suspended particles can adsorb cations and anions from aqueous solution due to chemical bonds or electrostatic interaction. Reduced flow velocity, typical for regulated stretches and estuaries of rivers, leads to a significant reduction in the mass of suspended solids in the aqueous medium along with chemical components due to their sedimentation and deposition in bottom sediments. It is shown in [38] that after 6 h of desilting the content of suspended forms of heavy metals in the Danube water is reduced by 70–80 %. Sorption processes are considered in more detail in Sect. 2.3.

One of the important indicators of adsorption is an adsorbent body's surface area, as it is this indicator that determines the presence of adsorption centers. Our calculations have shown that the surface area of an adsorbent sharply decreases with increasing the particle size (Fig. 2.26).

Fig. 2.26 The dependence of the surface area of the adsorbent on the size of suspended particles (at turbidity 5 mg/L) [67]



On this premise and on the basis of numerous experimental studies performed on water bodies of Ukraine, it has been established that the ion exchange capacity increases from psammitic (0.1–2.0 mm) to pellite fraction (<0.01 mm).

As an example, the data on heavy metals distribution in different particle-size fractions of bottom sediments of the Dnipro are presented (Table 2.6).

Radiographic analysis of pellite fraction (<0.01 mm) in the Dnipro reservoirs bottom sediments has shown that, as per the mineralogical composition, it includes fine quartz, carbonate and clay minerals—illite and montmorillonite. Organic matter in muddy sediments is associated with the presence of humic substances and waste products of planktonic organisms, whose development is determined by the intensity of photosynthesis.

It is characteristic that the distribution of organic matter between particles of different dimensions is subject to the general development pattern, namely the amount of organic matter increases with decreasing of a particle size.

Whereas the gross organic matter content in sand deposits of the Dnipro reservoirs varies in the range of 0.5–2.4 % (average 1.8 %), an average figure for silt particles is 12.6 % at variation range 10.0–18.0 %.

With the accumulation of suspended solids and formation of bottom sediments the active surface area of the particles is reduced by at least an order. This testifies to the fact that adsorption processes in aquatic ecosystems occur mainly in the water column at an interface “solution—suspended solid” and not in the bottom sediments. The main mass transfer of substances occurs in the direction “suspended solids—bottom sediments”. Under any conditions the role of inverse desorption process is much lesser.

According to [14], the cascade of the Dnipro reservoirs, as is typical for large lowland reservoirs, is characterized by high depositional capacity that varies from 89 % at the top, the Kyiv reservoir, to 99.5 % in the lower Kremenchug reservoir.

Increased water turbidity also inhibits the development of phytoplankton and bacterial plankton. The author of [90] analytically presented dependence between these parameters:

$$\beta_{\max} \approx 370\rho^{-1}, \quad (2.26)$$

where β_{\max} is the phytoplankton biomass, mg/L; ρ —water turbidity, g/L.

Table 2.6 Fluctuation intervals and average content of heavy metals (mg/kg of dry matter) in the surface layer of different types of bottom sediments in the Dnipro cascade reservoirs

Type of sediments	Variation limits	Org. substance (%)	<i>Fe</i>	<i>Mn</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>	<i>Ni</i>	<i>Co</i>	<i>Cd</i>
Kyiv reservoir										
Dirty sand, 0.05–0.1 mm	Min.	0.5	1682	50.2	14.0	2.8	2.4	14.0	2.0	0.8
	Max.	4.4	7400	149.0	29.0	8.6	17.0	34.0	12.0	1.2
	Medium	2.8	5421	119.0	22.0	6.4	14.0	28.0	9.0	1.0
Sandy silt, 0.01–0.05 mm	Min.	6.7	12875	271.0	41.0	8.0	15.0	28.0	14.0	0.8
	Max.	9.8	22876	885.0	80.0	12.0	23.0	48.0	21.0	1.5
	Medium	9.2	18291	625.0	68.0	10.0	19.0	40.0	19.0	1.1
Clayed silt, <0.01 mm	Min.	10.0	26000	848.0	86.0	14.0	20.0	46.0	16.0	0.6
	Max.	31.0	90030	5600.0	208.0	26.0	77.0	80.0	34.0	3.2
	Medium	20.0	53409	2298.0	119.0	18.5	57.4	62.4	25.0	1.9
Kaniv reservoir										
Dirty sand, 0.05–0.1 mm	Min.	1.0	859	104.0	19.2	3.0	7.0	18.0	5.0	0.3
	Max.	3.5	3400	128.0	28.0	7.0	10.0	32.0	13.0	1.1
	Medium	2.8	–	–	–	–	–	–	–	–
Sandy silt, 0.01–0.05 mm	Min.	4.7	8450	282.0	26.0	6.0	10.0	25.0	12.0	0.8
	Max.	7.7	11000	602.0	149.0	14.0	23.0	35.0	16.0	1.3
	Medium	6.5	9760	424.0	39.0	11.0	21.0	29.0	13.0	1.1
Clayed silt, <0.01 mm	Min.	–	21380	850.0	140.0	18.6	18.0	40.5	13.0	1.6
	Max.	–	32640	1820.0	440.0	40.8	32.0	72.8	16.0	4.8
Kremenchug reservoir										
Sand, >0.1 mm	Min.	–	574	54.0	19.6	0.9	2.0	9.0	3.7	0.3
	Max.	–	3260	108	29.5	6.2	4.9	17.0	7.6	0.5
	Medium	–	1540	82.0	22.7	3.4	3.1	12.3	5.8	0.4
Dirty sand, 0.05–0.1 mm	Min.	–	1124	84.7	23.5	1.8	1.6	12.2	6.6	0.5
	Max.	–	8650	166.4	42.3	7.5	8.7	21.5	14.0	0.9
	Medium	–	4267	129.3	38.5	5.1	5.3	18.6	9.7	0.7
Kakhovka reservoir										
Sand, >0.1 mm	Min.	–	1325	62.3	8.0	1.6	2.2	10.1	3.2	0.3
	Max.	–	3240	88.6	14.6	5.3	3.8	16.5	8.4	0.7
	Medium	–	1950	75.4	11.5	4.1	2.7	14.6	5.2	0.4
Dirty sand, 0.05–0.1 mm	Min.	–	5326	113.3	22.4	3.4	3.5	12.1	7.5	0.4
	Max.	–	10830	219.0	41.6	12.7	10.1	26.0	13.0	1.2
	Medium	–	7385	162.3	31.2	9.3	7.3	19.4	10.8	0.6

The effect of phytoplankton on the chemical composition of surface waters is described in Sect. 2.4.

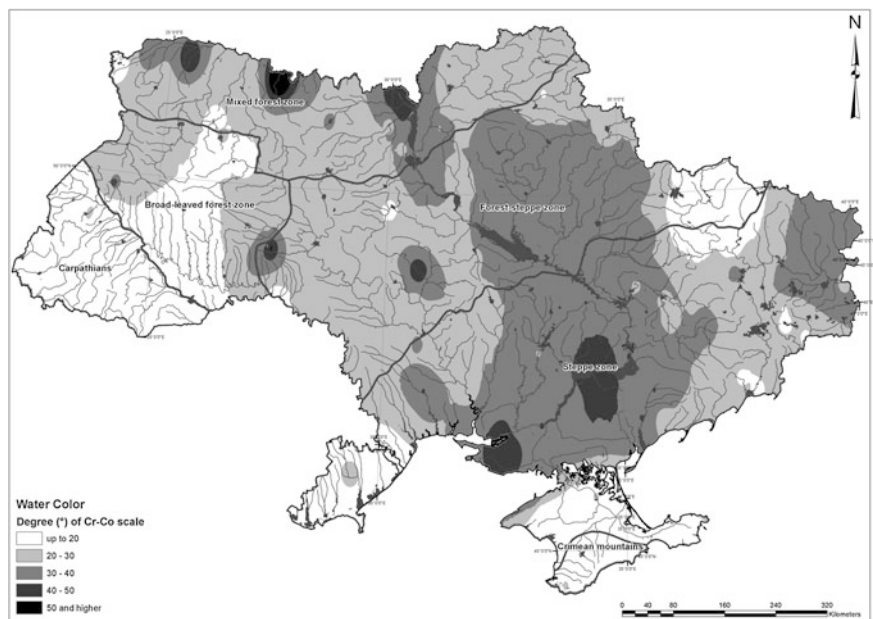


Fig. 2.27 Averaged color of surface waters in Ukraine (1989–2009) [50]

2.4.3 Water Color

Water color intensity is characterized by its color index, the value of which is determined by an intake of autochthonous and allochthonous substances of different nature, as well as anthropogenic influence.

Among the natural substances the greatest impact on water color is exerted by humic acids which due to active absorption of the wave of the lower (blue) part of the visible spectrum and ultraviolet radiation become yellow-brown. Surface waters also acquire a yellowish tint due to the presence of humic substances.

Territorial distribution of water color index in the surface waters of Ukraine is shown in Fig. 2.27. Darker water color is characteristic of North-Dnipro terraced low-lying region, the Poltava Upland region of forest-steppe zone and central steppe zone, and of such azonal system as the cascade of Dnipro reservoirs, where the average value of color increases to 40° of Cr–Co scale. The highest water color (50° and above) is registered in the Polissya Territory.

Water color profiles show that color is mainly due to the presence of humic substances and closely linked to zone-genetic features of humus formation.

Higher levels of humic substances in water lead to a shift of *pH* equilibrium values to higher acidity [66], and significantly affect phytoplankton development. The most likely cause of this dependence is inhibition of photosynthesis by reducing the photic zone. In the context of the lower portion of the Kyiv reservoir

Fig. 2.28 Dynamics of water color ($^{\circ}$ of Cr–Co scale) and number of phytoplankton during the growing season (bottom of the Kyiv reservoir, 1991)

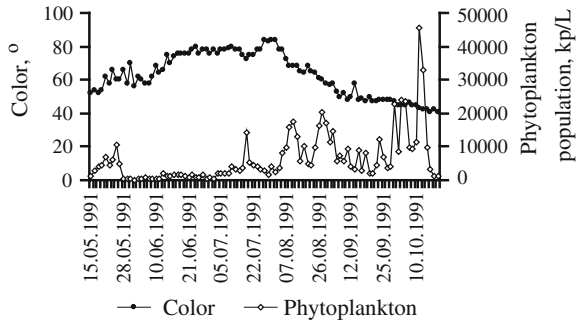


Fig. 2.29 Dynamics of water color ($^{\circ}$ of Cr–Co scale) and number of phytoplankton during the growing season (Desna River, v. Litky, 2000)

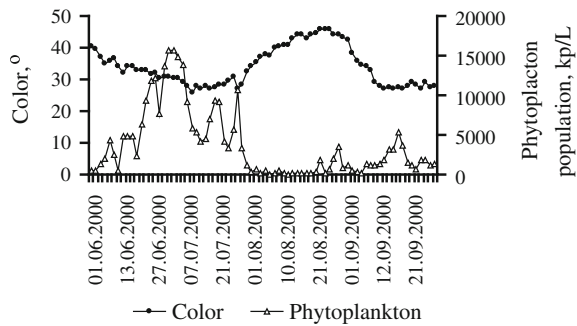
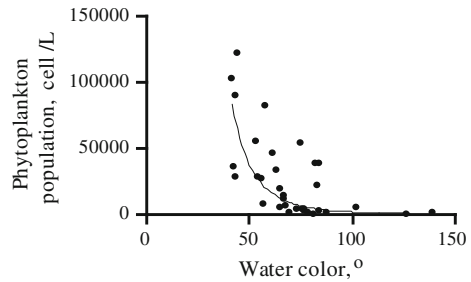


Fig. 2.30 The relationship between the number of phytoplankton and water color ($^{\circ}$ of Cr–Co scale) in lower portion of Kyiv reservoir, 1990–2001



we have shown that against the background of virtually homogeneous temperature conditions (water temperature fluctuations do not exceed 4°C), reduction of water color by twofold (from 84° to 41° of Cr–Co scale) led to almost ninefold increase in phytoplankton number (Fig. 2.28).

Reduction of water color in the Desna River from 40° to 30° of Cr–Co scale has led to an increase of phytoplankton population by 12-fold (Fig. 2.29).

The analysis of long-term data (1990–2001) allowed on the whole confirm an inverse relationship between the number of phytoplankton and water color in the lower portion of the Kyiv reservoir, presented as a graduated trend (Fig. 2.30).

2.5 Bottom Sediments

The¹ deposition of suspended particles in areas with active sedimentation processes leads to the formation of bottom sediments the boundaries of which are bedrock and the interface with the water body.

Bottom sediments belong to the porous objects, the skeleton of which is formed by solid particles and the pores are filled with water, trapped during the formation of sediment beds [55].

Solid particles enter water bodies due to the erosion of banks, which accounts for their mainly mineral composition; due to runoff from rivers, in which case they may have mineral or organic composition; and due to deposition of autochthonous organic matter. Suspended mineral solids are capable of absorbing organic matter of humic origin from the solution, forming organo-mineral complexes.

From the time of deposition of suspended particles bottom sediments undergo some diagenetic transformations related to consolidation of their mass, turbulent mixing of a surface layer, the life-sustaining activity of benthic organisms, decomposition of organic matter.

Bottom sediments belong to the open non-equilibrium thermodynamic systems and experience constant exchange of material with the environment [48]. The result is a high likelihood of bottom sediments affecting the chemical composition of water bodies. Mass transfer of substances between the solid and liquid phases is due to molecular diffusion process, quantitative parameters of which are determined by the Fick laws. This process is considered in detail in Sect. 2.3.

Macro-kinetics of the processes in bottom sediments is described by the equation:

$$\frac{\partial C}{\partial t} = D_{e\Phi} \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} + f(z, t) \quad (2.27)$$

where C is the concentration of a substance in a layer of bottom sediments with thickness z ; $D_{e\Phi}$ —effective diffusion coefficient with taking into account the porosity of the environment; $f(z, t)$ —the combined characteristics of chemical reactions, physical, chemical and biological processes that lead to changes in the concentration of the substance.

To determine effective diffusion coefficient one can use a number of formulas, among which the most common is:

$$D_{ef} = D_0 \cdot p^m \quad (2.28)$$

where D_0 is the molecular diffusion coefficient; p —porosity, $1.3 < m < 3$.

Since the diffusion process occurs in porous media, rather than in a continuous homogeneous body, the activity of material exchange is determined by the

¹See also Sect. 3.6.

properties of this environment, among the integral characteristics of which porosity is the most important. Paper [82] demonstrates direct linear correlation between soil porosity and total content of soluble substances (chloride ions, calcium, magnesium and petroleum products) as well as inverse correlation between the content of water-soluble components and the weight of wet soil and its skeleton.

Another important factor that will determine the content of water-soluble substances in sediment formations is their particle-size distribution. The nature of this relationship is discussed in Sect. 2.4.2.

Dissolved gases A long-term study cycle of the Volga and Dnipro reservoirs has shown that bottom sediments, due to decomposition of organic matter deposited in them, are able to materially affect the content of dissolved oxygen in the bottom layer of water [14, 46]. This process was most intensive during the first years after filling the reservoirs. Intensive oxygen consumption by flooded soils often led to its deficit.

The rate of oxygen consumption by bottom sediments is determined by the type of the soil, and in a variety from muddy sand to silt it increases 10 times [14]. In particular, oxygen consumption by bottom sediments in the Kaniv Reservoir of the Dnipro cascade ranged within 310.4–568.7 mg O_2/m^2 day. Obviously, this was due to the increased content of fine silt fraction in the bottom sediments. It is mainly represented by clay minerals and iron hydroxides, which show significant capacity for sorption of organic substances.

The decomposition of organic matter in bottom sediments is accompanied by formation of carbon dioxide, whose dynamics, as demonstrated in [14], is cyclical. The authors linked this to a decreased activity or demise of microorganisms. The amount of released CO_2 has a similar to oxygen dependence on the type of soil.

With formation of CO_2 under anaerobic conditions there was simultaneous desorption of HCO_3^- ions.

The ability of main ions to migration from the bottom sediments in the water can be clearly illustrated by materials obtained by us in the Kaniv Reservoir (Tables 2.7, 2.8). Apparently, the concentration of main ions in the solution of porous formations far exceeds their content in the water.

Nitrogen Nitrogen compounds enter bottom sediments almost exclusively with indigenous substances, and their transformation in the interface “bottom sediments-water” is closely associated with the decomposition of organic detritus (Fig. 2.31). About half of bottom sediment nitrogen has protein nature and is subject to hydrolysis to form amino acids. The latter are incorporated into proteins or mineralize with the release of ammonia. Ammonification plays a major role in the microbiological cycle of nitrogen in bottom sediments, and accounts for mineralization of $\sim 40\text{--}50\%$ N_{org} [46]. The resultant ammonia is partly captured by microorganisms, undergoes nitrification, adsorption by clay minerals or is removed from the bottom sediments into the water.

From 5 to 20 % of mineralized nitrogen undergoes further nitrification, resulting in the accumulation of NO_3^- ions in the bottom sediments. Another source of nitrate ions, similar in quantitative terms, is diffusion flow from the water [83]. The

Table 2.7 The concentrations of main ions (mg/L) in the solutions of porous bottom sediments (numerator) and in the water (denominator) of the Kaniv reservoir

Place and date of sampling	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}
Water basin of Kaniv HPP, 26.09.1997	$\frac{305.0}{207.4}$	$\frac{200.0}{38.0}$	$\frac{266.3}{33.7}$	$\frac{100.0}{-}$	$\frac{122.0}{-}$
Kaniv reservoir, Buoy 46, 26.9.1997	$\frac{427.0}{231.8}$	$\frac{88.0}{30.0}$	$\frac{10\ 6.5}{35.5}$	$\frac{120.0}{-}$	$\frac{85.4}{-}$
Water basin of Kaniv HPP, 06.04.1998	$\frac{549.0}{146.4}$	$\frac{72.0}{28.0}$	$\frac{142.0}{17.8}$	$\frac{80.0}{42.0}$	$\frac{109.6}{7.3}$
Kaniv reservoir, 50th km, 17.06.1998	$\frac{732.0}{183.0}$	$\frac{72.0}{28.0}$	$\frac{63.9}{21.3}$	$\frac{160.0}{58.0}$	$\frac{12.2}{6.1}$
Kaniv reservoir, 30th km, 17.06.1998	$\frac{488.0}{207.4}$	$\frac{160.0}{3\ 4.0}$	$\frac{56.8}{21.3}$	$\frac{120.0}{56.0}$	$\frac{24.4}{13.4}$
Kaniv reservoir, 50th km, 10.09.1998	$\frac{610.0}{183.0}$	$\frac{64.0}{50.0}$	$\frac{195.0}{23.1}$	$\frac{100.0}{50.0}$	$\frac{146.0}{21.9}$
Kaniv reservoir, Buoy 0–3, 10.09.1998	$\frac{183.0}{213.5}$	$\frac{48.0}{30.0}$	$\frac{124.3}{21.3}$	$\frac{140.0}{60.0}$	$\frac{12.2}{15.9}$
Kaniv reservoir, 50th km, 26.09.1998	$\frac{244.0}{231.8}$	$\frac{96.0}{40.0}$	$\frac{71.0}{26.6}$	$\frac{40.0}{58.0}$	$\frac{53.7}{25.6}$

Table 2.8 The concentrations of main ions (mg/L) in the water and solutions of porous bottom sediments of the Kyiv Reservoir, v. Sukholuchcha, 16.03.1999

Depth/layer of sampling	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Water, surface	189.1	62.0	28.1	72.0	9.7	31.0	3.5
3.5 m from the bottom	189.0	75.0	28.1	70.0	11.0	30.0	3.5
1.0 m from the bottom	189.0	75.0	28.0	71.0	10.0	31.0	3.5
0.3 m from the bottom	170.8	70.0	29.7	64.0	9.0	31.0	3.5
0.1 m from the bottom	152.5	65.0	28.9	54.0	10.1	32.0	3.5
0.02 m from the bottom	169.7	72.0	29.7	58.0	8.1	32.0	4.0
Interstitial solution, Layer 0–10 cm	274.0	48.0	51.1	80.0	7.1	15.0	6.0
Layer 10–20 cm	213.0	77.0	43.0	70.0	8.0	10.0	5.5
Layer 20–30 cm	213.5	151.0	26.6	80.0	7.0	15.0	7.5

accumulated nitrate nitrogen is consumed by bacteria, followed by the formation of N_{org} (30–40 %), or undergoes denitrification with restoring nitrogen gas state (60–70 %).

Nitrogen, produced in the process of denitrification, is released from the bottom sediments in the water and is partially bound by heterotrophic microorganisms.

Thus, it is ammonification that, as a basic process of microbiological transformation of nitrogen, determines the basic form of mineral nitrogen in the bottom sediments.

The research results on distribution of nitrogen compounds in the water and solutions of porous bottom sediments of the Kyiv reservoir are shown in Table 2.9.

Fig. 2.31 Nitrogen cycle in bottom sediments [32]

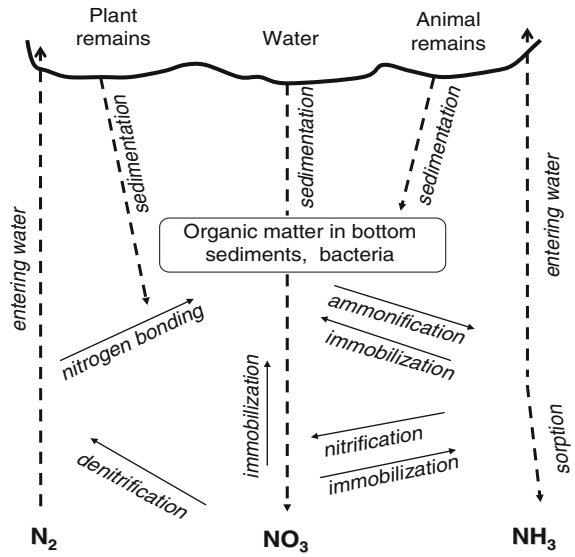


Table 2.9 The concentrations of nitrogen mineral compounds (mg N/L) in the water and solutions of porous bottom sediments of the Kyiv reservoir, v. Sukholuchcha, 16.03.1999

Depth	Layer of sampling	NH_4^+	NO_2^-	NO_3^-
Water	Surface	0.62	0.061	1.25
	3.5 m from the bottom	0.65	0.061	1.25
	1.0 m from the bottom	0.62	0.052	1.25
	0.3 m from the bottom	0.62	0.071	1.2
	0.1 m from the bottom	0.77	0.061	1.25
	0.02 m from the bottom	2.7	0.058	1.5
Interstitial solution	Later 0–10 cm	19.0	1.25	7.5
	Later 10–20 cm	29.0	1.27	8.0
	Later 20–30 cm	33.0	2.0	8.0

As studies of the Dnipro cascade reservoirs have shown, bottom sediments intensively release into water NH_4^+ ions until they reach an equilibrium concentration of 20 mg N/L, then the process trend is reversed [14].

The intensity of nitrogen diffusion from bottom sediments depends on the physical and chemical environment at an interface of phases: oxygen content, N_{org} , Eh, pH, t °C, and flow rate. The intensity of ammonium ions separation in bottom sediments varies within a wide range and depends on many factors, including the quality of organic matter in the soil. For instance, according to estimates up to 30 thous. t NH_4^+ are released from the bottom sediments of the Kremenchug reservoir into the water during the vegetation period [14].

Phosphorus Phosphorus is deposited in bottom sediments in mineral and organic forms, whose orders of magnitude are virtually identical.

Compounds of organic phosphorus (nucleic acids, phytin, lecithin) in bottom sediments undergo microbial mineralization, reaching 40–80 % P_{org} . The resulting mineral phosphorus compounds become mobilized due to microorganism activity and interaction with organic acids and, due to concentration gradient, they diffuse back into the water column.

The intensity of phosphorus diffusion from the bottom sediments depends on their mineralogical composition, water saturation with oxygen, Eh, t °C, and flow velocity.

The intensity of phosphates and P_{org} release from the bottom sediments of the Kremenchug reservoir in anaerobic conditions is 9 and 6 mg/m² day respectively, while in aerobic conditions phosphate diffusion is reduced by an order and remobilization of P_{org} practically does not occur [14].

Organic matter The accumulation of organic matter in bottom sediments depends on the balance between their supply (reservoir productivity, its average depth) and the intensity of decomposition. More simple organic compounds, that are formed thereby, diffuse in the bottom layers of water. Thus, soluble proteins continuously enter the water of the Kremenchug reservoir and their desorption from the bottom sediments has a cyclical pattern and ranges from zero to 50 mg/m² day [14].

Allochthonous organic substances of humus nature (HA and FA) are supplied with river runoffs due to leaching from a watershed. HA and FA content in the bottom sediments of the Dnipro reservoirs is characterized by considerable variability. The highest concentration values, as well as average and boundary values (minimum, maximum), were observed in the main Kyiv reservoir, and the lowest ones—in the closing Kakhovka reservoir. The difference between minimum and maximum values also decreases downstream the cascade of reservoirs (Fig. 2.32).

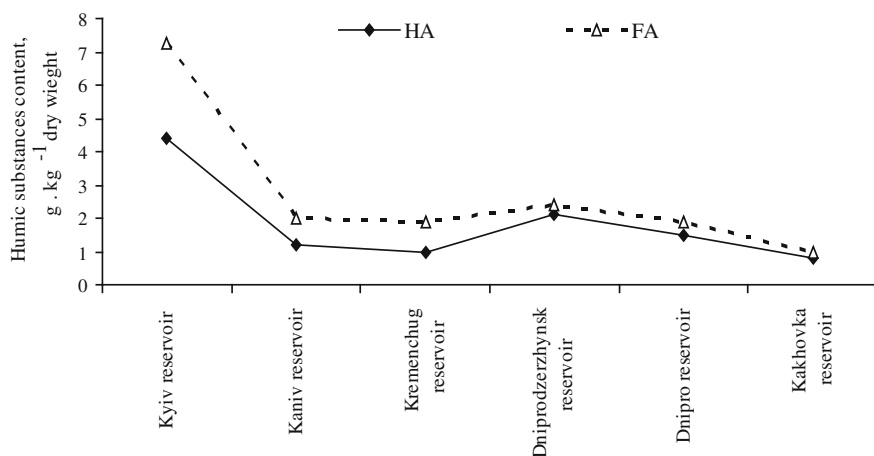


Fig. 2.32 The average content of HA and FA in the bottom sediments of the Dnipro cascade reservoirs, 2004

High molecular weight of most of humic substances minimizes the likelihood of their reentry from the bottom sediments to water.

Metals The results of field observations made in the Dnipro reservoirs and data of computer thermodynamic scale modeling showed that heavy metals in the solution phase are in a thermodynamically unstable state under physical and chemical conditions, specific for the aquatic environment of the Dnipro cascade reservoirs (excluding some winter periods with prolonged freeze-ups). This leads to the passage of a significant amount of metals to suspended form and their further depositing in the bottom sediments.

The probability of remobilization of heavy metals in the water is determined by the form, in which they are deposited in the bottom sediments or are present in the solution of a porous formation.

The contribution of metals to bottom sediments occurs in different ways, among which the most important are adsorption on suspended solids, co-precipitation with soluble compounds, biological consumption and as part of detritus.

The forms of heavy metals in the solid phase of bottom sediments were determined by their stepwise extraction, and the results are presented in Fig. 2.33.

A part of the metals that are incorporated in mobile fractions (exchange, carbonate and oxide) are able to reenter the water under a change of physical and chemical environmental conditions. Those of them that are bonded with organic substances or are included in the crystal lattice (residual fraction), belong to low-mobility forms.

As far as redistribution between heavy metals and water occurs through the solution of porous formations, quantitative content and the form of metals in the aqueous phase of bottom sediments is an important factor of secondary water pollution. Typically, the contents of heavy metals in solutions of porous formations exceed their concentrations in the water, especially it regards iron, manganese, zinc, cadmium. At the same time, iron, zinc, copper, lead and nickel are characterized by a high degree of complexing with organic substances (primarily humic), which reduces their ability to molecular diffusion. Manganese and cadmium in sludge solutions are represented mostly by uncomplexed (hydrated) ions, which are the most mobile form.

Material migration in a system “bottom sediments-water” largely depends on oxygen regimen and the changes in physical and chemical characteristics of aquatic environment. Formation of anaerobic conditions is a major factor of migration of part of heavy metals from the bottom sediments in the water, and it is manganese that is most sensitive to oxygen deficiency [40, 57]. There was a repeated migration of sizable amounts of manganese from the bottom sediments to the water in the Dnipro reservoirs under anaerobic conditions, resulting from long freeze-up periods in late winter time. Should the anaerobic conditions persist for longer periods the concentrations of manganese might increase 20–0 times compared with the periods of sufficient oxygen supply. The work [39] presents dependence of manganese content on dissolved oxygen concentrations in the waters of the Kyiv reservoir.

Lowering the pH in the bottom layer of water leads to the release of metals from oxide fractions of the bottom sediments and their subsequent migration into the

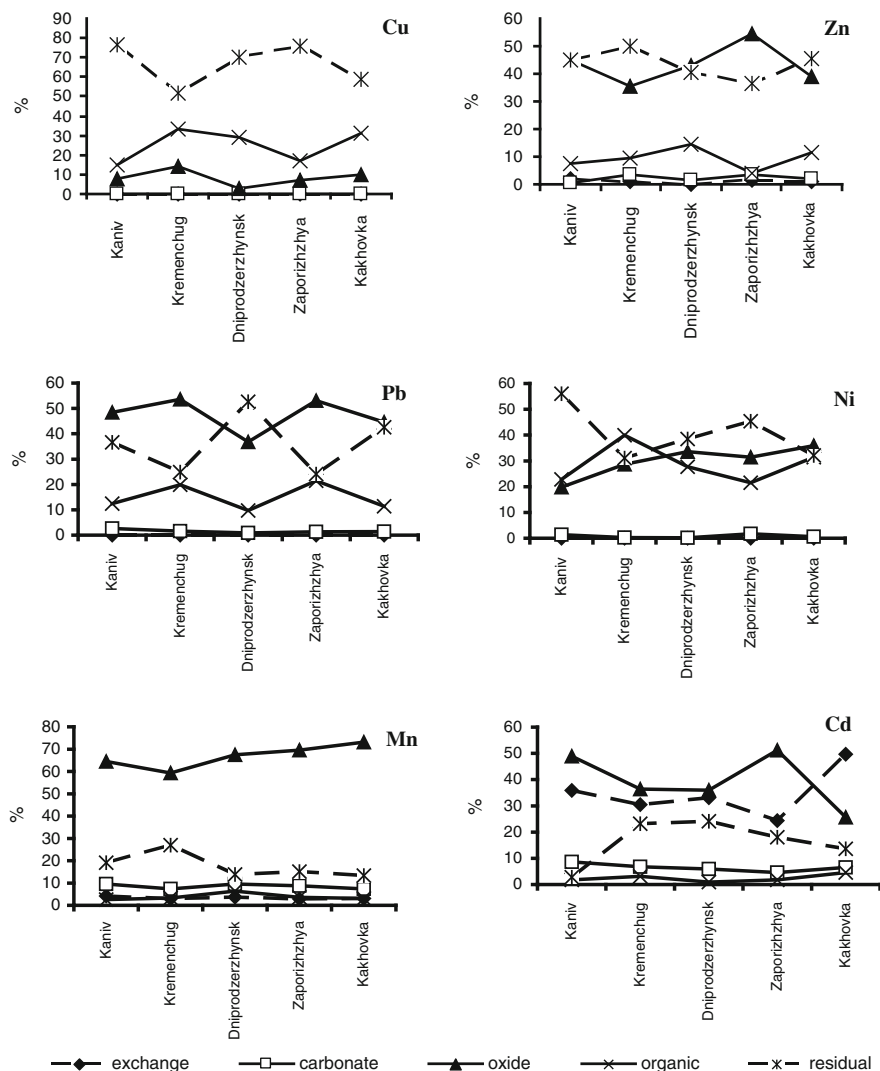


Fig. 2.33 Forms of heavy metals in the bottom sediments of the Dnipro reservoirs

water [44]. This is the case of manganese in the first place. Migration of other metals is much lower due to the more stable bonds with a solid phase of bottom sediments.

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