Volodymyr Osadchyy · Bogdan Nabyvanets
Petro Linnik · Nataliia Osadcha
Yurii Nabyvanets

Processes Determining Surface Water Chemistry

Springer

Processes Determining Surface Water Chemistry

Volodymyr Osadchyy · Bogdan Nabyvanets
Petro Linnik · Nataliia Osadcha
Yurii Nabyvanets

Processes Determining Surface Water Chemistry

Springer

Volodymyr Osadchyy
Ukrainian Hydrometeorological Institute
Kyiv
Ukraine

Nataliia Osadcha
Ukrainian Hydrometeorological Institute
Kyiv
Ukraine

Bogdan Nabyvanets
Ukrainian Hydrometeorological Institute
Kyiv
Ukraine

Yurii Nabyvanets
Ukrainian Hydrometeorological Institute
Kyiv
Ukraine

Petro Linnik
Institute of Hydrobiology
Kyiv
Ukraine

ISBN 978-3-319-42158-2 ISBN 978-3-319-42159-9 (eBook)
DOI 10.1007/978-3-319-42159-9

Library of Congress Control Number: 2016944921

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG Switzerland

Preface

This monograph presents major hydrological, physicochemical and biological processes determining the formation of hydro-physical properties and chemical composition of terrestrial surface waters. Generalized hydro-physical, hydrochemical and hydro-biological parameters affecting the surface water quality, in particular in Ukraine, are provided; a methodology for determining classes and categories of surface waters based on their ecological quality indexes is suggested.

As per hydrological processes, the authors place special emphasis on the interrelation between water runoff and chemical composition of water objects, on hydrodynamic processes, effects of hydro-physical factors on dissolved oxygen concentrations, water turbidity and color, as well as on the role of bottom sediments in forming water chemistry. For physicochemical processes the emphasis is placed on acid–base and redox equilibriums, settling out of slightly soluble compounds, heavy metals' complexing ability and their distribution in the «water—suspended solids—benthic sediment» system. For biological processes the priority is given to the role of hydrobionts in forming of surface water characteristics (pH, Eh, concentrations of dissolved oxygen, biogenic elements, organic compounds, as well as buffer capacity of freshwater ecosystems to bind heavy metals in complex compounds).

General description of anthropogenic factors affecting the process of forming natural waters' properties is presented.

The monograph is intended for specialists of ecological organizations, scientists, lecturers and students of higher education institutions who investigate the patterns of formation of water properties and work on the development of methodologies to model and design such properties.

Kyiv, Ukraine

Volodymyr Osadchyy
Bogdan Nabyvanets
Petro Linnik
Nataliia Osadcha
Yurii Nabyvanets

Contents

Chapter 1
Characteristics of Surface Water Quality

Surface water quality depends on the presence of numerous chemical ingredients which may be in dissolved, colloid-dispersed state or in the form of mineral or organic-mineral suspension. Qualitative composition and concentration of these ingredients determine certain physical, chemical and organoleptic properties of surface waters and allow for their use in different sectors of the economy. They affect the development and activity of aquatic organisms, which in turn play an important role in determining the chemistry of natural waters. Water quality is an integrating indicator reflecting the state of aquatic ecosystems per totality of hydro-physical, hydro-chemical and hydro-biological indicators.

Table 1.1 shows the main indicators of the chemical composition of the surface waters in Ukraine for the period from 1995 through 2009 [3].

1.1 Hydro-Physical Indicators

Hydro-physical indicators of surface water quality include temperature, the content of suspended solids (turbidity), transparency and color. Water temperature in the river basins of Ukraine varies widely from 0 to 32 °C. The rivers within the Azov Sea region have the highest temperature, the rivers of the forest and forest-steppe zones and of the Carpathians—the lowest one. The rivers of the forest and forest-steppe zones have the highest color due to high content of humic substances. The waters of the Danube River and some rivers of the Dnipro Basin are the muddiest ones.

V. Osadchyy et al., *Processes Determining Surface Water Chemistry*,
DOI 10.1007/978-3-319-42159-9_1

Table 1.1 Averaged chemical composition of water in the major river basins and rivers of the Azov Sea region and water bodies of the Crimea during the period of 1995−2009

Indicator	Dnipro	Danube	Dniester	Southern Bug	Western Bug (the Vistula basin)	Siversky Donets (the Don basin)	Rivers of Azov Sea region	Water bodies of Crimea
Temperature, °C	$\frac{13}{31\text{–}0}$	$\frac{12}{29\text{–}0}$	$\frac{10}{28\text{–}0}$	$\frac{10}{29\text{–}0}$	$\frac{10}{26\text{–}0}$	$\frac{12}{31\text{–}0}$	$\frac{13}{32\text{–}0}$	$\frac{12}{29\text{–}0}$
Suspended substances, mg/L	$\frac{11}{300\text{–}0}$	$\frac{76}{2150\text{–}0}$	$\frac{52}{1426\text{–}0}$	$\frac{20}{116\text{–}0}$	$\frac{27}{199\text{–}0}$	$\frac{18}{413\text{–}0}$	$\frac{27}{957\text{–}1}$	$\frac{24}{219\text{–}0}$
pH	$\frac{7.9}{9.6\text{–}6.0}$	$\frac{7.8}{9.6\text{–}6.0}$	$\frac{7.5}{8.9\text{–}6.0}$	$\frac{7.8}{9.4\text{–}6.1}$	$\frac{7.7}{8.9\text{–}6.0}$	$\frac{7.9}{8.9\text{–}6.0}$	$\frac{8.1}{8.9\text{–}6.5}$	$\frac{7.9}{9.3\text{–}6.7}$
Oxygen, mg/L	$\frac{9.9}{22.8\text{–}1.3}$	$\frac{10.0}{15.6\text{–}2.5}$	$\frac{10.5}{16.8\text{–}2.5}$	$\frac{11.3}{21.0\text{–}1.6}$	$\frac{8.1}{14.0\text{–}0}$	$\frac{8.3}{16.6\text{–}0.2}$	$\frac{9.6}{14.0\text{–}1.42}$	$\frac{10.8}{21.1\text{–}3.9}$
Carbon dioxide, mg/L	$\frac{7.1}{75.2\text{–}0}$	$\frac{4.4}{61.6\text{–}0}$	$\frac{7.5}{44.0\text{–}0}$	$\frac{7.8}{26.1\text{–}0}$	$\frac{11.9}{20.0\text{–}0}$	$\frac{7.7}{52.8\text{–}0}$	$\frac{7.1}{25.2\text{–}0}$	$\frac{3.8}{36.0\text{–}0}$
Hydrocarbonate ions, mg/L	$\frac{229}{781\text{–}28}$	$\frac{178}{400\text{–}15}$	$\frac{198}{681\text{–}15}$	$\frac{343}{750\text{–}127}$	$\frac{306}{525\text{–}122}$	$\frac{299}{659\text{–}103}$	$\frac{342}{702\text{–}49}$	$\frac{241}{582\text{–}82}$
Sulfate ions, mg/L	$\frac{82}{2810\text{–}2}$	$\frac{42}{218\text{–}2}$	$\frac{42}{1588\text{–}2}$	$\frac{78}{904\text{–}1.9}$	$\frac{39}{394\text{–}5}$	$\frac{350}{3336\text{–}6.9}$	$\frac{945}{4205\text{–}69}$	$\frac{102}{678\text{–}3}$
Chloride ions, mg/L	$\frac{48}{2850\text{–}3.5}$	$\frac{28}{230\text{–}1.3}$	$\frac{67}{6165\text{–}0.2}$	$\frac{52}{355\text{–}5.7}$	$\frac{39}{146\text{–}4}$	$\frac{233}{1268\text{–}9.2}$	$\frac{407}{2570\text{–}21.3}$	$\frac{41}{468\text{–}0.7}$
Calcium, mg/L	$\frac{66}{577\text{–}5}$	$\frac{46}{497\text{–}4}$	$\frac{61}{426\text{–}5}$	$\frac{76}{220\text{–}7.3}$	$\frac{99}{232\text{–}12}$	$\frac{154}{662\text{–}7}$	$\frac{208}{846\text{–}9.1}$	$\frac{73}{414\text{–}9}$

(continued)

Table 1.1 (continued)

Indicator	Dnipro	Danube	Dniester	Southern Bug	Western Bug (the Vistula basin)	Siversky Donets (the Don basin)	Rivers of Azov Sea region	Water bodies of Crimea
Magnesium, mg/L	$\frac{20}{367\text{–}1}$	$\frac{12}{292\text{–}1}$	$\frac{13}{329\text{–}1}$	$\frac{30}{276\text{–}1}$	$\frac{11}{112\text{–}1}$	$\frac{49}{500\text{–}3}$	$\frac{101}{457\text{–}2.43}$	$\frac{23}{127\text{–}1}$
Sodium, mg/L	$\frac{50}{1370\text{–}1}$	$\frac{34}{295\text{–}0}$	$\frac{38}{1033\text{–}0}$	$\frac{57}{446\text{–}1}$	$\frac{27}{165\text{–}0}$	$\frac{174}{1169\text{–}2}$	$\frac{449}{1866\text{–}1.25}$	$\frac{38}{306\text{–}0.7}$
Potassium, mg/L	$\frac{8}{78\text{–}0}$	$\frac{9}{46\text{–}0}$	$\frac{16}{83\text{–}0}$	$\frac{13}{95\text{–}0}$	0	0	0	$\frac{15}{85\text{–}0}$
Sum of ions, mg/L	$\frac{497}{5360\text{–}120}$	$\frac{332}{657\text{–}87}$	$\frac{410}{8620\text{–}69}$	$\frac{641}{2030\text{–}321}$	$\frac{520}{978\text{–}220}$	$\frac{1233}{5236\text{–}350}$	$\frac{2454}{7814\text{–}407}$	$\frac{533}{1680\text{–}167}$
Hardness (mmol-eq/L)	$\frac{4.9}{40.0\text{–}0.5}$	$\frac{3.4}{7.68\text{–}0.7}$	$\frac{4.1}{33.8\text{–}0.7}$	$\frac{6.3}{24.2\text{–}1.7}$	$\frac{6.0}{25.0\text{–}2.0}$	$\frac{14.0}{55.0\text{–}1.0}$	$\frac{18.6}{65.6\text{–}2.20}$	$\frac{5.5}{25.3\text{–}1.0}$
NH_4^+, mg N/L	$\frac{0.4}{21.5\text{–}0}$	$\frac{0.4}{9.2\text{–}0}$	$\frac{0.9}{10.9\text{–}0}$	$\frac{0.4}{10.0\text{–}0}$	$\frac{1.9}{12.3\text{–}0}$	$\frac{0.7}{21.6\text{–}0.01}$	$\frac{0.8}{13.2\text{–}0.01}$	$\frac{0.1}{8.8\text{–}0}$
NO_2^-, mg N/L	$\frac{0.02}{1.06\text{–}0}$	$\frac{0.02}{0.56\text{–}0}$	$\frac{0.02}{1.19\text{–}0}$	$\frac{0.04}{0.79\text{–}0}$	$\frac{0.09}{1.29\text{–}0}$	$\frac{0.09}{1.15\text{–}0}$	$\frac{0.17}{1.79\text{–}0}$	$\frac{0.02}{1.82\text{–}0}$
NO_3^-, mg N/L	$\frac{0.23}{8.03\text{–}0}$	$\frac{0.85}{8.60\text{–}0}$	$\frac{0.45}{7.42\text{–}0}$	$\frac{0.39}{10.5\text{–}0}$	$\frac{0.31}{88.2\text{–}0}$	$\frac{1.43}{14.1\text{–}0.01}$	$\frac{2.70}{15.0\text{–}0}$	$\frac{1.40}{19.0\text{–}0}$
$NH_4^+ + NO_2^- + NO_3^-$, mg N/L	$\frac{0.58}{22.0\text{–}0.01}$	$\frac{1.25}{13.3\text{–}0.01}$	$\frac{1.36}{20.5\text{–}0}$	$\frac{0.89}{16.0\text{–}0.03}$	$\frac{2.09}{12.6\text{–}0.01}$	$\frac{2.16}{22.2\text{–}0.02}$	$\frac{3.70}{18.4\text{–}0.25}$	$\frac{1.98}{24.3\text{–}0}$

(continued)

Table 1.1 (continued)

Indicator	Dnipro	Danube	Dniester	Southern Bug	Western Bug (the Vistula basin)	Siversky Donets (the Don basin)	Rivers of Azov Sea region	Water bodies of Crimea
Phosphates, mg P/L	$\frac{0.14}{3.41–0}$	$\frac{0.06}{3.80–0}$	$\frac{0.08}{3.40–0}$	$\frac{0.12}{3.35–0}$	$\frac{0.28}{3.09–0}$	$\frac{0.36}{7.60–0.005}$	$\frac{0.19}{2.75–0.002}$	$\frac{0.06}{0.93–0}$
Phosphorus tot., mg P/L	$\frac{0.27}{7.54–0}$	$\frac{0.11}{7.57–0}$	$\frac{0.14}{5.70–0}$	$\frac{0.24}{5.15–0}$	$\frac{0.50}{6.24–0}$	$\frac{0.65}{12.0–0.007}$	$\frac{0.37}{3.79–0.002}$	$\frac{0.14}{8.82–0}$
Silicon tot., mg/L	$\frac{4.5}{53.0–0}$	$\frac{2.6}{20.0–0}$	$\frac{3.2}{15.4–0}$	$\frac{5.0}{38.0–0}$	$\frac{4.3}{12.6–0}$	$\frac{5.8}{32.0–0.1}$	$\frac{3.5}{36.0–0.2}$	$\frac{4.5}{37.8–0}$
Iron tot., mg/L	$\frac{0.23}{9.1–0}$	$\frac{0.31}{8.82–0.01}$	$\frac{0.36}{9.05–0}$	$\frac{0.21}{8.60–0}$	$\frac{0.30}{4.01–0}$	$\frac{0.19}{7.00–0.01}$	$\frac{0.20}{10.0–0.01}$	$\frac{0.11}{2.92–0.1}$
Copper, μg/L	$\frac{4.9}{116.0–0}$	$\frac{8.7}{96.8–0}$	$\frac{7.5}{73.0–0}$	$\frac{5.3}{99.0–0}$	$\frac{6.8}{163.0–0}$	$\frac{4.1}{91.2–0}$	$\frac{5.0}{68.4–0}$	$\frac{3.3}{21.2–0}$
Manganese, μg/L	$\frac{51}{960–0}$	$\frac{34}{864–0}$	$\frac{49}{838–0}$	$\frac{51}{840–1}$	$\frac{52}{840–0}$	$\frac{53}{700–0}$	$\frac{78}{960–2}$	$\frac{14}{220–0}$
Zink, μg/L	$\frac{38}{989–0}$	$\frac{28}{572–0}$	$\frac{21}{583–0}$	$\frac{33}{991–0}$	$\frac{33}{719–0}$	$\frac{34}{538–0}$	$\frac{32}{918–0}$	$\frac{6}{482–0}$
Chromium (VI), μg/L	$\frac{5.3}{98.0–0}$	$\frac{4.1}{54.0–0}$	$\frac{5.4}{90.0–0}$	$\frac{5.5}{41.0–0}$	$\frac{8.2}{75.0–0}$	$\frac{6.9}{66.0–0}$	$\frac{4.2}{29.3–0}$	$\frac{2.9}{54.0–0}$
COD_{Mn}, mg O/L	$\frac{8.7}{46.3–1.3}$	$\frac{4.3}{21.2–0.49}$	$\frac{8.2}{15.5–2.2}$	$\frac{7.3}{29.6–0.3}$	$\frac{5.3}{40.8–1.6}$	$\frac{8.2}{30.0–2.75}$	$\frac{7.6}{21.8–2.00}$	$\frac{8.8}{11.8–3}$

(continued)

Table 1.1 (continued)

Indicator	Dnipro	Danube	Dniester	Southern Bug	Western Bug (the Vistula basin)	Siversky Donets (the Don basin)	Rivers of Azov Sea region	Water bodies of Crimea
COD_{Cr}, mg O/L	$\frac{29}{140\text{–}1.3}$	$\frac{17}{139\text{–}1}$	$\frac{32}{124\text{–}4}$	$\frac{21}{73\text{–}1}$	$\frac{35}{106\text{–}2}$	$\frac{29}{109\text{–}2.9}$	$\frac{28}{122\text{–}5}$	$\frac{13}{43\text{–}2}$
BOD_5, mg O_2/L	$\frac{2.7}{40.0\text{–}0}$	$\frac{2.5}{11.6\text{–}0.1}$	$\frac{3.6}{22.2\text{–}0.7}$	$\frac{3.0}{14.6\text{–}0.1}$	$\frac{4.4}{72.0\text{–}0.3}$	$\frac{3.3}{10.1\text{–}0}$	$\frac{3.2}{20.0\text{–}0.2}$	$\frac{2.5}{10.7\text{–}0.1}$
Phenols, mg/L	$\frac{0.002}{0.075\text{–}0}$	$\frac{0.004}{0.100\text{–}0}$	$\frac{0.003}{0.038\text{–}0}$	$\frac{0.003}{0.05\text{–}0}$	$\frac{0.001}{0.03\text{–}0}$	$\frac{0.003}{0.32\text{–}0}$	$\frac{0.001}{0.09\text{–}0}$	$\frac{0}{0.004\text{–}0}$
Petroleum hydrocarbons, mg/L	$\frac{0.06}{3.51\text{–}0}$	$\frac{0.09}{2.70\text{–}0}$	$\frac{0.19}{4.72\text{–}0}$	$\frac{0.05}{2.69\text{–}0}$	$\frac{0.02}{1.10\text{–}0}$	$\frac{0.13}{4.89\text{–}0}$	$\frac{0.12}{4.80\text{–}0}$	$\frac{0.03}{0.35\text{–}0}$
SS, mg/L	$\frac{0.03}{1.00\text{–}0}$	$\frac{0.02}{0.81\text{–}0}$	$\frac{0.03}{1.78\text{–}0}$	$\frac{0.04}{0.95\text{–}0}$	$\frac{0.04}{0.85\text{–}0}$	$\frac{0.12}{0.93\text{–}0}$	$\frac{0.01}{0.11\text{–}0}$	$\frac{0.01}{0.11\text{–}0}$
п, п′- DDE, g/L	$\frac{0.001}{0.150\text{–}0}$	$\frac{0.001}{0.160\text{–}0}$	$\frac{0}{0.09\text{–}0}$	$\frac{0}{0.06\text{–}0}$	$\frac{0.001}{0.08\text{–}0}$	$\frac{0.007}{0.07\text{–}0}$	0	$\frac{0}{0.01\text{–}0}$
DDT, μg/L	$\frac{0}{0.17\text{–}0}$	$\frac{0}{0.12\text{–}0}$	$\frac{0}{0.03\text{–}0}$	$\frac{0}{0.01\text{–}0}$	$\frac{0}{0.01\text{–}0}$	0	0	0
Alpha-Hexachlorocyclohexane (α-HCH) μg/L	$\frac{0}{0.070\text{–}0}$	$\frac{0}{0.380\text{–}0}$	$\frac{0}{0.010\text{–}0}$	$\frac{0}{0.014\text{–}0}$	$\frac{0}{0.002\text{–}0}$	$\frac{0}{0.095\text{–}0}$	$\frac{0}{0.038\text{–}0}$	$\frac{0}{0.046\text{–}0}$
Gamma Hexachlorocyclohexane (γ-HCH, lindane) μg/L	$\frac{0}{0.060\text{–}0}$	$\frac{0}{0.086\text{–}0}$	$\frac{0}{0.005\text{–}0}$	$\frac{0}{0.013\text{–}0}$	$\frac{0}{0.020\text{–}0}$	$\frac{0}{0.097\text{–}0}$	$\frac{0}{0.009\text{–}0}$	$\frac{0}{0.060\text{–}0}$

(continued)

Table 1.1 (continued)

Indicator	Dnipro	Danube	Dniester	Southern Bug	Western Bug (the Vistula basin)	Siversky Donets (the Don basin)	Rivers of Azov Sea region	Water bodies of Crimea
Beta Hexachlorocyclohexane (β–HCH), μg/L	$\frac{0}{2.00\text{–}0}$	$\frac{0}{0.030\text{–}0}$	0	0	$\frac{0}{0.008\text{–}0}$	$\frac{0}{0.052\text{–}0}$	0	$\frac{0}{0.002\text{–}0}$
Hexachlorobenzene (HCB), μg/L	$\frac{0}{0.030\text{–}0}$	$\frac{0}{0.008\text{–}0}$	0	0	$\frac{0}{0.003\text{–}0}$	$\frac{0}{0.069\text{–}0}$	0	0
Color, degrees	$\frac{34}{257\text{–}0}$	$\frac{15}{149\text{–}0}$	$\frac{18}{177\text{–}0}$	$\frac{21}{80\text{–}0}$	$\frac{26}{67\text{–}7}$	$\frac{23}{70\text{–}2}$	$\frac{23}{78\text{–}0}$	$\frac{10}{91\text{–}0}$
Transparency, cm (font)	$\frac{25}{55\text{–}0}$	$\frac{20}{58\text{–}0}$	$\frac{25}{55\text{–}0}$	$\frac{23}{38\text{–}0}$	$\frac{20}{42\text{–}1}$	$\frac{21}{60\text{–}1}$	$\frac{19}{35\text{–}0}$	$\frac{21}{27\text{–}0}$
Ionic strength, μ	$\frac{0.01}{0.19\text{–}0.0007}$	$\frac{0.007}{0.067\text{–}0.0005}$	$\frac{0.009}{0.20\text{–}0.0005}$	$\frac{0.013}{0.07\text{–}0.002}$	$\frac{0.010}{0.039\text{–}0.002}$	$\frac{0.031}{0.192\text{–}0.002}$	$\frac{0.057}{0.250\text{–}0.003}$	$\frac{0.011}{0.063\text{–}0.001}$

Notes Numerator: average, denominator: max.–min

Figure “0” means that the content of a determined ingredient is lower than the limit of quantification by the methods described in the monograph [2]

A dash means that the ingredient is not defined

COD—chemical oxygen demand, COD_{Cr}—with bichromate as an oxidant,—with permanganate an oxidant

BOD_5—biochemical oxygen demand, per five days

1.2 Hydro-Chemical Indicators

Extremely wide range of hydro-chemical parameters implies various conditions of forming water chemistry in water bodies of Ukraine depending on the physical and geographic zoning and anthropogenic factors. In particular, the lowest water salt content is observed in the rivers of the Danube Basin, which is dominated by mountain streams, and the highest—in the rivers of the Azov Sea region, where due to the dry climate soluble compounds accumulate in the soil and conditions emerge for the formation of brackish water (Fig. 1.1).

The value of pH is fairly stable, usually ranging within 7.9–8.1. However, under the specific conditions of intensive photosynthesis in the summer and reduction of carbon dioxide to almost zero because of its consumption by hydrobionts, pH value can reach 9.5–10. At the same time, given the decomposition of organic substances and accumulation of carbon dioxide, water pH may decrease to 5.9–6.0.

Concentrations of dissolved oxygen and carbon dioxide fluctuate within wide limits and usually change by inverse relation.

Nitrogen is present in natural waters in the form of inorganic (NH_4^+, NO_2^-, NO_3^-) and organic (proteins, amines, amino acids, etc.) compounds. Nitrogen inorganic compounds, especially nitrates, are absorbed by hydrobionts during photosynthesis,

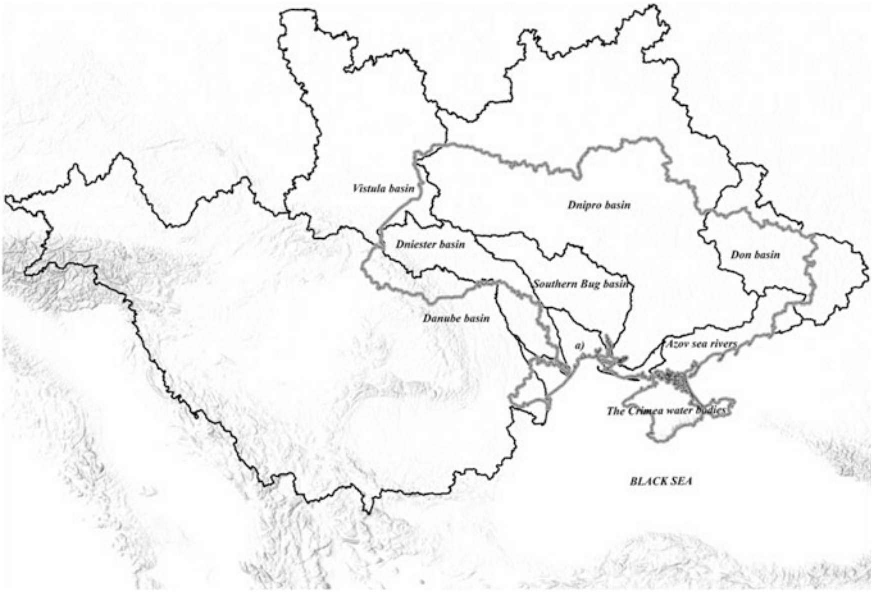


Fig. 1.1 The main river basins in Ukraine

therefore during intensive growth their concentration can be reduced to almost zero. The concentration of nitrogen compounds increases with biochemical decomposition of organic substances and due to contamination of natural waters with municipal sewage and fertilizer leaching from the soil by rain. The lowest concentrations of inorganic nitrogen compounds are observed in the rivers of the Dnipro Basin, and the highest, especially NH_4^+—in the rivers of the Dniester and Siversky Donets Basins and the Azov Sea region.

As to the phosphates level, the cleanest are the rivers of the Danube Basin and the Crimean rivers, the most polluted are the rivers of the Siversky Donets Basin.

The concentration of iron compounds is usually less than 0.5 mg Fe/L and in most surface waters is at the level of 0.2–0.3 mg Fe/L. A somewhat higher content of iron compounds is present in certain rivers of the Dniester and Danube Basins (the Transcarpathia) (0.5–1 mg Fe/L). In places of anthropogenic pollution the concentration of iron compounds can reach 10 mg Fe/L.

The content of trace elements-heavy metal compounds is much lower and is within μg/L. Thus, the concentration of manganese compounds in most rivers of Ukraine is less than 100 μg Mn/L, and only in some rivers of the Dniester, Dnipro and Danube Basins (the Transcarpathia) exceeds this value. In places of anthropogenic pollution the concentration of manganese compounds can reach 800–900 μg Mn/L.

The average content of copper compounds is not more than 10 μg Cu/L. In some rivers of the Dniester and Danube Basins and the left bank of the Dnipro Basin it is 20–25 μg Cu/L and in places of anthropogenic pollution it may exceed 100 μg Cu/L.

The concentration of zinc compounds is usually less than 50 μg Zn/L. However, in lower reaches of the Dnipro and in some rivers of the Transcarpathia, the Dniester and Siversky Donets Basins it reaches 100–150 μg Zn/L, apparently due to anthropogenic pollution.

The concentration of chromium (VI) compounds is much lower—10 μg Cr/L, though in places of anthropogenic pollution it can reach 50−100 μg Cr/L.

Among the organic compounds of natural origin humic and fulvic acids make up the largest share, the content of which is at 1–300 mg/L, especially in forest and wetland areas. Concentrations of other organic compounds are much lower—amines account for 10–200 μg N/L, amino acids—2–5 μg N/L, proteins—50–000 μg/L per albumin, carbonyl compounds—1–0 μg/L per acetic aldehyde (in the waters of lakes up to 40−0 μg/L), organic carboxylic and hydroxycarboxylic acids—10–00 μmol eq/L, esters—10–00 μmol eq/L etc. [1, 2, 6].

Among anthropogenic organic compounds in surface waters of Ukraine most abundant are phenols (up to 0.2 mg/L), mineral oils (5 mg/L), synthetic surfactants (up to 1 mg/L), pesticides (0.1 μg/L), aromatic hydrocarbons and fats (up to milligram quantities in mg/L) [2, 3].

More information on organic compounds in natural waters is given in Chap. 4.

1.3 Hydro-Biological Indicators

Hydro-biological indices are an important characteristic of surface water quality. The monitoring of hydro-biological indicators in Ukraine is insufficient, therefore there is no possibility to provide generalized characteristics of river basins water quality by biotic indices, similar to abiotic indicators listed in Table 1.1.

The most characteristic biotic indicators of surface water quality, including Ukraine, are provided in [4, 5]. Boundary values of biotic indicators are the following:

- Phytoplankton biomass (mg/L) from <0.5 to >50;
- Index of purification—from 1.0 to <0.5;
- Self-pollution index (A/R) of 1.1 to >2.5;
- Bacterioplankton population (million cells/mL) from <0.5 to >10.0;
- Population of saprophytic bacteria (thous. cells/cm^3) from <1.0 to >100.0;
- the Pantle–Buck saprobity index from <1.0 to >3.5;
- the Goodnight−Whitley saprobity index from 1–0 to 91–00.

References

1. Linnik PN, Nabivanets BY (1986) Formy migratsii metallov v presnykh poverkhnostnykh vodakh. (Patters of metal migration in fresh surface water). Gydrometizdat, Leningrad
2. Nabivanets BY, Osadchy VI, Osadcha NM et al (2007) Analitychna khimiya poverkhnevykh vod (Analytical chemistry of surface water). Nauk Dumka, Kyiv
3. Osadchy VI, Nabivanets BY, Osadcha NM et al (2008) Gidrokhemichny dovidnyk (Hydrochemical handbook). Nika-Cetre, Kyiv
4. Romanenko VD (ed) (2006) Metody gidroekologichnykh doslidzhen poverkhnostnykh vod (Methods of hydroecoligical studies of surface water). LOGOS, Kyiv
5. Romanenko VD, Zhukinsky VM, Oksiyuk OP et al (1998) Metodika ekologichnoy otsinki yakosti poverkhnevykh vod za vidpovidnymy kategoriyamy (Technique for ecological evaluation of surface water quality by competent categories). Symbol-T, Kyiv
6. Varshal GM, Koscheeva IY, Sirotkina Is et al (1979) Izuchenie organicheskikh veschestv poverkhnostnykh vod i ikh vzaimodeystviya s metallami (Studying surface water organic substances and their interaction with metal ions). Geochemistry 4: 598–606

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 30–40 J/m^2 mm or 1.8 J/m^2 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 6.7×10^3 J and 1.7×10^9 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

V. Osadchyy et al., *Processes Determining Surface Water Chemistry*,
DOI 10.1007/978-3-319-42159-9_2

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 waterlogged 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 132–262 km^3/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 −1133 mg/L, although an average annual volume of the Siversky Donets runoff is more than 90 times lower −4.26 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 ($\sim$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.

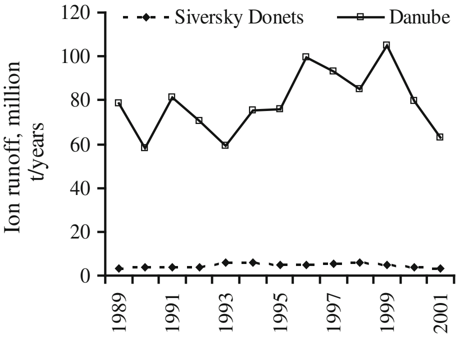


Fig. 2.1 Ion runoff in the Danube and Siversky Donets rivers (in Ukraine), 1989–2001 [67]

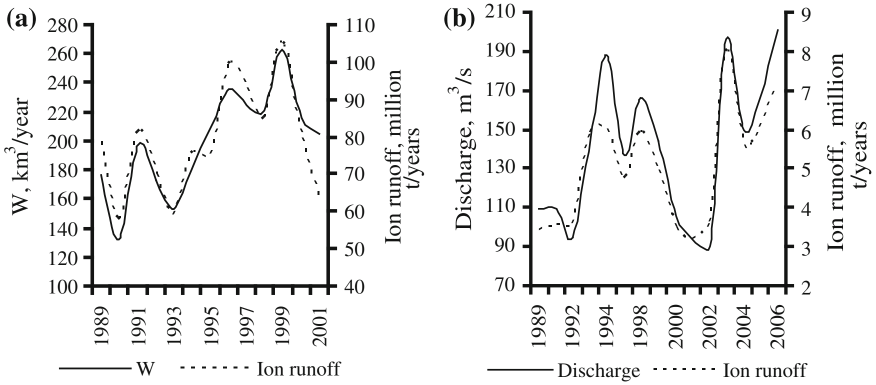
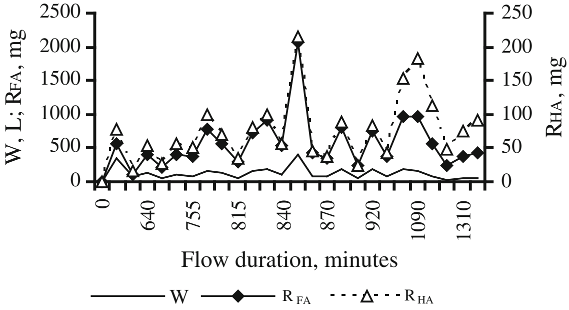


Fig. 2.2 Long-term dynamics of **a** ion and water runoff (W) in the Danube, city of Reni **b** water discharge and ion runoff in the Siversky Donets, Kruzhylivka village [67]

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

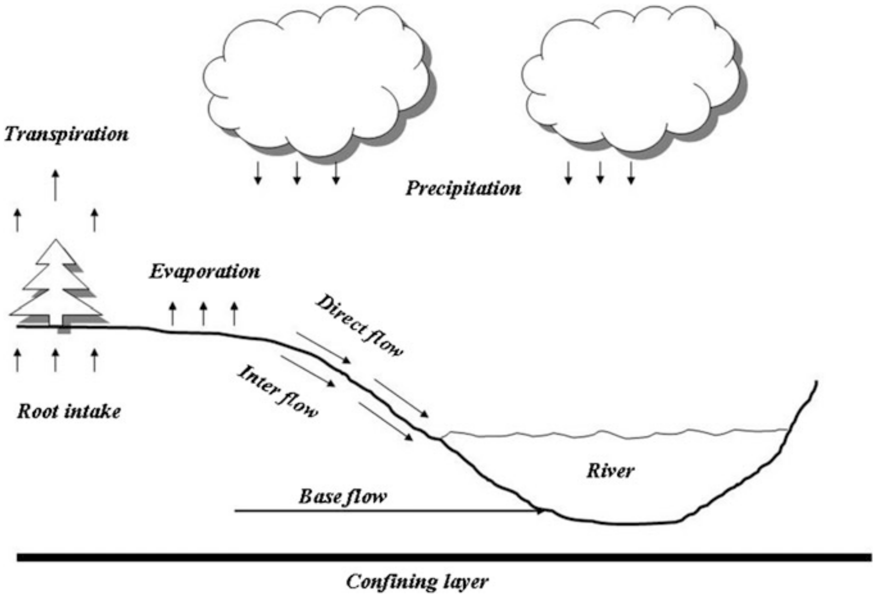


Fig. 2.4 Scheme illustrating water runoff phenomenon

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 a of 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 $N_{miner.}$ 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 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 ($CaSO_4 \cdot 2H_2O$), calcite ($SaCO_3$), dolomite ($CaMg(CO_3)_2$).

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

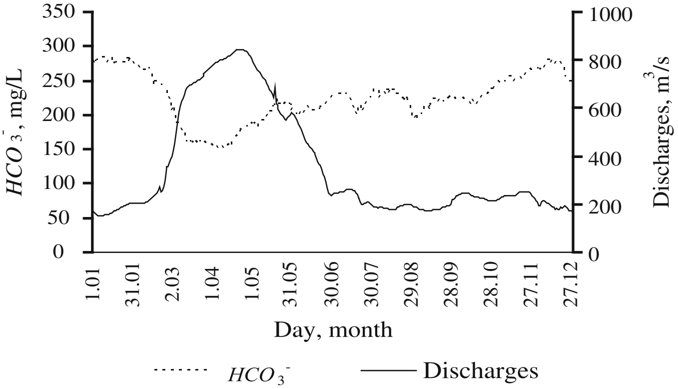
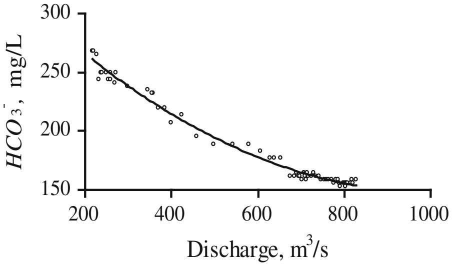


Fig. 2.5 Annual dynamics of hydrocarbon ions content and water discharge in the Desna River near outlet station (Litky village), 1995 [67]

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):

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

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

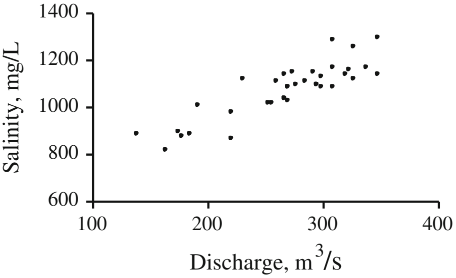


Fig. 2.7 The relationship between discharge and salinity of water in the Siversky Donets River, city of Lysychansk, 1999 [67]

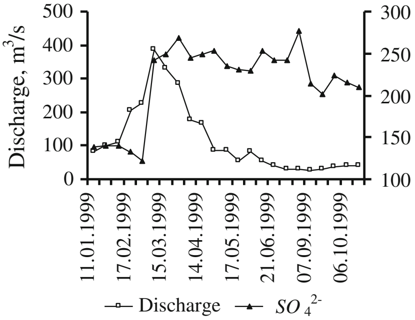


Fig. 2.8 Annual dynamics of water flow and concentration of sulfate ions in the Siversky Donets River, city of Lysychansk, 1999 [67]

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).

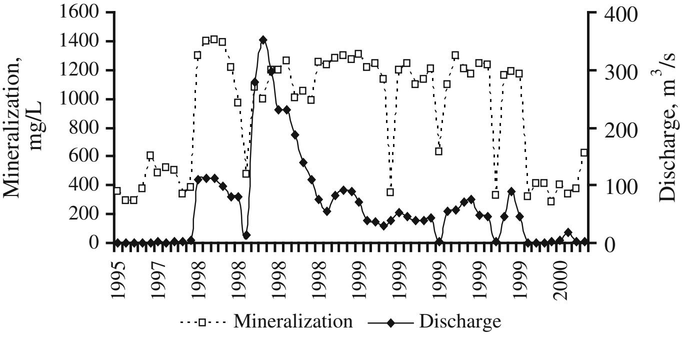


Fig. 2.9 Dynamics of water mineralization and discharge in the Black River (Crimea), during the period of 1995–2000

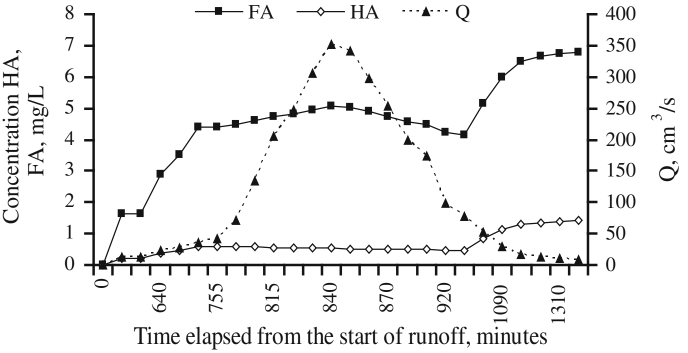


Fig. 2.10 Dynamics of humic and fulvic acid concentrations at various stages of generation of water runoff (according to the experimental simulation) [64]

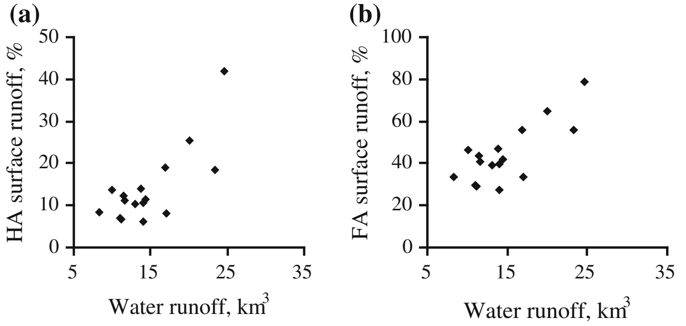


Fig. 2.11 Dependence of relative share of surface runoff on water content **a** HA and **b** FA [65]

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

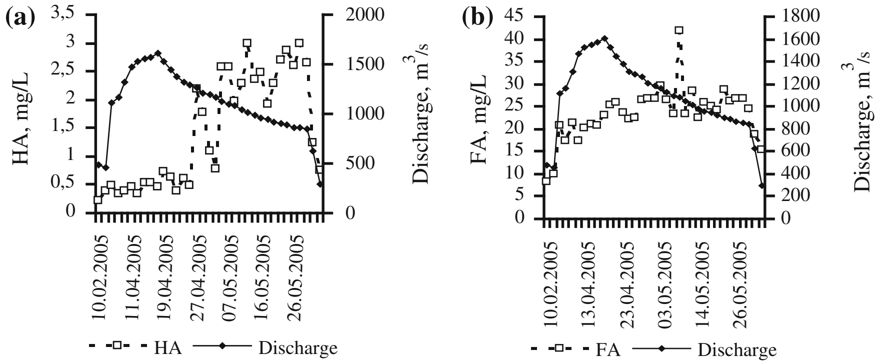


Fig. 2.12 Dynamics of the change of water flow and concentrations of **a** humic and **b** fulvic acids in the Prypiat River, city of Chernobyl, during the flood in 2005 [64]

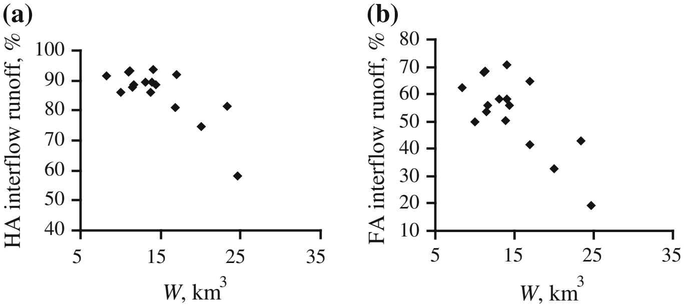


Fig. 2.13 Dependence of relative portion of interflow runoff of **a** humic and **b** fulvic acids in the basin of the Prypiat River on water content [64]

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 Mezhygirya-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 Donbass 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].

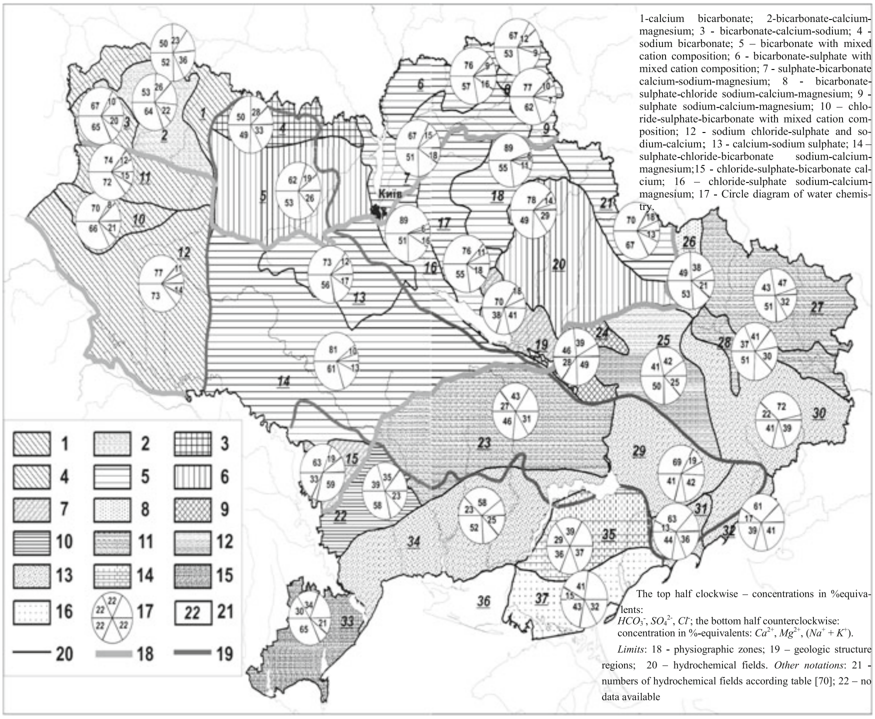
   Fresh waters in the Carpathians are found only in the Quaternary sediments. The deeper Paleogene and Cretaceous sediments carry abundant sodium chloride brines with high salinity.

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).

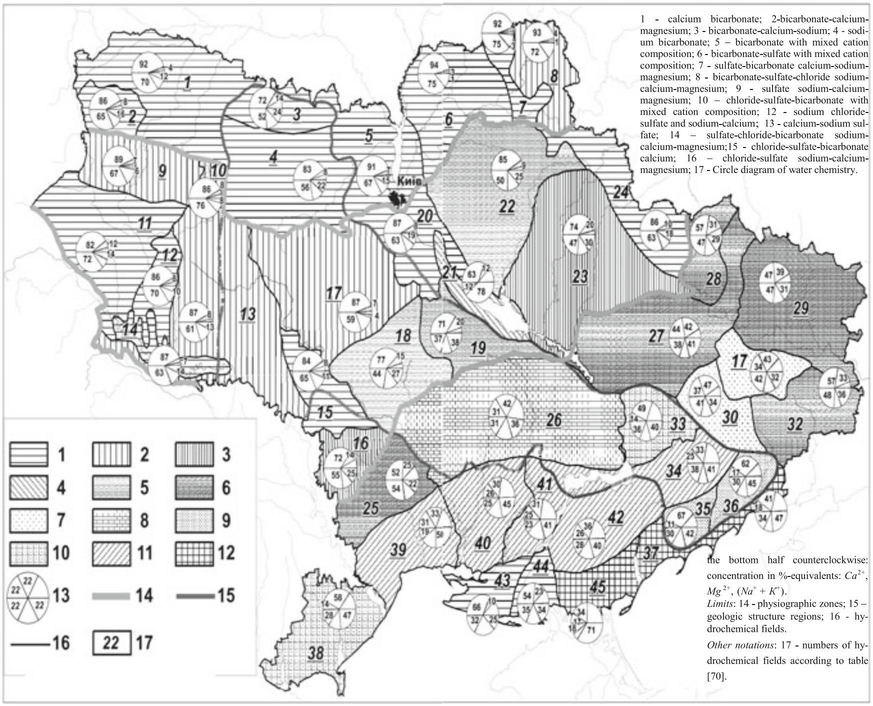


1-calcium bicarbonate; 2-bicarbonate-calcium-magnesium; 3 - bicarbonate-calcium-sodium; 4 - sodium bicarbonate; 5 – bicarbonate with mixed cation composition; 6 - bicarbonate-sulphate with mixed cation composition; 7 - sulphate-bicarbonate calcium-sodium-magnesium; 8 - bicarbonate-sulphate-chloride sodium-calcium-magnesium; 9 - sulphate sodium-calcium-magnesium; 10 – chloride-sulphate-bicarbonate with mixed cation composition; 12 - sodium chloride-sulphate and sodium-calcium; 13 - calcium-sodium sulphate; 14 – sulphate-chloride-bicarbonate sodium-calcium-magnesium;15 - chloride-sulphate-bicarbonate calcium; 16 – chloride-sulphate sodium-calcium-magnesium; 17 - Circle diagram of water chemistry.

The top half clockwise – concentrations in %equivalents: HCO_3^-, SO_4^{2-}, Cl^-; the bottom half counterclockwise: concentration in %-equivalents: Ca^{2+}, Mg^{2+}, $(Na^+ + K^+)$.

Limits: 18 - physiographic zones; 19 – geologic structure regions; 20 – hydrochemical fields. *Other notations*: 21 - numbers of hydrochemical fields according table [70]; 22 – no data available

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


1 - calcium bicarbonate; 2-bicarbonate-calcium-magnesium; 3 - bicarbonate-calcium-sodium; 4 - sodium bicarbonate; 5 – bicarbonate with mixed cation composition; 6 - bicarbonate-sulfate with mixed cation composition; 7 - sulfate-bicarbonate calcium-sodium-magnesium; 8 - bicarbonate-sulfate-chloride sodium-calcium-magnesium; 9 - sulfate sodium-calcium-magnesium; 10 – chloride-sulfate-bicarbonate with mixed cation composition; 12 - sodium chloride-sulfate and sodium-calcium; 13 - calcium-sodium sulfate; 14 – sulfate-chloride-bicarbonate sodium-calcium-magnesium;15 - chloride-sulfate-bicarbonate calcium; 16 – chloride-sulfate sodium-calcium-magnesium; 17 - Circle diagram of water chemistry.

the bottom half counterclockwise: concentration in %-equivalents: Ca^{2+}, Mg^{2+}, (Na^{+} + K^{+}).

Limits: 14 - physiographic zones; 15 – geologic structure regions; 16 - hydrochemical fields.

Other notations: 17 - numbers of hydrochemical fields according to table [70].

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

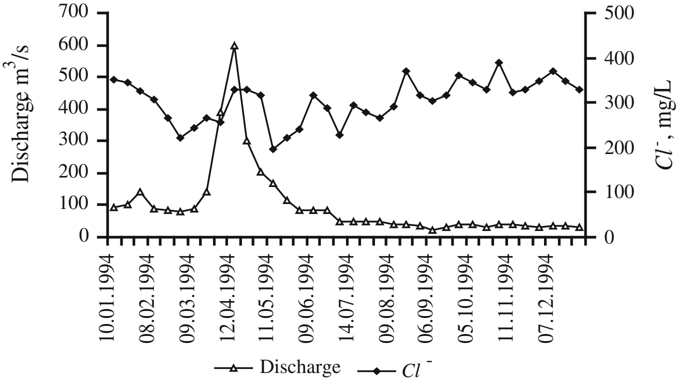


Fig. 2.16 Annual dynamics of water discharge and chloride ion content in the Siversky Donets River, the city of Lysychansk, 1994 [67]

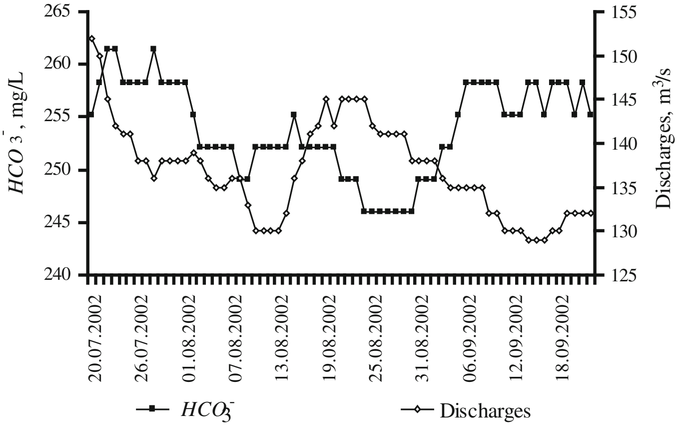


Fig. 2.17 The dynamics of hydrocarbon ions and water discharge during the summer-autumn low water (case study of the Desna River, vil. Litky, 2002) [67]

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:

$$(\mathrm{Ip}+\mathrm{It}+\mathrm{Iu}+\mathrm{Id}+\mathrm{P})-(\mathrm{Rp}+\mathrm{Rw}+\mathrm{Rs}+\mathrm{E})=\mathrm{A}. \tag{2.1}$$

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 km^3. 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 km^3 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 km^3/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 ($W_{\mathrm{inflow},\ \mathrm{runoff}}$) exceeds the volume contained in it (V).

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

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].

$$B = 1 - \left(\frac{V_0}{V_k}\right)^{1 + \frac{W_{runoff} : V_{\hat{e}}}{1 - V_0 : V_{\hat{e}}}}, \tag{2.2}$$

where V_0, V_k are the volumes of the reservoir at the beginning and the end of the base period, m^3; W_{runoff}—runoff for the same period, m^3.

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

$$B' = 0.5 \cdot V^{-1}(V + Qbp \cdot t - 14,1b \cdot h \cdot \surd t), \tag{2.3}$$

where Q_{bp} is the average for the base period volume of water entering a reservoir, m^3/s; *V*—volume of the reservoir, m^3; *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 or 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):

$$C_\kappa = C_0 + (C_{in} \frac{W_{in}}{W_{in} + W_{prec} - W_{evaap}} - C_0) : B \tag{2.4}$$

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, m^3; W_{evap}—the volume of water evaporated from the water surface, m^3. 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

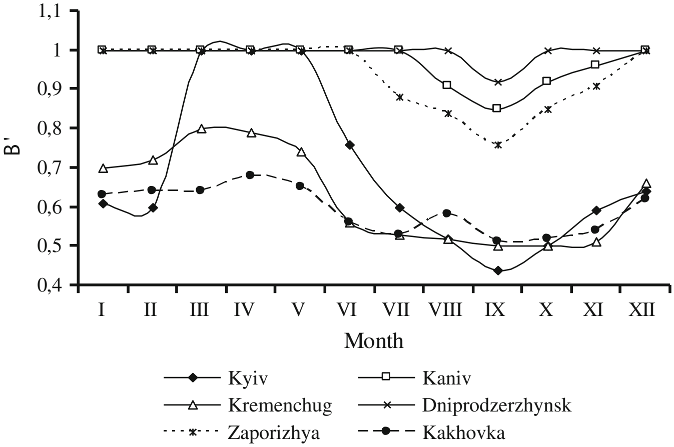


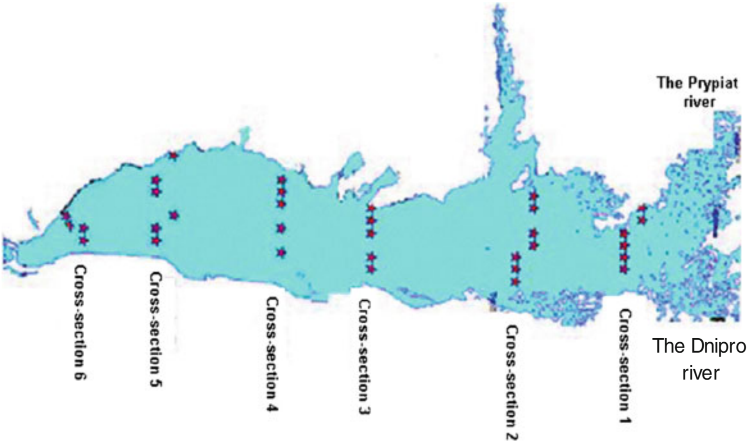
Fig. 2.18 Water replacement rates in the Dnipro reservoirs [14, 90]

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 distrophization.

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



Cross-section number	6	5	4	3	2	1
Distance from the dam of the Kyiv HPP, km	5.7	15.0	27.4	36.7	51.3	62.4

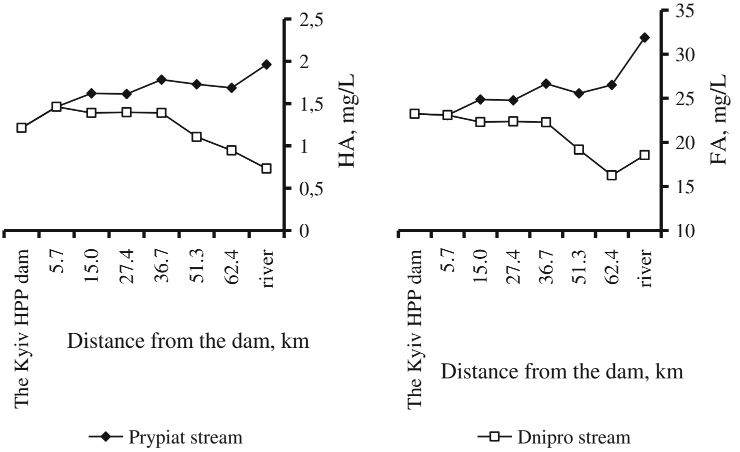


Fig. 2.19 Changing of HA and FA content along the Kyiv reservoir during summer low water, 1999 [64]

out that the two genetically different water masses of the Prypiat and the Dnipro 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:

$$Ca^{2+}\,(\mathrm{mM/L}) > HCO_3^- + CO_3^{2-}\,(\mathrm{mM/L}),$$

or in the form of balance of charges

$$2\mathrm{m}_{Ca^{2+}} > \mathrm{m}_{HCO_3^-} + 2\mathrm{m}_{CO_3^{2-}},$$

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 Ca^{2+} (mM/L) > HCO_3^- + CO^{2+} (mM/L), calcium will start accumulating in water and it will precipitate not only as $CaCO_3$, but also as $CaSO_4$.

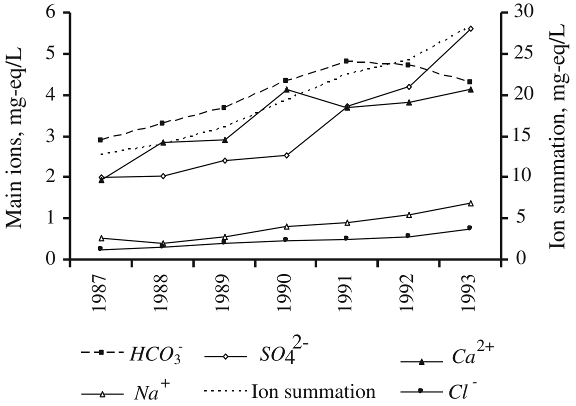


Fig. 2.20 Dynamics of main ions content and water salinity in the cooling pond of the Zaporizhzhya NPP during its operation in non-blowdown regime (1987–1993) [67]

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).

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

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

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 = 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:

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

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 dz 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]:

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

where C is the concentration of pollutants, g/L; V_{av}—the average flow rate, m/s; D_{av}—the average turbulent diffusion coefficient, m^2/s; x, y, z—the coordinates of analysis grid.

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

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

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]:

$$C_{\max} = C_{\mathrm{bg}} + C_{\mathrm{ww}} - C_{\mathrm{bg}}/n, \tag{2.10}$$

where C_{max} is the maximum concentration of a substance in a contaminated stream, $\mathrm{g/m^3}$; C_{bg}—the concentration of a substance in cross-section above the waste water release site (background concentration), $\mathrm{g/m^3}$; C_{ww}—concentrations of substances in wastewater, $\mathrm{g/m^3}$; n—reciprocal dilution of waste water at a given distance from the release site.

Reciprocal dilution of waste water is calculated by the formula:

$$n = \frac{\gamma \cdot Q + q_{ww}}{q_{ww}}, \tag{2.11}$$

where Q is the water runoff in a river; $\mathrm{m^3/s}$; q_{ww}—wastewater discharge, $\mathrm{m^3/s}$; γ—mixing ratio, which is calculated by the formula:

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

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:

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

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.

$$D = \frac{V_{av} \cdot H_{av} \cdot g}{2\, m\, c} \tag{2.14}$$

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 $10 < p < 60$ m = 0.7c + 6, at s $\geq$ 60 m = 48 = 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:

$$c = \frac{V_{av}}{\sqrt{\mathrm{RI}}} \tag{2.15}$$

where V_{av} is the average flow rate, m/s; R = F $\cdot$ χ—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:

$$c = \frac{1}{n_r} \cdot R^y \tag{2.16}$$

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

$$R < 1\mathrm{m}\ y = \mathbf{1},\ \mathbf{5}\sqrt{\mathbf{n}_r}\quad R > 1\mathrm{m}\ \ y = \mathbf{1},\ \mathbf{3}\sqrt{\mathbf{n}_r}$$

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 χ = 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:

$$D = \frac{v_{av} \cdot H_{av}}{200} \tag{2.17}$$

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 (~4 °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]:

$$A_z = \frac{\gamma_h}{4\rho a_0} wh \tag{2.18}$$

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_o—wind factor, the recommended value of which is 0.0125.

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

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):

$$K_L = \frac{r_{\max}^2}{4t_{\max}} \tag{2.20}$$

where KL 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]:

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

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-saprobiotic 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 m^3/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, physicochemical 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

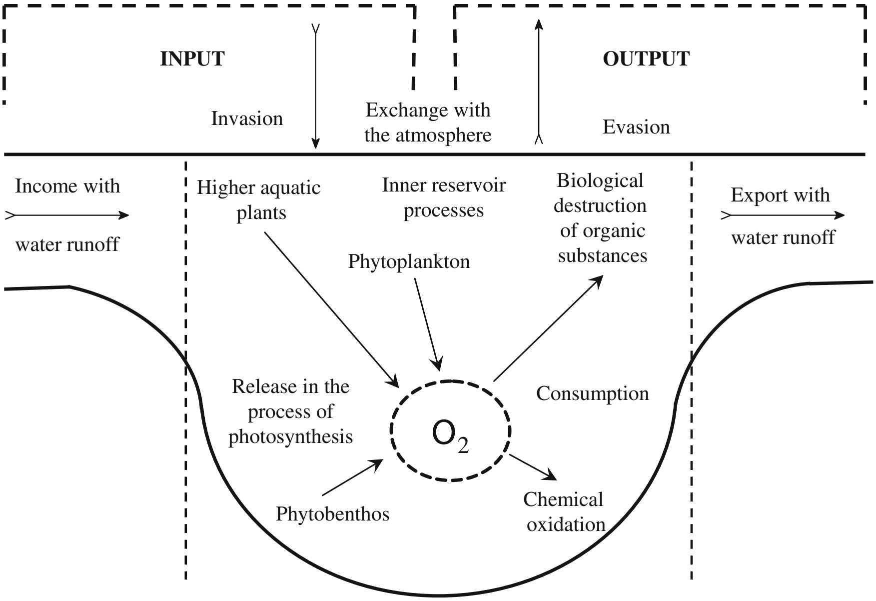


Fig. 2.21 Diagram of dissolved oxygen circulation in aquatic ecosystems [78]

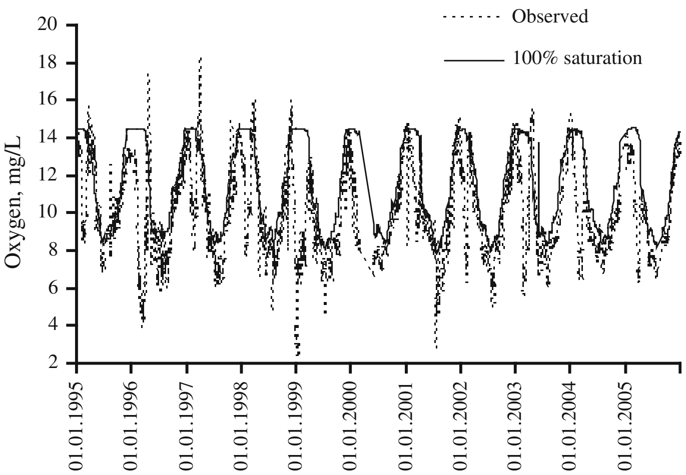


Fig. 2.22 Long-term (1995–2005) dynamics of dissolved oxygen concentrations in the Kyiv reservoir, vill. Novopetrivtsi, compared to 100 % saturation concentration

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 g/m^2 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:

$$Cs = 14.62 - 0.4042 - \mathrm{T} + 0.00842 - \mathrm{T}^2 - 0.00009 - \mathrm{T}^3[7], \qquad (2.22)$$

where T is the water temperature, °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:

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

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):

$$K_2 = 3.68\sqrt{\frac{V}{h^3}} \tag{2.24}$$

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

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

$$K_2(\mathrm{T}) = K_2(20^\circ\mathrm{C}) \cdot 1{,}04^{\mathrm{T}-20} \tag{2.25}$$

Typically, the value of reaeration coefficient (1/24 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/m^2 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/m^2 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).

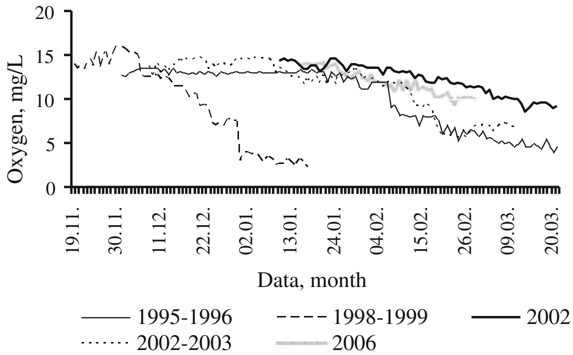


Fig. 2.23 The content of dissolved oxygen in the near-dam section of the Kyiv reservoir during the freezing periods in 1995–2006

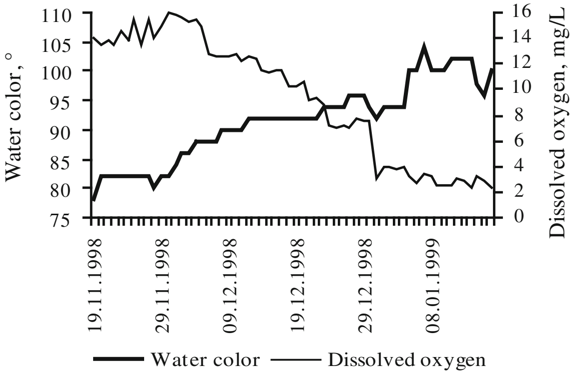


Fig. 2.24 The dynamics of the dissolved oxygen content and water color in the near-dam water of the Kyiv reservoir during the freeze-up of 1998–1999

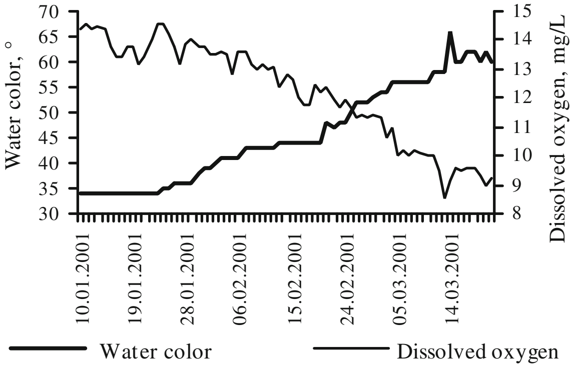


Fig. 2.25 The dynamics of the dissolved oxygen content and water color in the near-dam water of the Kyiv reservoir during the freeze-up of 2001

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).

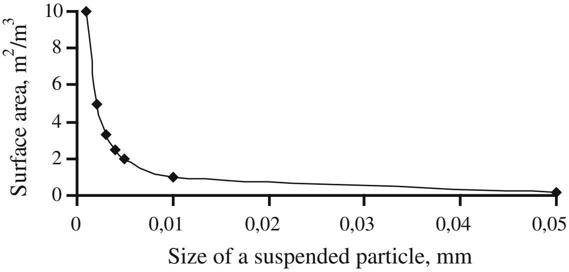


Fig. 2.26 The dependence of the surface area of the adsorbent on the size of suspended particles (at turbidity 5 mg/L) [67]

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:

$$\beta \max \approx 370\rho^{-1}, \tag{2.26}$$

where βmax 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 (%)	*Fe*	*Mn*	*Zn*	*Cu*	*Pb*	*Ni*	*Co*	*Cd*
	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.

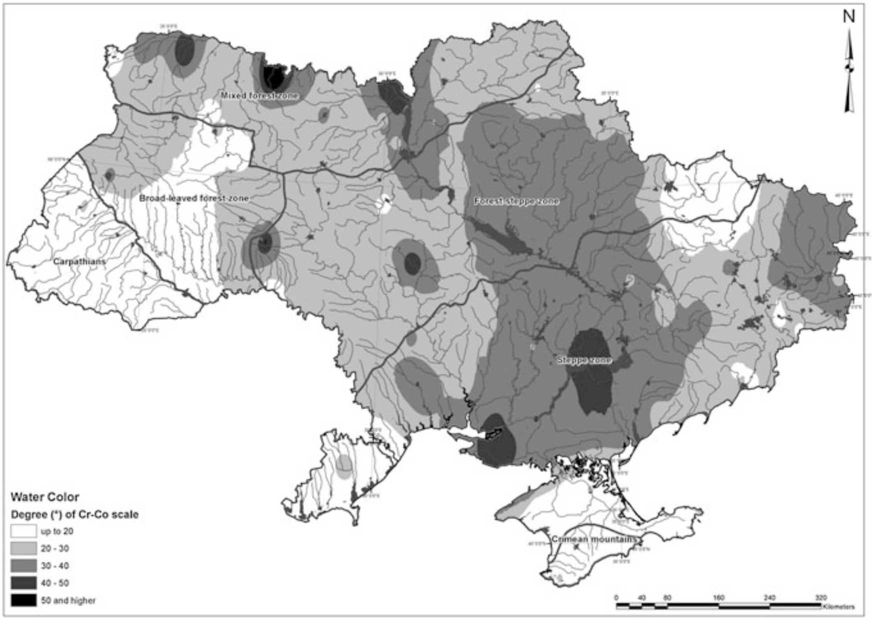


Fig. 2.27 Averaged color of surface waters in Ukraine (1989–2009) [50]

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

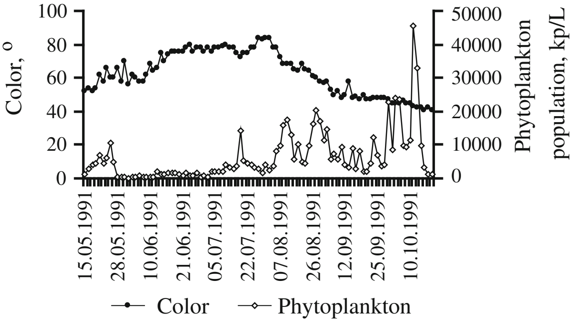


Fig. 2.28 Dynamics of water color (° of Cr–Co scale) and number of phytoplankton during the growing season (bottom of the Kyiv reservoir, 1991)

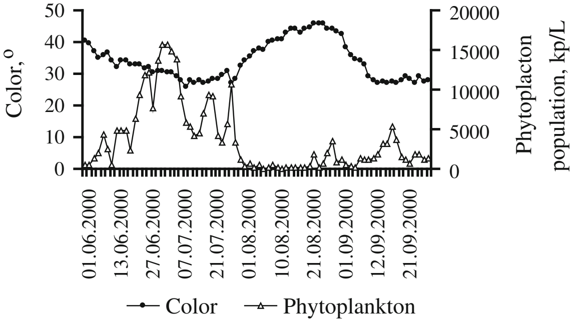


Fig. 2.29 Dynamics of water color (° of Cr–Co scale) and number of phytoplankton during the growing season (Desna River, v. Litky, 2000)

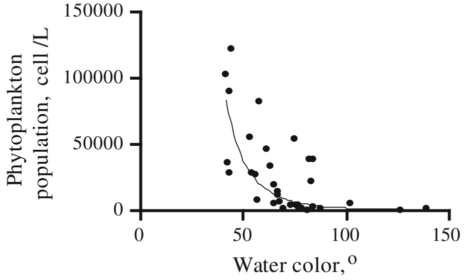


Fig. 2.30 The relationship between the number of phytoplankton and water color (° of Cr–Co scale) in lower portion of Kyiv reservoir, 1990–2001

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

The[1] 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:

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

where C is the concentration of a substance in a layer of bottom sediments with thickness z; Def—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:

$$D_{ef} = D_0 \cdot p^{\mathrm{m}} \tag{2.28}$$

where $D0$ is the molecular diffusion coefficient; p—porosity, $1.3 < \mathrm{m} < 3$.

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

---

[1] See 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$40–50 % $\mathrm{N}_{\mathrm{org}}$ [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	305.0 207.4	200.0 38.0	266.3 33.7	100.0 –	122.0 –
Kaniv reservoir, Buoy 46, 26.9.1997	427.0 231.8	88.0 30.0	10 6.5 35.5	120.0 –	85.4 –
Water basin of Kaniv HPP, 06.04.1998	549.0 146.4	72.0 28.0	142.0 17.8	80.0 42.0	109.6 7.3
Kaniv reservoir, 50th km, 17.06.1998	732.0 183.0	72.0 28.0	63.9 21.3	160.0 58.0	12.2 6.1
Kaniv reservoir, 30th km, 17.06.1998	488.0 207.4	160.0 3 4.0	56.8 21.3	120.0 56.0	24.4 13.4
Kaniv reservoir, 50th km, 10.09.1998	610.0 183.0	64.0 50.0	195.0 23.1	100.0 50.0	146.0 21.9
Kaniv reservoir, Buoy 0–3, 10.09.1998	183.0 213.5	48.0 30.0	124.3 21.3	140.0 60.0	12.2 15.9
Kaniv reservoir, 50th km, 26.09.1998	244.0 231.8	96.0 40.0	71.0 26.6	40.0 58.0	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. Sukholuchchya, 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.

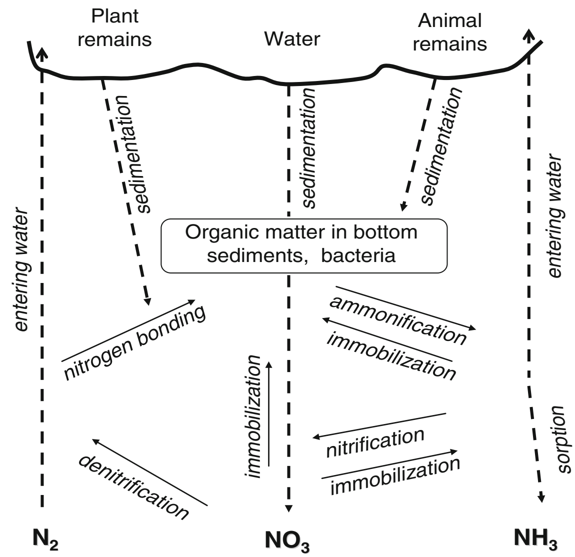


Fig. 2.31 Nitrogen cycle in bottom sediments [32]

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. Sukholuchchya, 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/m^2 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/m^2 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).

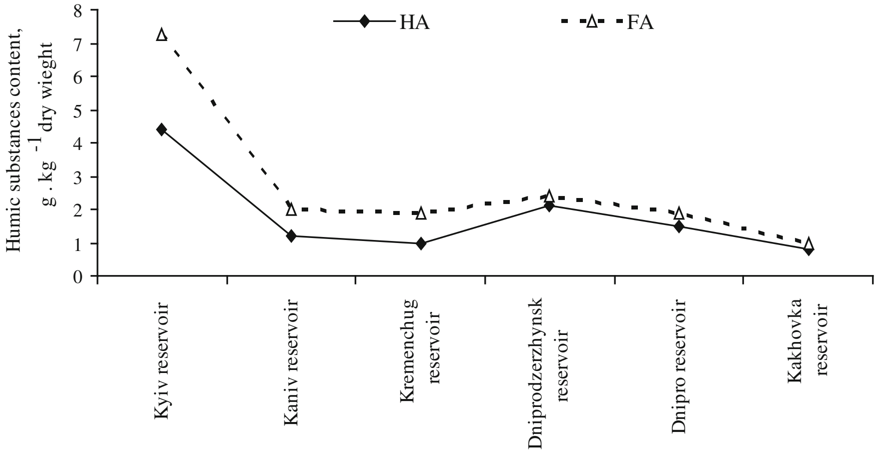


Fig. 2.32 The average content of HA and FA in the bottom sediments of the Dnipro cascade reservoirs, 2004

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

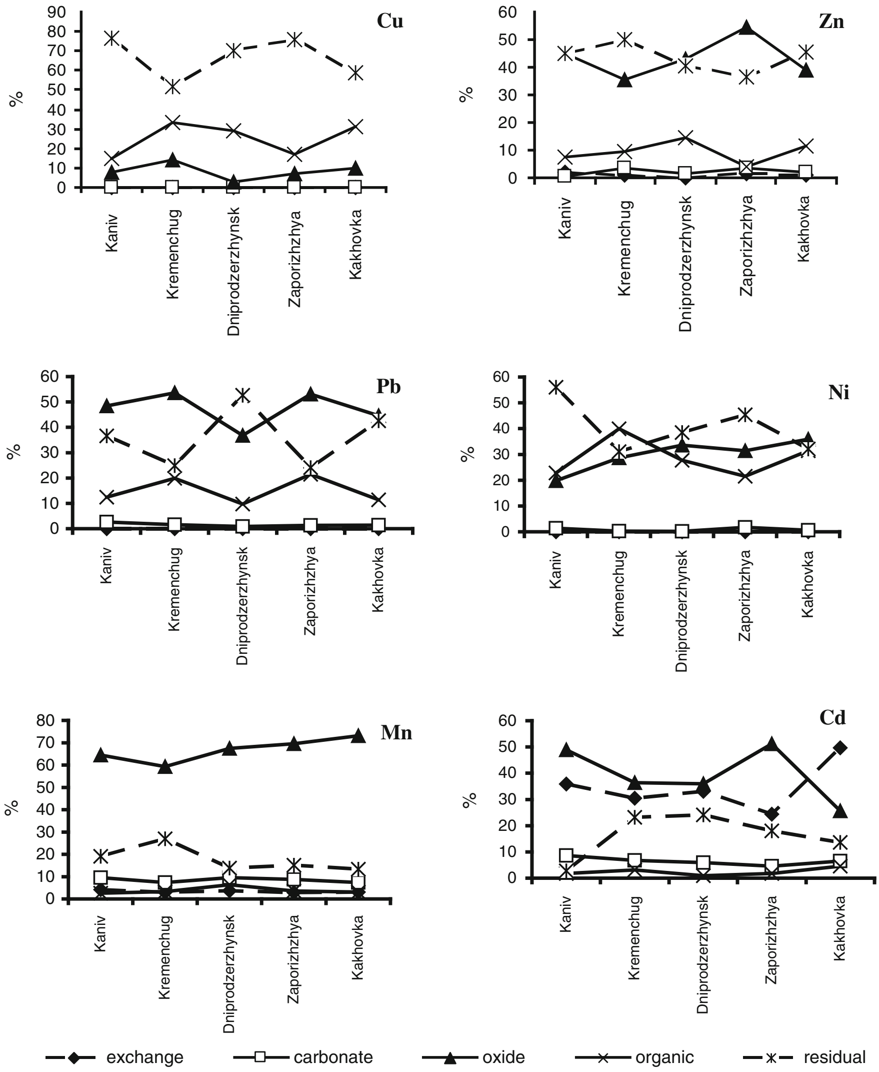


Fig. 2.33 Forms of heavy metals in the bottom sediments of the Dnipro reservoirs

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.

References

1. Alekin OA (1970) Osnovy gidrokhimii (Principles of hydrochemistry). Gydrometeoizdat, Leningrad
2. Alekin OA, Brazhnikova LV (1964) Stok rastvorennykh veshchestv s territorii SSSR (Dissolved substance runoff from the USSR area). Nauka, Moscow
3. Almazov AM, Denisova AI, Maystrenko YuG et al (1967) Gidrokhimiya Dnepra, ego vodokhranilisch i pritokov (Hydrochemistry of the Dnieper, its reservoirs and tributaries). Nauk Dumka, Kyiv
4. Avakyan AB, Saltankin VP, Sharapov VA (1987) Vodokhranilischa (Reservoirs). Myisl, Moscow
5. Bestsennaya MA (1968) Naturnoye izucheniye razbavleniya stochnykh vod v rekakh i proverka metodov rascheta (Field study of sewage dilution in rivers and calculation method testing). Works of GGI Issue 156:163–178
6. Braslavsky AP (1961) Raschet mineralizatsii vody v vodokhranilischakh (Water salinity calculation in reservoirs). Gydrochemistry Mater 32:72–96
7. Brekhovskikh VF (1988) Gidrofizicheskiye faktory formirovaniya kislorodnogo rezhima vodoyomov (Hydrophysical factors of pond oxigen regime forming). Nauka, Moscow
8. Budnik SV (2010) Taly stok so sklonov (Snowmelt hillwash). ZhGU Press, Zhitomir
9. Butorin NV (1969) Gidrolodicheskie protsessy I dinamika vodnykh mass v vodokhranilischakh volzhskogo kaskada (Hydrological processes and water body dynamics in the reservoirs of the Volga cascade). Nauka, Leningrad
10. Chebotarev AI (1975) Obschaya gidrologiya (General hydrology). Hydrometeoizdat, Leningrad
11. Copeland BJ, Duffer WP (1964) Use of clear plastic dome to measure gaseous diffusion rates in natural waters. Limnol Oceanogr 9(4):494–499
12. Demin YL, Filatov NN (1989) Osobennosti dinamiki vod raznotipnykh ozer (Water dynamics peculiarities of different lakes. Hydrophysical process and field modeling in enclosed ponds and seas). Nauka, Moscov, pp 79–93
13. Denisova AI (1979) Formirovaniya gidrokhemicheskogo rezhima vodokhranilisch Dnepra i metody ego prognozirovaniya (Hydrochemical regime formation in the Dnieper reservoirs and its forecasting methods). Nauk Dumka, Kyiv
14. Denisova AI, Timchenko VM, Nahshina EP et al (1989) Gidrologiya i gidrokhimiya Dnepra i ego vodokhranilisch (The Dnieper and its reservoirs' hydrology and hydrochemistry). Naukova Dumka, Kyiv
15. Driver J (1985) Geokhimiya prirodnykh vod (Natural water geochemistry). Mir, Moscow
16. Felzenbaum AI (1960) Teoreticheskie osnovy i metody raschyota ustanovivshikhsya morskikh techeny (Theoretical framework and calculation methods for steady marine currents). AN USSR, Moscow
17. Filatov NN (1983) Dinamika ozyor (Lake dynamics). Hydrometeizdat, Leningrad
18. Fzench RH (1984) Lake modelling: state of art. Crit Rev Environ Control 13(4):311–357
19. Gedroyts KK (1922) Uchenie o poglotitelnoy sposobnosty pochv (Soil absorption science). Ed pub com Nar com of agriculture, Petrograd
20. Glazovskaya MA (1988) Geokhimiya prirodnykh i tekhnogennykh landshaftov SRSR (Geochemistry of natural and technogenic landscapes of the USSR). Vyisshaya shkola, Moscov
21. Gorbachova LO (2005) Chynnyky, struktura I dinamika vynosu rozchinnenogo tseziyu—137 z vodnym stokom u baseyni Pripyati (Factors, structure and dynamics of dissolved Caesium—137 export with aqueous runoff in the Pripyat basin). Dissertation, Taras Shevchenko National University of Kyiv
22. Gorev LN, Nikanorov AM, PeleshenkoVI (1989) Regionalnaya gidrokhimiya (Regional hydrochemistry). Vyischa shkola, Kyiv

23. Vasilenko EV, GrebinVV (2010) Metodychni aspekty vydilennya podzemnoy skladovoy u zhyvlenni richok (Methodological aspects of underground component distinction in groundwater inflow). Hydrol Hydrochem Hydroecology 4(21):8–15
24. Gulyaeva OO (2010) Techi v Dneprovskomu vodoskhovischi: rezultaty modelyuvannya (Currents in the Dniester reservoir: modeling results). Scien. records of Ternopol ped. u-y (Special issue hydroecology) 2(43): 136–139. (Series: Biology)
25. Hatchinson D (1969) Limnologiya (Limnology). Progress, Moscow
26. Imboden DM, Schwarzenbach RP (1985) Chemical process in lakes. In: Stum W (ed) Spatial and temporal distribution of chemical substances in lakes: modelling concepts. Wiley, New York p, pp 385–403
27. Kaganer MS (ed) (1967) Resursy poverkhnostnykh vod SSSR. Ukraina i Moldavia. Bassein Severskogo Dontsa i reki Priazovya (Surface water resources of the USSR. Ukraine and Moldova. The Severski Donets basin and the Azov sea region rivers. vol.6, Issue 3). Hydrometeoizdat, Leningrad
28. Kaganer MS (ed) (1976) Kaskad Dneprovskikh vodokhranilisch (The Dnieper's reservoir cascade). Hydrometeoizdat, Leningrad
29. Kamzist ZhS, Shevchenko OL (2009) Gidrogeologiya Ukrayiny (Hydrogeology of Ukraine). Inkos, Kyiv
30. Karaushev AV (1969) Rechnaya gidravlika (River hydraulics). Hydrometeoizdat, Leningrad
31. Karaushev AV (ed) (1987) Metodicheskie osnovy otsenki i reglamentirovaniya antropogennogo vliyaniya na kachestvo poverkhnostnykh vod (Methodological framework for assessment and regulation of anthropogenic influence on surface water quality). Hydrometizdat, Leningrad
32. Kemp AWL, Mudrochowa A (1972) Distribution and forms of nitrogen in a lake Ontario sediment core. Limnol Oceanogr 17(6):855–867
33. Klebanov DO, Osadcha NM, Osadchy VI (2003) Otsinka vynosu khimichnykh elementiv vodami Dunayu u suchasny period (Assessment of chemical component export by the Dnieper water at our times). UkrNDGMI Sci. Works 251:119–134
34. NatN Kolosova, Kolosova NN (1961) Biogennye elementy i ikh stok v reke Volge u g. Kuybysheva do eyo zaregulirovaniya (1951–1954 gg.) (Nutrients and their runoff in the Volga river near Kuybyishev city before its regulation (1951–1954)). Hydrochemical Mater 31–32:68–78
35. Kopistyansky MM (1988) Protyeroziyni gidrotekhnichni sporudy. (Erosion preventive constructions) (Erosion preventive constructions). Urozhay, Kyiv
36. Kovalenko VV, Viktorova NV, Gaidukova EV (2006) Modelirovanie gidrologicheskikh protsessov (Hydrological process modelling), St.Petersburg, pp 479–481
37. Kriventsov MI, Tarasov MN (1976) Prognozirovanie mineralizatsii i soderzhanie glavnykh ionov v vode vodokhranilisch (Water salinity forecasting and principle ion content in the water of reservoirs). Hydrometeoizdat, Leningrad
38. Linnik PN (1989) Formy nakhozhdeniya tyazhyolykh metallov v prirodnykh vodakh-sostavnaya chast ekologo-toksilogicheskoy kharakteristiki vodnykh ekosistem (Heavy metal occurrence forms in natural water -ecologico-toxicological characteristics constituent of aquatic ecosystems). Water Resour 1:123–134
39. Linnik PN (2003) Prichiny ukhudsheniya kachestva vody v Kievskom i Kanevskom vodokhranilischakh (Water quality impairment agents in Kiev and Kanev reservoirs). Chem and Water Technol 25(4):384–398
40. Linnik PN, Timchenko OV, Zubko AV et al (2008) Kislorodny rezhim vodoyomov kak vazhneyshy factor migratsii razlichnykh form metallov v sisteme donnye otlozheniya-voda (Oxigen regime of reservoirs as the most important factor of different occurrence form migration in the bottom sediments-water system). Hydrobiol J 44(6):94–116
41. Linnik PN, Zhuravlyova LA, Samoylenko VN et al (1993) Vliyanie rezhima ekspluatatsii na kachestvo vody Dneprovskykh vodokhranilisch i ustevoy oblasty Dnepra (Operating mode influence on the water quality of the Dnieper reservoirs and its mouth area). Hydrobiol J 29 (1):86–98

42. Linnik PN, Zubko AV (2007) Gumusovye veschestva kak vazhny factor v migratsii matallov v sisteme donnye otlozheniya—voda (Humic substances as an important factor of metal migration in the bottom sediments-water system). Ecol Chem 16(2):69–84
43. Linnik PN, Zubko AV, Zubenko IB et al (2005) Adsorbatsiya tyazhyolykh metallov donnymi otlozheniyami v prisutstvii gumusovykh veschestv (Heavy metal adsorbation by bottom sediments before humic substances). Hydrobiol J 41(3):104–119
44. Linnik PN, Zubko AV, Zubenko IB et al (2009) Vliyanie pH na migratsiyu razlichnykh form metallov v sisteme donnye otlozheniya–voda v eksperimentalnykh usloviyakh (Influence of pH on different metal occurrence form migration in the bottom sediments-water system in experimental conditions). Hydrobiol J 45(1):99–110
45. Litvinov AS, Roschupko VF (2000) Mnogoletnyaya i sezonnaya izmenchivost vodnogd balansa vodoobmena vodokhranilisch verkhney Volgi (Long-time and seasonal water balance variability and exchange of the Upper Volga reservoirs). Water Resour 27(4): 424–434
46. Martyinova MV (1984) Azot i fosfor v donnykh otlozheniyakh ozer i vodokhranilisch (Nitrogen and phosphorus in bottom sediments of lakes and reservoirs). Nauka, Moscov
47. Mihaylov VO (1978) Usovershenstvovanie metodiki raschyota razbavleniya stochnykh vod v rekakh (Improvement of the calculation technique for sewage dilution in rivers). Works of GGI 249:94–108
48. Mizandrontsev IB (1990) Khimicheskie protsessy v donnykh otlozheniyakh vodoyomov (Chemical processes in the bottom sediments of reservoirs). Nauka, Novosibirsk
49. Moskovkin VM, Gahov VF (1981) K metodike raschyota kineticheskoy energii osadkov (On the calculation technique for kinetic energy of precipitation). Soil Sci 2:150–152
50. Nabivanets BY, Osadchy VI, Osadcha NM et al (2007) K metodike raschyota kineticheskoy energii osadkov (Analitical chemistry of surface water). Nauk dumka, Kyiv
51. Nahshina EP (1968) Ionny i biogenny stok rek basseyna verkhnego Dnepra (Ion and biogenic sink of the Upper Dnieper basin rivers). Hydrochem Mater 48:14–22
52. Nahshina EP (1989) Mikroelementy v vodokhranilischakh Dnepra (Micronutrients in the Dnieper reservoirs). Nauk dumka, Kyiv
53. Nikanorov AM (2001) Gidrokhimiya (Hydrochemistry). Hydrometizdat, St-Peterburg
54. Nikora VI (1981) Rechnoy potok kak dissipativnaya sistema (Stream flow as a dissipative system). Meteorol Hydrol 12:84–88
55. Novikov BI (1985) Donnye otlozheniya dneprovskikh vodokhranilisch (Bottom sediments of the Dnieper reservoirs). Nauk Dumka, Kyiv
56. Oksiyuk OP, Timchenko VM, Davyidov OA et al (1999) Sostooyanie ekosistemy Kievskogo uchastka Kanevskogo vodokhranilischa i puti ego regulirovaniya (Ecosystem condition of Kiev zone of Kanev reservoir and ways of its regulation). VIPOL, Kiev
57. Oksiyuk OP, Timchenko VM, Polischuk VS et al (1996) Upravlenie sostoyaniem ekosistem i kachestvom vody v ustevom uchastke Dnepra chast 1 (Ecosystem condition and water quality management in the Dnieper mouth area, part 1). VIPOL, Kiev
58. Oksiyuk OP, Timchenko VM, Polischuk VS et al (1999) Zavisimost sostoyaniya ekosistemy ustevogo uchastka Dnepra ot popuskov Kakhovskoy GES v letny period (The dependence of ecosystem condition of the Dnieper mouth area on Kahovskaya HPP releases in summer-time). Hydrobiol J 35(1):67–76
59. Oksiyuk OP, Timchenko VM, Yakushin VM et al (2000) Prognozirovanie i puti uluchsheniya kislorodnogo rezhima Kievskogo vodokhranilischa v zimny period (Forecasting and ways of improvement of Kiev reservoir oxygen regime in winter season). VIPOL, Kiev
60. Oksiyuk OP, Timchenko VM, Yakushin VM et al (2001) Kislorodny balans Kievskogo vodokhranilischa v zimny period (Kiev reservoir oxygen balance in winter season). Hydrobiol J. Kiev 37(3):10–22
61. Oksiyuk OP, Timchenko VM, Polischuk VS et al (1997) Upravlenie sostoyaniem ekosistem i kachestvom vody v ustevom uchastke Dnepra chast 2 (Ecosystem condition and water quality management in the Dnieper mouth area, part 2). VIPOL, Kiev

62. Orlov DS (1992) Khimiya pochv (Soil chemistry). MGU Press, Moscov
63. Orlov DS (1998) Detoksitsiruyuschaya sposobnost guminovykh kislot po otnosheniyu k gerbitsidu trifluralinu (Humic acid detoxic ability with regard to trifluraline herbicide). Soil Sci 9:1049–1057
64. Osadcha NM (2011) Zakonomirnosti migratsii gumusovykh rechovyn u poverkhnevykh vodakh Ukrayiny (Humic substance migration regularities in the surface water of Ukraine). Dissertation, Taras Shevchenko National University of Kyiv
65. Osadcha NM, Osadchy VI (2002) Stik rozchinenykh gumusovykh rechovyn z baseynu Pripyati: rozrakhunok, chynnyky, richny rozpodil (Dissolved humic substance runoff from the Pripyat basin: calculation, factors, annual distribution). Ukr Geogr J 1:51–57
66. Osadcha NM, Osadchy VI (2003) Doslidzhennya umov formuvannya velychyny pH vodnykh ekosistem Dnipra, Dunayu, Zakhidnogo Bugu (Research of *pH* value formation conditions for the Dnieper, Danube, Western Bug water ecosystems). Sci works of Ukr NDGMI 252:40–52
67. Osadchy VI (2008) Metodologichni osnovy doslidzhennya chynnykiv ta protsessiv formuvannya khimichnogo skladu poverkhnevykh vod Ukrayiny (Methodological fundation of study of factors and chemical surface water composition formation processes of Ukraine). Dissertation, Taras Shevchenko National University of Kyiv
68. Paal LL (1972) Raschet razbavlenia stochnykh vod v rekakh (Calculation of sewage dilution in rivers // Water quality and river and inland water body fishery). MGU press, Moscov, pp 35–50
69. Peleshenko VI (1975) Otsenka vzaimosvyazi khimicheskogo sostava razlichnykh tipov prirodnykh vod (na primere ravninnoy chasti Ukrainy) (Relation assessment of chemical water composition of different types of natural water (the case of plain part of Ukraine)). Vyischa shkola, Kyiv
70. Peleshenko VI (ed) (1979) Gidrokhemicheskoe kartirovanie s primeneniem veroyatnostno-staticheskikh metodov (Hydrochemical mapping with application of statistically distributed methods). Vyischa shkola, Kyiv
71. Perelman AI, Kasimov NS (1999) Geokhimiya landshafta (Geochemistry of landscape). MGU, Moscow
72. Polyinov BB (1951) Izbrannye trydi (Selected works). AN SRSR press, Moscov–Leningrad
73. Polyinov BB (1952) Geograficheskie raboty (Geographic works). Geographiz, Moscov
74. Pritula LM (2010) Kharakteristika serednorichnogo ionnogo stoku richky Desny (Ion average annual flow characteristics of the Desna river). Hydrology, hydrochemistry and hydroecology, vol II(19). Nika-Centre, Kiev, pp 147–154
75. Raschyot razbavleniya stochnykh vod v rekakh Urala: Metod, rekomendatsii (1976) (Sewage dilution calculation in the Urals rivers): Methodological recommendations. Sverdlovsk
76. Rodi V, Kolman V (ed) (1984) Modeli turbulentnosti okruzhayuschey sredy (Environment turbulence models. Calculation methods of turbulent currents). Mir, Moscow, pp 227–322
77. Rodziller ID (1984) Prognoz kachestva vody vodoyomov-priyomnikov stochnykh vod (Water quality prediction of sewage water receivers). Ctroyizdat, Moscow
78. Romanenko VD (2004) Osnovy gidroekologii (Fundamentals of hydroecology). Geneza, Kiev
79. Romas IM (2004) Otsinka gidrologo-gidrochemichnykh kharakteristik minimalnogo stoku richok baseynu Dnipra (v mezhakh Ukrayiny) (Assessment of hydrologo-hydrochemical characteristics of a minimal river runoff of the Dnieper basin rivers (within Ukraine)) Dissertation, Taras Shevchenko National University of Kiev
80. Ruban SA, Shinkarevsky MA (2005) Gidrogeologichny otsinki ta prognozy rezhimu pidzemnykh vod Ukrayiny (Hydrogeological assessments and predictions of ground water dynamics of Ukraine). Ukr.DGRI, Kyiv
81. Samoylenko VN (1988) Faktory, opredelyayuschie obmen kislorodom mezhdu vodoyomamy i atmosferoy (na primere ustevoy oblasti Dnepra) (Factors determining oxygen respiration between reservoirs and atmosphere (the case of the Dnieper mouth area)). Hydrobiol J 24(4):101–104

82. Savitsky VN, Osadchy VI, Romas NI, Chebotko KA (1990) Khimichesky sostav i nekotorye svoistva donnykh otlozheny ustevoy chaste Dneprovsko-Bugskogo limana (Chemical water composition and some properties of bottom sediments of the mouth area of the Dnieper-Bug liman). Water Resour 2:121–129
83. Seryishev VA (1989) Obmen biogennykh elementov v sisteme voda—donnye otlozheniya melkovodiy Bratskogo vodokhranilischa (Nutrient change in the water-bottom sediment system of the shallow place of Bratsk reservoir). Water Resour 5:107–114
84. Skopintsev BA, Bikbulatova EM (1986) O chimicheskoy prirode organicheskogo veschestva vody rek SSSR (On chemical nature of organic matter of the USSR river water). Water Resour 3:85–89
85. Sokolovsky DL (1968) Rechnoy stok (osnovy teorii i metodiki raschetov) (River runoff (foundations of the theory and calculation methodology)). Hydrometeoizdat, Leningrad
86. Suurkask VA, Tutt MA (1971) O koeffitsientakh turbulentnoy diffusii v raschetakh smesheniya stochnykh vod v vodotokakh (On the coefficient of turbulent diffusion in the calculations of sewage water mixing in streams). Works of Tallinn polytechnic institute ser. A 309:51–55
87. Temam R (1981) Uravnenie Navier-Stoksa. Teoriya I chislenny analiz (Navier—Stokes equation. Theory and numerical analysis. the 2nd edn). Mir, Moscow
88. Timchenko VM (1986) Gidrologicheskie factory formirovaniya gidrobiologicheskogo rezhima Dunaya i limanov Severo-Zapadnogo Prichernomorya (Hydrological factors of hydrobiological regime formation of the Danube and North-West Black Sea region limans. Hydrobiology of the Danube and West-North Black Sea region limans). Nauk Dumka, Kyiv, pp 3–19
89. Timchenko VM (2006) Ekologicheskaya gidrologiya dneprovskikh vodokhranilisch (Ecological hydrology of the Dnieper reservoirs). Hydrolog J 42(3):81–96
90. Timchenko VM (2006) Ekologicheskaya gidrologiya vodoyomov Ukrainy (Ecological hydrology of the ponds of Ukraine). Nauk Dumka, Kyiv
91. Timchenko VM (2008) Gidrologichesky rezhim kak veduschy factor upravleniya ekosistemami vodoyomov (Hydrological regime as a leading factor of reservoir ecosystem management). Inter-Agency scientific collection of Ukraine. Ecology 2008, vol 50 (1). Odessa, pp 366–371
92. Timchenko VM (2010) Model optymizatsii yakosti vodnogo seredovyscha kaskadnykh vodoskhovysch (na prykladi dniprovskykh) (Water environment quality optimization model of cascade reservoirs(the case of Dnieper)). Sci Rec Ternopol Nat Ped u-ty.-Ser Biology Spec Issue Hydroecology 2(43):478–481
93. Timchenko VM (2010) Vodoobmennye protsessy kak factor formirovaniya potokov energii v ekosistemakh dneprovskikh vodokhranilisch (Water exchange processes as an energy flux forming factor in the Dnieper reservoir ecosystem). Hydrobiol J 46(3):105–120
94. Timchenko VM, Korobka AA (1999) O vliyanii techeniy na raspredelenie fitoplanktona v vodoyomakh (na primere Kremenchugskogo vodokhranilischa) (On current influence on the phytoplankton distribution in ponds (the case of Kremenchug reservoir)). Hydrobiol J 35(2):90–96
95. Timchenko VM, Oksiyuk OP (2002) Kislorodny rezhime rechnykh uchastkov dneprovskikh vodokhranilisch v zimny period I ego uluchshenie popuskami GES (Oxygen regime of the Dnieper reservoir river sites in winter season and its improvement by HPP releases). Hydrobiol J 38(60):89–98
96. Timchenko VM, Oksiyuk OP, Timchenko OV (2003) Vozmozhnost regulirovaniya kislorodnogo rezhima dneprovskikh vodokhranilisch v zimny period i ego uluchshenie popuskami GES (Oxygen regime control ability of the Dnieper reservoir in winter season and its improvement by HPP releases). Hydrol Hydrochem Hydroecology 5:195–204
97. Timchenko VM, Shershevsky AI (1987) Otsenka vodoobmena na Nizhnem Dnepre v sovremennykh usloviyakh (Water exchange assessment on the Lower Dnieper in modern conditions). Sci Works UkrNIGMI 220:87–101

98. Timchenko VM, Timchenko OV (2006) Zastosuvannya modelyuvannya dinamiki vod pri pozbortsi sposobiv polipshennya kysnevogo rezhimu kaskadnykh vodoskhovysch (Water dynamics modelling application during the ways of developing oxygen regime improvement of cascade reservoirs). Nat Almanac, Kherson, Ser: Biol 8:234–251
99. Trofimov SYA, Karavanova EI (2009) Zhidkaya faza pochv (Soil solution). MGU press, Moscow
100. YaYa Tseeb, Maystrenko YuG (eds) (1972) Kievskoe vodokhranilische (Kiev reservoir). Nauk Dumka, Kyiv
101. Tsunodai Sh, Tanaka N (1980) Flux of oxygen across the air–sea interface as determined by the analysis of dissolved components in sea water. Geochem J 14(5):227–234
102. Varshal GM, Velyuhanova TK, Baranova NN (1984) Kompleksoobrazovanie zolota (III) s fulvokislotami I geokhimicheskaya rol etogo protsessa (Complexation of gold (III) with fulvic acids and geochemical role of the process). Geocmistry 3:413–420
103. Vernadsky VI (1933–1936) Istoriya prirodnykh vod (History of natural water), Issue 1–3. Pub. AN USSR, Moscow, P 1
104. Vernadsky VI (1954) Izbramnnye sochineniya (Selected works), vol I. Pub. AN USSR, Moscow
105. Vernadsky VI (1965) Khimicheskoe stroenie biosfery Zemli I eyo okruzheniya (Chemical constitution of terrestrial biosphere and its environment). Nauka, Moscow
106. Vladimirov AM (1976) Gidrologicheskie aspekty problemy kachestva vody (Hydroecological aspects of water quality problem. In: Works of the fourth All-Union hydrological scientific meeting Water quality and scientific principles of its protection), vol 9. Hydrometeoizdat, Leningrad, pp 105–112
107. Voronkov PP (1963) Formirovanie khimicheskogo sostava atmosfernykh vod I vliyanie ego na pochvennye rastvory I sklonovye vody (Chemical composition formation of meteorological water and its influence on soil solutions and hillslope water). Works GGI 102:21–35
108. Voronkov PP (1963) Gidrokhemicheskie osnovaniya vydeleniya mestnogo stoka i sposoby raschleneniya ego gidrografa (Hydrochemical fundamentals of local runoff distinguishing and separation of its hydrograph). Meteorol hydrol 8:27–8
109. Voropayev GV, Avakyan AB (eds) (1986) Vodokhranilischa I ikh vozdeystvie na okruzhayuschuyu sredu (Reservoirs and their influence on environment). Nauka, Moscow
110. Yashin IM, Raskatov VA, Shishov LL (2003) Vodnaya migratsiya khimicheskikh elementov v pochvennom pokrove (Chemical element aqueous migration in soil cover). MSHA press, Moscow
111. Zakrevsky DV, Peleshenko VI, Hilchevsky VK (1988) Stok khimicheskikh komponentov rek Ukrainskoy SSR (Chemical component runoff of the Ukranian SSR rivers). Water Res 15(6):63–3
112. Zenin AA (1967) Izmenenie khimicheskogo sostava ravninnykh rek evropeyskoy chasti SSSR v rezultate zaregulirovaniya (Water chemistry change of sluggish rivers of the European part of the USSR as a result of regulation). Hydrochem Mater 45:1–21
113. Zhuravlyova LA (1988) Gidrokhimiya ustevoy oblasti Dnepra i Yuzhnogo Buga v usloviyakh zaregulirovaniya rechnogo stoka (Hydrochemistry of the Dnieper and South Bug mouth area in available stream flow). Nauk Dumka, Kyiv
114. Znamensky VA (1981) Gidrologicheskie protsessy i ikh rol v formirovanii kachestva vody (Hydrological processes and their role in the water quality formation). Hydrometizdat, Leningrad
115. Zogorski JS, Faust SD (1973) Atmospheric reaeration capasity of streams, part 1. Env Lett 4(1):35–39

Chapter 3
Physico-Chemical Processes

The direction and completeness of chemical process is calculated with the use of thermodynamic equilibrium constants K_p, which are listed in reference books, given for ionic strength $\mu = 0$, i.e. ionic activity coefficient $f_i = 1$. However, the ionic strength of natural water never equals to zero due to the presence of salt components (main ions). It is calculated by equation:

$$\mu = \frac{1}{2}\sum C_i \cdot Z_i^2 \tag{3.1}$$

where C_i—concentration of main ions mol/L; Z_i—their charge.

Therefore, the calculation of chemical equilibrium in natural water is to be performed with the use of **concentration** equilibrium constants K_p', related to **thermodynamic** constants K_p according to scheme and formula:

$$mA + nB \rightleftarrows A_mB_n$$

$$K_p = \frac{a_{A_mB_n}}{a_A^m \cdot a_B^n} = \frac{[A_mB_n] \cdot f_{A_mB_n}}{[A]^m \cdot [B]^n \cdot f_A^m \cdot f_B^n} = K_p' \cdot \frac{f_{A_mB_n}}{f_A^m \cdot f_B^n} \tag{3.2}$$

where a—ion activity; f_i—ionic activity coefficient. For molecules activity coefficients are taken as 1.

Activity coefficients of some ions based on ionic strength are shown in Annex 3, and the graph and equation of μ—dependence on f_i—respectively in Fig. 3.1 and in Table 3.1. Activity coefficients are calculated by the Davis equation [15]:

$$-\frac{\lg f_i}{Z_i^2} = \frac{0.511 \cdot \sqrt{\mu}}{1 + 1.5 \cdot \sqrt{\mu}} - 0.2\mu$$

V. Osadchyy et al., *Processes Determining Surface Water Chemistry*,
DOI 10.1007/978-3-319-42159-9_3

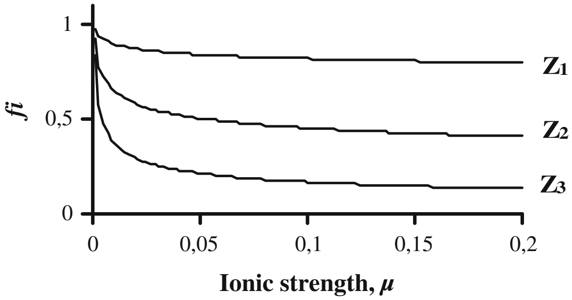


Fig. 3.1 Dependence of activity coefficients of f_i ions with charge Z_i on ionic strength μ

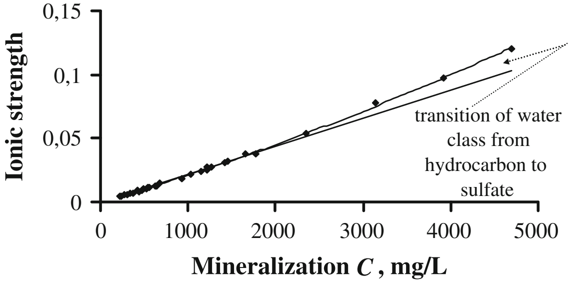
Table 3.1 Dependence of activity coefficients on ionic strength μ and mineralization of water C for ions with different charges

Charge of cations and anions	Dependence of f_1 on μ	R*	Dependence of f_i on C (mg/L)	R*
Z = 1	$f_1 = 0.7490 \cdot \mu^{-0.0389}$	0.9930	$f_1 = 1.1585 \cdot C^{-0.0419}$	0.9904
Z = 2	$f_2 = 0.3171 \cdot \mu^{-0.1545}$	0.9930	$f_2 = 1.7912 \cdot C^{-0.1661}$	0.9902
Z = 3	$f_3 = 0.0755 \cdot \mu^{-0.3474}$	0.9929	$f_3 = 3.7110 \cdot C^{-0.3737}$	0.9901

3.1 Dependence of Ionic Activity Coefficients on Ionic Strength and Mineralization of Surface Water

Ionic strength of surface water in Ukraine is normally within 0.003–0.1 mg/L, although in some cases it can be much lower ($\mu = 0.0014$, mineralization 69 mg/L, Vorona river, 2006) or significantly higher ($\mu = 0.24$, mineralization 7814 mg/L, Lozuvatka river, 2005) [25].

Ionic strength significantly affects equilibrium constants of the chemical processes that occur in natural water. For example, by changing the ionic strength from 0 to 0.1 carbonic acid dissociation constants K_1 and K_2 respectively increase from 4.3×10^{-7} to 6.8×10^{-7} (by 1.6 times) and from 4.7×10^{-11} to 12×10^{-11} (by 2.6 times); solubility product of $Fe(OH)_3$ increases from 6.3×10^{-38} to 80×10^{-38} (by 12.7 times); stability constant of iron hydroxide fulvate complex $FeFA(OH)_2^-$ decreases from 6.4×10^{31} to 3.2×10^{30} (by 20 times) etc.



C – average values for 1995–2006

Fig. 3.2 Dependence of ionic strength of surface water in Ukraine on mineralization

Table 3.2 Ionic activity coefficients f_i, calculated according to values of μ and C

Ionic strength μ	Mineralization C (mg/L)	Z = 1			Z = 2			Z = 3		
		$f_1 \rightarrow \mu$	$f_1 \rightarrow C$	Δ	$f_1 \rightarrow \mu$	$f_2 \rightarrow C$	Δ	$f_3 \rightarrow \mu$	$f_3 \rightarrow C$	Δ
0.001	51	0.980	0.983	0.003	0.922	0.932	0.010	0.832	0.842	0.010
0.0025	127	0.946	0.946	0	0.800	0.801	0.001	0.605	0.597	0.008
0.005	251	0.920	0.919	0.001	0.719	0.715	0.004	0.476	0.471	0.005
0.01	493	0.896	0.893	0.003	0.646	0.687	0.041	0.374	0.366	0.008
0.025	1175	0.865	0.862	0.003	0.561	0.554	0.007	0.272	0.264	0.008
0.05	2200	0.842	0.839	0.003	0.504	0.499	0.005	0.214	0.209	0.005
0.10	3970	0.819	0.819	0	0.453	0.453	0	0.168	0.168	0
0.15	5478	0.806	0.808	0.002	0.425	0.429	0.004	0.146	0.149	0.003
0.20	6826	0.797	0.800	0.003	0.407	0.413	0.006	0.132	0.137	0.005

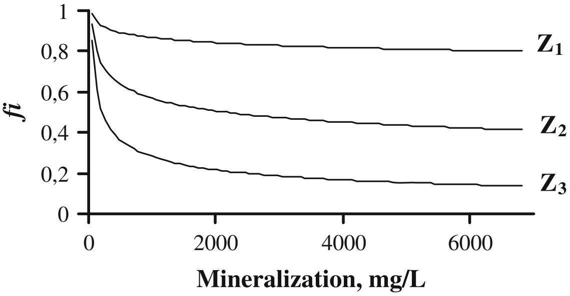


Fig. 3.3 Dependence of activity coefficients of f_i ions with charge Z_i on water mineralization

The dependence of ionic strength of surface water in Ukraine on mineralization C (mg/L) is shown in Fig. 3.2 and expressed by equation:

$$\mu = 1.42 \cdot 10^{-9} \cdot C^2 + 1.96 \cdot 10^{-5} \cdot C \tag{3.3}$$

Correlation coefficient R = 0.997. To calculate this dependence, averaged data on river water mineralization of m main eight river basins in Ukraine over 1995–2006 years were used and of each basin two water bodies considered with the minimum and maximum mineralization (15 rivers, 1 reservoir and 7 lakes) [25].

Table 3.2 presents activity coefficients of ions with different charges, calculated according to values of μ and C. They are virtually identical. Thus, *activity coefficients of ions can be calculated directly by values of water mineralization.*

Since ionic activity coefficients depend on ionic strength, they should also depend on water mineralization. This dependence is shown in Fig. 3.3, and the corresponding equations are given in Table 3.1.

Examples of real ionic strength calculated by the content of main ions according to Eqs. (3.1) and (3.3) for some water bodies in Ukraine are presented in Table 3.3. Rivers, lakes and reservoirs located in different physiographic zones were selected for calculations, and for each object—the years with the lowest and highest water mineralization [25]. The data in Table 3.3 imply that a statistically significant deviation from the actual ionic strength calculated by Eq. (3.3) is different for water in different physico-geographic zones.

The largest deviation (up to 20 % with consideration of confidence interval based on an average value) is observed for the rivers of the Carpathian Mountains, the smallest (5 %)—for the rivers of Crimea, due, apparently, to different physical and geographical conditions in forming the ionic composition of the water. If the deviation of the real ionic strength of water calculated from the Eq. (3.3) is higher, it indicates a significant impact of natural or anthropogenic factors on the formation of the ionic composition of water, specific for a given water body.

Calculations show that the deviation of 25–30 % in ionic strength, found on the basis of concentration of main ions, from the value calculated by Eq. (3.3), leads to a change in the concentration equilibrium constants by no more than 1.2–1.3 times, i.e. 20–30 %. This change in concentration equilibrium constants has little effect on the results of hydro-chemical calculations.

Table 3.3 The actual and calculated by Eq. (3.3) ionic strength of water in rivers, lakes and reservoirs, located in different natural zones of Ukraine

Natural area and average deviation of μ from the calculated one, % x ± Δx	Rivers, lakes	Years	Averaged mineralization, *C* (mg/L)	Ionic strength μ		
				Real (calculated by Eq. (3.1))	Calculated by Eq. (3.3)	Deviation from the calculated (%)
Carpathians % x = 12.6 ± 6.6	Bila Tysa	1997	144	0.0035	0.0028	+25.0
		2000	477	0.0096	0.0097	–1.0
	Latorytsya	1995	211	0.0038	0.0042	–9.5
		2001	230	0.0067	0.0046	+45.7
	Rika	1977	177	0.0034	0.0035	–2.9
		2001	312	0.0056	0.0062	–9.7
	Tereblya	1997	164	0.0031	0.0033	–6.1
		2005	315	0.0055	0.0063	–12.7
	Opir	1997	203	0.0047	0.0040	+17.5
		2006	297	0.0058	0.0059	–1.7
	Prut	1997	265	0.0066	0.0053	24.5
		2001	444	0.0087	0.0090	–3.3
	Stryi	1997	210	0.0049	0.0042	+16.7
		1999	316	0.0064	0.0063	+1.6
	Cheremosh	1996	198	0.0041	0.0036	+5.1
		2003	457	0.0076	0.0093	–18.3
	Vorona	2006	69	0.0016	0.0014	–12.5
		2000	709	0.0130	0.0146	–10.1

(continued)

Table 3.3 (continued)

Natural area and average deviation of μ from the calculated one, % x ± Δx	Rivers, lakes	Years	Averaged mineralization, *C* (mg/L)	Ionic strength μ		
				Real (calculated by Eq. (3.1))	Calculated by Eq. (3.3)	Deviation from the calculated (%)
Forest zone % x = 8.9 ± 3.8	Gorin'	2006	363	0.0070	0.0073	–4.1
		2001	481	0.0085	0.0098	–13.2
	Prypiat	2002	334	0.0071	0.0067	+5.9
		2006	482	0.0086	0.0098	+12.2
	Styr	1996	389	0.0081	0.0078	+3.8
		2001	472	0.0094	0.0096	–2.1
	Teteriv	2003	369	0.0074	0.0074	0
		1995	534	0.0109	0.0108	+0.9
	Turiya	1996	387	0.0074	0.0078	–5.1
		2000	482	0.0093	0.0098	–5.1
	Ubort'	1997	225	0.0048	0.0045	+6.7
		2005	511	0.0080	0.0103	–22.3
	Uzh	1999	190	0.0040	0.0038	+2.6
		1997	288	0.0071	0.0058	+22.4
	Lake Svityaz'	1996	169	0.0038	0.0034	+11.8
		1999	423	0.0064	0.0085	–24.7
Forest-steppe zone % x = 11.4 ± 4.0	Buzhok	2006	419	0.0082	0.0085	–3.5
		1995	667	0.0136	0.0137	–0.7
	Buzhok	2006	216	0.0035	0.0043	–18.6
		2001	796	0.0210	0.0165	+27.3
	Desna	2000	334	0.0064	0.0067	–4.8
		1997	391	0.0076	0.0079	–3.8

(continued)

Table 3.3 (continued)

Natural area and average deviation of μ from the calculated one, $\%\ x \pm \Delta x$	Rivers, lakes	Years	Averaged mineralization, C (mg/L)	Ionic strength μ		
				Real (calculated by Eq. (3.1))	Calculated by Eq. (3.3)	Deviation from the calculated (%)
Forest-steppe zone $\%\ x = 11.4 \pm 4.0$	Western Bug	1999	469	0.0092	0.0095	–3.2
		1995	543	0.0115	0.0111	+3.6
	Psel	1998	575	0.0121	0.0117	+3.4
		2004	770	0.0150	0.0159	–5.7
	Rata	1999	372	0.0075	0.0074	+1.4
		1997	514	0.0105	0.0104	+0.9
	Ros’	2003	446	0.0087	0.0090	–3.3
		2004	584	0.0099	0.0119	–16.8
	Sula	2003	680	0.0143	0.0140	+2.1
		1997	1034	0.0208	0.0218	–4.6
Steppe zone $\%\ x = 6.0 \pm 2.0$	Kazennyi Torets’	1195	1914	0.0433	0.0427	+1.4
		2006	2712	0.0620	0.0636	–2.5
	Kal’mius	1995	2245	0.0474	0.0512	–7.4
		2006	2997	0.0730	0.0714	+2.2
	Mius	2003	1083	0.0238	0.0229	+3.9
		2006	1819	0.0386	0.0404	–4.9
	Obytichna	2004	4262	0.1060	0.1093	–3.0
		2005	4983	0.1132	0.1329	–14.8
	Oril’	1995	1273	0.0288	0.0273	+5.5
		1998	1629	0.0379	0.0357	+6.2
	Samara	2001	2671	0.0650	0.0625	+4.0
		2006	3365	0.0764	0.0820	–6.8
	Sukhyi Torets’	2003	1224	0.0281	0.0261	+7.7
		2006	2052	0.0492	0.0462	+6.5
	Lake Sasyk	1999	1494	0.0319	0.0325	–1.9
		2006	2122	0.0461	0.0480	–3.9

(continued)

Table 3.3 (continued)

Natural area and average deviation of μ from the calculated one, % x ± Δx	Rivers, lakes	Years	Averaged mineralization, *C* (mg/L)	Ionic strength μ		
				Real (calculated by Eq. (3.1))	Calculated by Eq. (3.3)	Deviation from the calculated (%)
Crimea % x = 3.8 ± 1.4	Bel'bek	2002	377	0.0074	0.0076	–2.6
		1995	631	0.0141	0.0129	+9.3
	Biyuk-Uzenbash	2002	296	0.0060	0.0059	+1.7
		2003	404	0.0075	0.0082	–8.5
	Derekoyka	2005	340	0.0068	0.0068	0
		1995	455	0.0090	0.0093	–3.2
	Kacha	2005	379	0.0080	0.0076	+5.3
		1995	683	0.0136	0.0140	–2.8
	Kuchuk-Uzenbash	1999	335	0.0063	0.0067	–5.9
		2003	427	0.0087	0.0086	+1.2
	Taraktash	2006	766	0.0166	0.0158	+5.1
		2002	1355	0.0274	0.0292	–6.2
	Uskug	1999	503	0.0101	0.0102	–0.9
		2000	798	0.0171	0.0165	+3.6
	Chorna	1995	314	0.0064	0.0063	+1.6
		1998	1143	0.0250	0.0243	+2.9

(continued)

Table 3.3 (continued)

Natural area and average deviation of μ from the calculated one, % x ± Δx	Rivers, lakes	Years	Averaged mineralization, *C* (mg/L)	Ionic strength μ		
				Real (calculated by Eq. (3.1))	Calculated by Eq. (3.3)	Deviation from the calculated (%)
Cascade of Dnipro reservoirs % x = 5.2± 1.5	Kyiv	1998	262	0.0053	0.0052	+2.0
		1995	352	0.0070	0.0069	+1.5
	Kaniv	1999	287	0.0059	0.0057	+3.5
		2003	333	0.0064	0.0067	–4.8
	Kremenchuk	2006	317	0.0066	0.0064	+3.1
		1998	378	0.0080	0.0076	+5.3
	Dniprodzerzhynsk	1996	311	0.0059	0.0062	–4.8
		1998	377	0.0081	0.0076	+6.6
	Dnipro (Zaporizhzhya)	2006	256	0.0054	0.0051	+5.9
		1996	495	0.0090	0.0100	–10.0
	Kakhovka	2004	334	0.0073	0.0067	+8.9
		2001	367	0.0071	0.0074	–4.1
Reservoirs of Crimea % x = 5.7 ± 4.3	Ayans’ke	1999	257	0.0048	0.0050	–4.0
		1997	411	0.0085	0.0083	+2.4
	Partyzans’ke	2002	316	0.0061	0.0063	–3.2
		1999	420	0.0080	0.0085	–5.8
	Simferopolske	1996	311	0.0064	0.0062	+3.2
		1995	647	0.0132	0.0133	–0.8
	Feodosiys’ke	2001	357	0.0069	0.0072	–4.2
		2004	503	0.0105	0.0102	+2.9
	Chornorichens’ke	1995	288	0.0057	0.0058	–1.7
		2000	396	0.0071	0.0080	–11.3
	Shchaslyve	2006	277	0.0054	0.0055	–1.8
		2000	390	0.0058	0.007	–26.6

Thus, the ionic strength of water of a certain object, calculated by Eq. (3.3) on the basis of mineralization, can be used to attain ionic activity coefficients by the equations given in Table 3.1. At the same time, *activity coefficients of ions can be calculated, as described above, also directly by water mineralization* (Table 3.1), without resorting to calculation of ionic strength.

3.2 Acid-Base Balance

The major acid-base processes that occur in natural water are the dissociation of weak organic and inorganic acids and bases, as well as the hydrolysis of metal ions. The acidity of aqueous media is influenced by a variety of natural and anthropogenic factors such as dissolved carbon dioxide, heavy metals, organic acids and bases—products of aquatic organisms metabolism, acid rains, waste water etc. An integral indicator of these factors which **directly** affects the acid-base balance is the concentration of H^+ ions in water.

3.2.1 Dissociation of Acids

Products of dissociation of acids are anions, which are part of many soluble complex compounds and slightly soluble precipitates. In the first case, they contribute to the migration of heavy metals in aquatic ecosystems, in the second—to their accumulation and consolidation of sediments in the form of slightly soluble carbonates, phosphates, sulfides and others. The concentration of each form of acid HnA ($n \leq 4$) in mol/dm^3 is calculated by equations (for notational simplicity, ion charges are not indicated):

$$[A] = C/\left(1 + \frac{[H]}{K'_n} + \frac{[H]^2}{K'_n \cdot K'_{n-1}} + \frac{[H]^3}{K'_n \cdot K'_{n-1} \cdot K'_{n-2}} + \frac{[H]^4}{K'_n \cdot K'_{n-1} \cdot K'_{n-2} \cdot K'_{n-3}}\right); \left[[HA] = [A] \cdot \frac{[H]}{K'_n}\right];$$

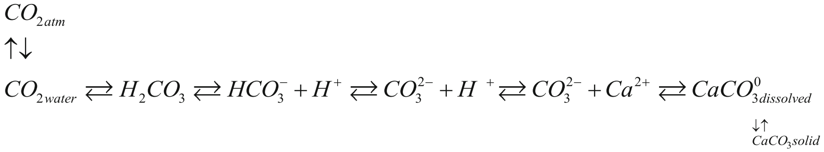
$$\begin{aligned} &[H_2A] = [A] \cdot \frac{[H]^2}{K'_n \cdot K'_{n-1}}; [H_3A] = [A] \cdot \frac{[H]^3}{K'_n \cdot K'_{n-1} \cdot K'_{n-2}}; \\ &[H_4A] = [A] \cdot \frac{[H^+]^4}{K'_n \cdot K'_{n-1} \cdot K'_{n-2} \cdot K'_{n-3}}, \end{aligned} \tag{3.4}$$

where C—total acid concentration (the sum of all forms), mol/L; K'_n, K'_{n-1}, K'_{n-2} and K'_{n-3}—acid dissociation concentration constants calculated according to formula (3.2). They depend on mineralization (ionic strength) of water, and temperature, which affects thermodynamic equilibrium constants.

In calculating the relative content of each form in percentage in Eq. (3.4) instead of C we put 100.

3.2.2 Carbonic Acid. Carbonate System. Aggressive Carbon Dioxide

The components of a carbonate system are carbonic acid H_2CO_3 ($CO_2 \cdot H_2O$), products of its dissociation and calcium carbonate. The relationship between these components can be expressed by the scheme [21]:



$$\begin{array}{l} CO_{2atm} \\ \uparrow\downarrow \\ CO_{2water} \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^- + H^+ \rightleftarrows CO_3^{2-} + H^+ \rightleftarrows CO_3^{2-} + Ca^{2+} \rightleftarrows CaCO^0_{3dissolved} \\ \hfill \downarrow\uparrow \\ \hfill CaCO_{3solid} \end{array} \tag{3.5}$$

State of equilibrium in aqueous solution and between the solution and solid phase is calculated with the use of carbonic acid dissociation constants and solubility product (SP) of calcium carbonate:

$$K_1 = \frac{[H^+] \cdot [HCO_3^-] \cdot f_{H^+} \cdot f_{HCO_3^-}}{[H_2CO_3]} \tag{3.6}$$

$$K_2 = \frac{[H^+] \cdot [CO_3^{2-}] \cdot f_{H^+} \cdot f_{CO_3^{2-}}}{[HCO_3^-] \cdot f_{HCO_3^-}} \tag{3.7}$$

$$SP_{CaCO_3} = [Ca^{2+}] \cdot [CO_3^{2-}] \cdot f_{Ca^{2+}} \cdot f_{CO_3^{2-}} \tag{3.8}$$

The concentration of each form of carbonic acid in mol/L is calculated by equations [6, 21]:

$$[CO_3^{2-}] = \frac{A}{2 + \left(a_{H^+} \cdot f_{CO_3^{2-}} / K_2 \cdot f_{HCO_3^-}\right)} \tag{3.9}$$

$$[HCO_3^-] = \frac{A}{1 + \left(2K_2 \cdot f_{HCO_3^-} / a_{H^+} \cdot f_{CO_3^{2-}}\right)} \tag{3.10}$$

$$[H_2CO_3] = \frac{a_{H^+} \cdot [HCO_3^-] \cdot f_{HCO_3^-}}{K_1} \tag{3.11}$$

where A-alkalinity of water ($[HCO_3^-] + 2[CO_3^{2-}]$) which is determined by titration of water sample with alkaline solution to pH 4.0 [19]; a_{H^+}—activity of hydrogen ions, which is determined by pH-potentiometry.

Fig. 3.4 Relative content (% moles) of various forms of carbonic acid depending on *pH* and water temperature

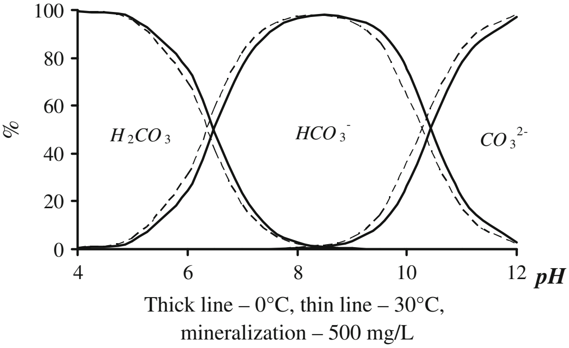
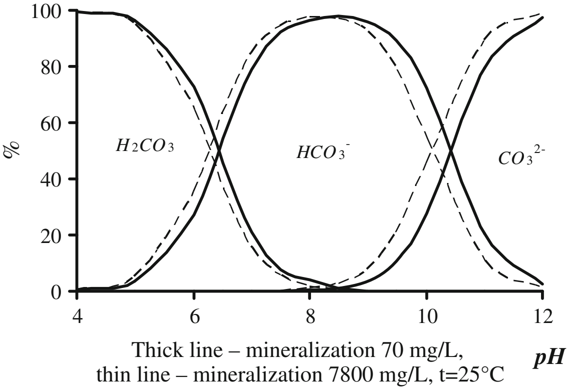


Fig. 3.5 Relative content (% moles) of various forms of carbonic acid depending on *pH* and water mineralization



Effect of water *pH* on the relative amount of molecules and anions of carbonic acid is shown in Figs. 3.4 and 3.5. Calculations were performed by the Eq. (3.4) with the use of activity coefficients of ions H^+, HCO_3^- and CO_3^{2-}. It is evident that dissociation of carbonic acid little depends on temperature in the range of 0–30 °C and water mineralization in the range of 70–7800 mg/L, typical for surface water in Ukraine [25]. At $pH \leq 9.5$ the difference in the content of individual components with the variation in temperature and mineralization within these limits does not exceed 10 %.

From Figs. 3.4 and 3.5 it follows that in the range of *pH* 5–8.5 molecules of carbonic acid and bicarbonate ions dominate in the solution. This is a typical buffer system, *pH* of which is calculated by equation [28]:

$$pH = pK_1^{'} + \lg \frac{C_{HCO_3^-}}{C_{H_2CO_3}} \tag{3.11a}$$

where $pK_1^{'}$—the first concentration constant of carbonic acid dissociation, which depends on the temperature and mineralization (ionic strength) of water. Buffer capacity of natural water increases with an increase of its hydrocarbonate (temporary) hardness. Natural water has the maximum buffer capacity with *pH* 6.3–6.4 when $C_{HCO_3^-} = C_{H_2CO_3}$ (see Figs. 3.4 and 3.5).

With entry into natural water of H^+ ions, such as acidic waste water, acid rains, as a result of the hydrolysis of metal ions, etc., HCO_3^- concentration decreases and the concentration H_2CO_3 increases according to reaction

$HCO_3^- + H^+ \rightleftarrows H_2CO_3$. Therefore, pH of the water is calculated by equation:

$$pH = pK_1' + \lg\frac{C_{HCO_3^-} - [H^+]}{C_{H_2CO_3} + [H^+]} \tag{3.11b}$$

If natural water has an entry of OH^- ions, for example, with alkaline wastewater, due to hydrolysis of salts of weak acids, etc., the pH of water is calculated by equation:

$$pH = pK_1' + \lg\frac{C_{HCO_3^-} + [OH^-]}{C_{H_2CO_3} - [OH^-]} \tag{3.11c}$$

For example, highly acidic waste water gets into natural water with t = 25 °C, mineralization of 500 mg/L ($pK_1' = 6.27$), $pH = 7.00$, $C_{HCO_3^-} = 100\,\text{mg/L}$ $(1.64 \times 10^{-3}\,\text{mol/L})^3$. In this case, according to Eq. 3.11b, pH of water will drop to just 5.96 instead of 3.00 in the absence of buffer action of carbonate system. At higher concentration $C_{HCO_3^-} = 500\,\text{mg/L}\,(8.20 \times 10^{-3}\,\text{mol/L})$ and $C_{H_2CO_3} = 1.53 \times 10^{-3}\,\text{mol/L}$ under the same conditions water pH will drop to just 6.72.

Thus, the carbonate buffer system is an important factor in stabilizing pH of natural water.

The relationship between the solubility of calcium carbonate and concentration of components of the carbonate system is expressed by the equation:

$$\downarrow CaCO_3 + CO_2 + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \tag{3.12}$$

$$Kp = \frac{[Ca^{2+}] \cdot [HCO_3^-]^2}{[H_2CO_3]} = \frac{SP'_{CaCO_3} \cdot K_1'}{K_2'} \tag{3.13}$$

where K_1', K_2' and SP'_{CaCO_3}—concentration constants of carbonic acid dissociation and product of calcium carbonate solubility, which depend on temperature and mineralization (ionic strength) of water.

According to Eq. (3.13) we find the concentration of Ca^{2+} ions which pass into solution when $CaCO_3$ is dissolved:

$$[Ca^{2+}] = \frac{SP'_{CaCO_3} \cdot K_1' \cdot [H_2CO_3]}{K_2' \cdot [HCO_3^-]^2} = \frac{SP'_{CaCO_3}}{[CO_3^{2-}]} \tag{3.14}$$

where

$$\left[CO_3^{2-}\right] = K_2^{'} \cdot \left[HCO_3^{-}\right]/[H^+] \tag{3.14.1}$$

However, during the dissolution of $CaCO_3$ not only Ca^{2+} and CO_3 ions pass into solution, but also $CaCO_3$ molecules, whose concentration depends on water temperature. Therefore, the solubility of calcium carbonate is equal to:

$$S(molCaCO_3/L) = \left[Ca^{2+}\right] + \left[CaCO_3^0\right] \tag{3.15}$$

$$\left[CaCO_3^0\right] = \beta_{CaCO_3^0}^{'} \cdot \left[Ca^{2+}\right] \cdot \left[CO_3^{2-}\right] = \beta_{CaCO_3^0}^{'} \cdot SP_{CaCO_3}^{'} \tag{3.16}$$

where $\beta_{CaCO_3^0}^{'}$—concentration constant of complex stability (ion associate) $CaCO_3^0$.

By combining Eqs. (3.13)–(3.16), we obtain the final equation for calculating the solubility of $CaCO_3$ depending on the concentration of H^+ (pH) and concentration of hydrocarbon ions:

$$S(mgCaCO_3/\mathrm{L}) = \left(\frac{[H^+]}{K_2' \cdot \left[HCO_3^-\right]} + \beta'_{CaCO_3}\right) \cdot SP_{CaCo_3} \cdot 1000 \cdot 100 \tag{3.17}$$

where 100—molecular weight of $CaCO_3$.

The solubility of $CaCO_3$, expressed in calcium concentrations, is calculated by equation:

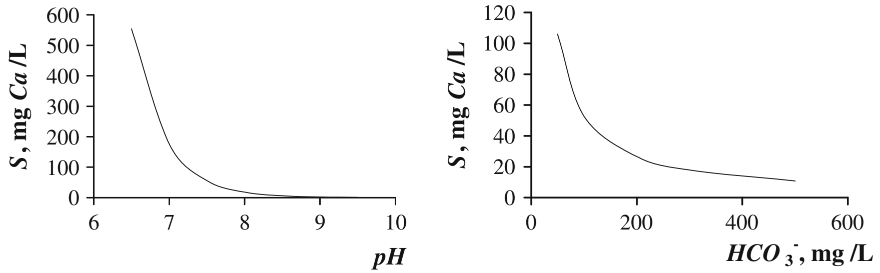
$$S(mgCa/L) = S(mgCaCO_3/L) \cdot 0.40 \tag{3.18}$$

where 0.40—ratio of atomic mass of calcium (40) to molecular weight of calcium carbonate (100).

Figure 3.6 shows the effect of pH, concentration of HCO_3^-, temperature and water mineralization on the solubility of calcium carbonate (influence of complex formation is discussed in Sect. 3.5). Indicator intervals, most typical for surface water in Ukraine [25], were selected for calculations. The influence of each parameter on the solubility of $CaCO_3$ was calculated with mean values of all other parameters. The solubility of calcium carbonate is most influenced by pH and concentration of hydrocarbon ions. The effect of temperature and mineralization (ionic strength) of water is much lesser.

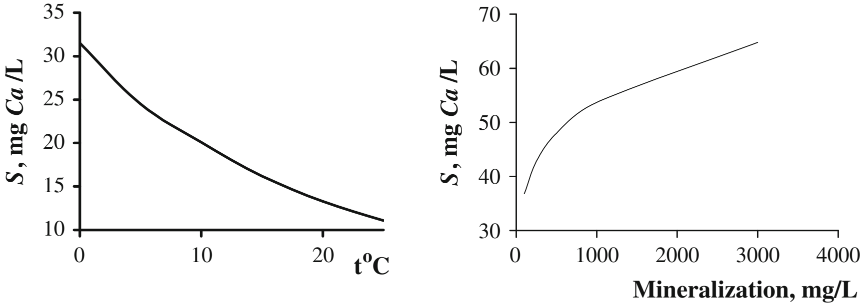
Index of water **saturation** with calcium carbonate is equal to [10]:

$$SI = \lg\left(\frac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}}}{SP_{CaCO_3}}\right) = \lg\left(\frac{\left[Ca^{2+}\right] \cdot \left[CO_3^{2-}\right] \cdot f_{Ca^{2+}} \cdot f_{CO_3^{3-}}}{SP_{CaCO_3}}\right) \tag{3.19}$$



Effect of *pH* on solubility of $CaCO^3$
HCO_3^- =300 mg/L, t=150°C,
mineralization = 500 mg/L

Effect of HCO_3^- on solubility of $CaCO_3$
pH=8, t=150C, mineralization = 500 mg/L



Effect of temperature on solubility of $CaCO_3$
pH=8, HCO_3^- = 300 mg/L,
mineralization = 500 mg/L

Effect of mineralization on solubility of $CaCO_3$
pH=8, HCO_3^-=100 mg/L, t=15°C

Fig. 3.6 Influence of various factors on solubility (*S*) of calcium carbonate in surface water

where concentrations of Ca^{2+} and CO_3^{2-} are expressed in mol/L; f_i—corresponding ion activity coefficients that depend on water mineralization (see Table 3.1); SP_{CaCO_3}—thermodynamic product of calcium carbonate solubility, which depends on temperature. Concentration of CO_3^{2-} ions is calculated by Eq. (3.9) or (3.14.1), Ca^{2+} ions—by Eq. (3.14). Alkalinity A, concentrations of HCO_3^- and H^+ (a_{H^+}) are defined experimentally.

If SI > 0, the water is supersaturated with calcium carbonate. In such water under certain conditions—higher temperature, intense mixing, etc., precipitate of $CaCO_3$ is formed, which is a good sorbent. Therefore this process contributes to self-purification of natural water from various chemical compounds (see Sect. 3.6). When SI < 0, there is a dissolution of $CaCO_3$ and as a result—self-contamination of water with compounds sorbed by calcium carbonate.

Aggressive carbon dioxide Equilibrium concentration of free carbon dioxide, which corresponds to reaction (3.12), is calculated by equation:

$$C_{CO_2} = \frac{K_2'}{K_1' \cdot SP'_{CaCO_3}} \cdot \left[Ca^{2+}\right] \cdot \left[HCO_3^-\right]^2 \cdot f_{Ca^{2+}} \cdot f^2_{HCO_3^-} \tag{3.20}$$

If experimentally determined CO_2 concentration (mol/L) exceeds the calculated one by Eq. 3.20, it indicates the presence in water of aggressive carbon dioxide. Its concentration is defined by graphic [6] or experimental [6, 19] method.

3.2.3 Phosphoric, Silicic and Chromic Acids

Phosphorus is present in natural water in the form of inorganic (phosphates) and organic (nucleic acids, nucleoproteins, phospholipids, etc.) compounds. The relationship between them and living organisms is expressed in the following diagram:

$$\begin{tikzcd}
& P_{\text{org. suspensions, colloids}} \arrow[d, shift left] & P_{\text{non-org. suspensions, colloids, precipitates}} \arrow[d, shift left] \\
P_{\text{living organisms}} \arrow[r] & P_{\text{org. soluble}} \arrow[u, shift left, "\text{seston, detritus}"'] \arrow[r] & P_{\text{non-org. soluble}} \arrow[u, shift left, "\text{metal phosphates}"'] \arrow[d, shift left] \\
& & \text{orthophosphates} \rightleftarrows \text{polyphosphates} \arrow[u, shift left] \arrow[ull]
\end{tikzcd} \tag{3.21}$$

The dependence of the relative content of different forms of phosphoric acid on water *pH* is shown in Fig. 3.7. Natural water is dominated by $H_2PO_4^-$ and especially HPO_4^{2-}ions. Increased mineralization of water leads to a marked shift of their dominance areas into more acidic environment. Anions of phosphoric acid are part of many complex and slowly soluble compounds.

Silicium is present in surface water mainly in the form of suspensions and colloids of slightly soluble hydrated dioxide $SiO_2 \cdot nH_2O$. Orthosilicic acid $H_4SiO_4(SiO_2 \cdot 2H_2O)$ is characterized by solubility of approximately 6 mg/L.

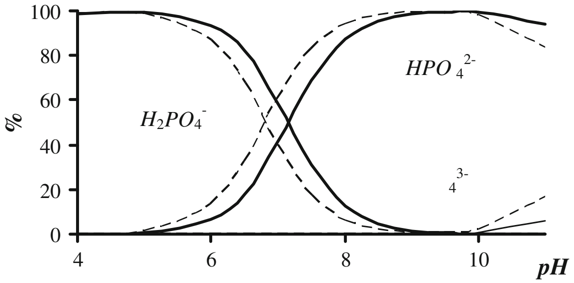
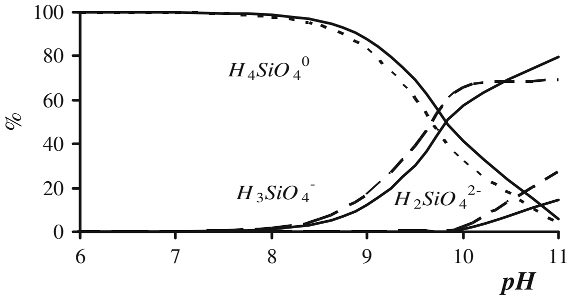


Fig. 3.7 Relative content (% moles) of different forms of phosphoric acid depending on *pH* and mineralization of water

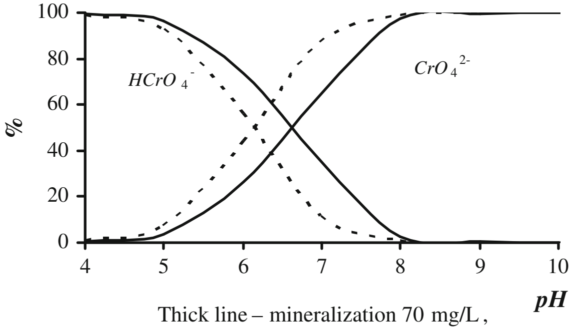
Thick line – mineralization 70 mg/L,
thin line – mineralization 7800 mg/L, t=25°C

Fig. 3.8 Relative content (% moles) of different forms of silicic acid depending on *pH* and mineralization of water



Thick line – mineralization 70 mg/L,
thin line – mineralization 7800 mg/L, t=25°C

Fig. 3.9 Relative content (% moles) of different forms of chromic acid depending on *pH* and mineralization of water



Thick line – mineralization 70 mg/L,
thin line – mineralization 7800 mg/L, t=25°C

Dissociation of the acid occurs at $pH > 8$, depending on water mineralization (Fig. 3.8). Hydrated silicon dioxide is a good sorbent (see Sect. 3.6), so its presence in water facilitates the process of self-purification, and dissolution at $pH > 8$—self-pollution of water by sorbed compounds. Silicon dioxide is inert and does not enter into chemical reactions with components of natural water.

Chrome is present in natural water under aerobic conditions (Eh > +0.1 v) as $HCrO_4^-$ and CrO_4^{2-}, depending on *pH* of the media (Fig. 3.9). Dichromate ions $Cr_2O_7^{2-}$ can be formed only at concentrations Cr (VI) $> 1 \times 10^{-2}$ mol/L, which is not typical for unpolluted surface water. Mineralization (ionic strength) of water significantly affects the relative content of CrO_4^{2-} and $HCrO_4^-$; chromic acid molecules are practically not formed. CrO_4^{2-} ions are involved in redox processes (see Sect. 3.4).

3.2.4 Organic Acids

Dissociation of weak acids depends mainly on their dissociation constants and *pH*; water mineralization and temperature have little effect on the dissociation (see

Table 3.4 *pH* dominance intervals of some anions in organic acids[a]

Acid	pK'_a	Acid anion	*pH* dominance interval (≥ 50 %)
Valeric HA	4.76	A^-	≥ 4.8
Tartaric H_2A	$pK'_1 = 2.79$	HA	2.8–4.3
	$pK'_2 = 4.33$	A^2	≥ 4.3
Enanthic HA	4.79	A^-	≥ 4.8
Caproic HA	4.79	A^-	≥ 4.8
Citric H_3A	$pK'_1 = 3.03$	H_2A^-	3.0–4.5
	$pK'_2 = 4.46$	HA^{2-}	4.5–6.1
	$pK'_3 = 6.10$	A^{3-}	≥ 6.1
Acetic HA	4.66	A^-	≥ 4.7
Propionic HA	5.79	A^-	≥ 5.8
Oxalic H_2A	$pK'_1 = 1.15$	HA^-	1.2–4.1
	$pK'_2 = 4.07$	A^{2-}	≥ 4.1
Fulvic acids H_2A	$pK'_1 = 2.60$	HA^-	2.6–4.1
	$pK'_2 = 4.11$	A^{2-}	≥ 4.1

Water mineralization 500 mg/L, t = 20–25 °C; K'_a—concentration constants of acid dissociation

[a] With $pH \geq 6$ amino acids in surface water are almost completely dissociated into carboxyl groups

example in Figs. 3.4 and 3.5). For the three major acids, this effect is somewhat larger (see Fig. 3.7).

Table 3.4 shows the results of calculating the *pH* dominance range (≥ 50 %) of anions of some organic acids, most common in surface water. The data in Table 3.4 imply that under most typical *pH* values 6.0–9.5 surface water is dominated by non-protonated anions of organic acids, which usually make up complex compounds of metals (see Sect. 3.3.2) and increase the solubility of slightly soluble compounds (see Sect. 3.5.2). The latter contributes to the migration of metal ions in natural ecosystems.

3.2.5 Dissociation of Bases. Ammonium Ions, Ammonia. Amines

Among the bases contained in natural water, the most common is ammonia (ammonium hydroxide) and products of its dissociation. They are part of the redox system $NH^+–NO^-–NO^-$ (see Sect. 3.4.1) and play an important role in the life of aquatic organisms. At high concentrations inorganic nitrogen compounds, especially NH_3, have toxic effect.

Ammonium ions are the products of dissociation of ammonium hydroxide:

$$NH_4OH(NH_3 \cdot H_2O) \rightleftarrows NH_4^+ + OH^- \tag{3.22}$$

The content of toxic ammonia NH_3 in surface water increases with growing pH and temperature and decreases with an increase of water mineralization (Table 3.5).

The concentration of toxic ammonia (mg N/L) is calculated by equation:

$$[NH_3] = [NH_4OH] = \frac{C}{1 + \frac{K'}{[OH^-]}} \tag{3.23}$$

where C—total concentration of ammonia nitrogen (mgN/L), K'—concentration constant of ammonium hydroxide dissociation, which depends on the temperature and mineralization of water. Equation (3.23) is a joint result of equations

$$K^{'} = \left[NH_4^+\right] \cdot [OH^-]/[NH_4OH] \text{ and } C = \left[NH_4^+\right] + [NH_4OH].$$

Figure 3.10 shows an area with excess of toxic ammonia above maximal allowable concentration (MAC–0.05 mg/L), depending on temperature, pH and total ammonia nitrogen concentration.

Increased water mineralization slightly reduces the formation of NH_3, but this effect is negligible (see Table 3.5).

Among organic bases in uncontaminated surface water the most common are low-boiling aliphatic amines such as dimethylamine, ethylamine, diethylamine, trimethylamine, and others (see Sect. 4.3.4). Higher boiling aliphatic and aromatic amines were not detected.

Amines and ammonia molecules are part of complex compounds of some metals—copper, cobalt, zinc, nickel, mercury and others, and affect the solubility of slightly soluble compounds. The data in Table 3.6 imply that under the conditions of surface water in Ukraine ($pH \leq 9.5$) the formation of complex compounds of metals with ammonia is most likely, and to a lesser extent with trimethylamine.

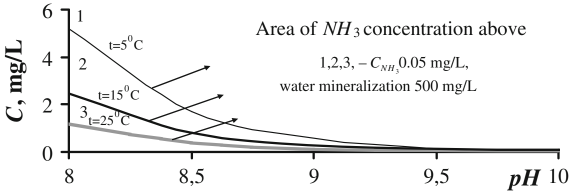


Fig. 3.10 Effect of pH and total ammonia nitrogen content C (mg/L) on the content of toxic NH_3 above the MAC (0.05 mg/L) at different temperatures

Table 3.5 Effect of *pH*, temperature and water mineralization on the relative content of ammonia (% of total ammonia nitrogen content) *K*—concentration constant of ammonium hydroxide dissociation

t (°C)	Mineralization[a] (mg/L)	K′	Content of NH_3 (%) with *pH*							
			6	7	8	8.5	9	9.5	10	10.5
25	70	1.872×10^{-5}	0.05	0.53	5.01	14.5	34.8	62.8	84.3	94.4
	7800	2.782×10^{-5}	0.04	0.36	3.47	10.2	24.5	53.2	78.2	91.9
15	70	3.882×10^{-5}	0.03	0.26	2.51	5.57	20.5	44.9	72.1	89.1
	7800	5.762×10^{-5}	0.02	0.17	1.71	5.20	14.8	35.4	63.5	84.6
5	70	8.292×10^{-5}	0.01	0.12	1.19	3.67	10.8	27.6	54.7	79.2
	7800	1.232×10^{-4}	0.01	0.08	0.81	2.50	7.5	20.4	44.8	72.0

[a] Minimum and maximum mineralization of surface water in Ukraine [25]

3.2.6 Hydrolysis of Metal Ions[1]

Hydrolysis belongs to important processes of transformation and migration of metal ions in aquatic ecosystems. Hydrolysis occurs mainly as the first degree:

$$Me(H_2O)_n^{z+} + H_2O \rightleftarrows \left[Me(H_2O)_{n-1}OH\right]^{(z-1)+} + H_3O^+$$

or more simply

$$Me^z + H_2O \rightleftarrows Me(OH)^{(z-1)+} + H^+ \tag{3.24}$$

The next degrees of hydrolysis occur more rarely because of interference of H^+ ions released during hydrolysis. A more complete hydrolysis to form hydroxo complexes, $Me(OH)_2^{z-2}$ $Me(OH)_3^{z-3}$ etc. and slightly soluble hydroxides occurs with increasing *pH*.

Equilibrium constant (3.24) at ionic strength $\mu = 0$ is the thermodynamic constant of hydrolysis:

$$K_{1H} = \frac{\left[Me(OH)^{(z-1)+}\right] \cdot [H^+]}{[Me^{z+}]} \cdot \frac{f_{MeOH^{(z-1)+}} \cdot f_{H^+}}{f_{Me^{z+}}} = K_{H_2O} \cdot \beta_{MeOH} \tag{3.25}$$

where—product of water ions, which is 1×10^{-14} at 25 °C; β_{MeOH}—thermodynamic stability constants of hydroxo $MeOH^{(z-1)+}$; f_i—activity coefficients of corresponding ions.

---

[1] Influence of complexation processes on metals hydroxides hydrolysis and solubility is considered in Sects. 3.3.3 and 3.5.3.

Table 3.6 *pH* dominance of ammonia molecules and some amines

Base	Ammonia	Trimethylamine	Dimethylamine	Ethylamine	Diethylamine	Methylamine
pK_B'	4.66	4.09	3.17	3.01	2.82	2.24
pH dominance (≥ 50 %)	9.2	9.8	10.7	10.9	11.1	11.7

Mineralization 500 mg/L; t = 25 °C; K_B'—concentration constants of acids dissociation

The process of hydrolysis is closely related to chemical properties of metal cation, namely its hydration energy, which in turn depends on the ratio of square of ion charge (z^2) to its crystal-chemical radius (r). With growing z and decreasing r, ability to hydrolysis of metal cations increases, with greater effect of ion charge. Therefore, hydrolysis constants increase with growing ion charge, and for ions with equal charges decreases with increasing their radius.

Using Eq. (3.25) solution acidity can be calculated, at which begins hydrolysis of metal cations. Let us take for the start of hydrolysis such state of equilibrium (3.24), when hydrolysis occurs for 1 %, or $\left[Me(OH)^{(z-1)+}\right] = 1\ \%$, $[Me^{z+}] = 99\ \%$. Then from Eq. (3.25) we obtain:

$$[H^+]_{1\%} = K_{1\Gamma} \cdot \frac{99}{1} \cdot \frac{f_{Me^{z+}}}{f_{H^+} \cdot f_{Me^{(z-1)+}}} \approx 100 \cdot K_{1\Gamma} \cdot \frac{f_{Me^{z+}}}{f_{H^+} \cdot f_{MeOH^{(z-1)+}}} \tag{3.26}$$

The last degree of hydrolysis during which molecules of $Me(OH)z$ are formed looks like follows:

$$Me(OH)^+_{z-1} + H_2O \rightleftarrows Me(OH)^0_z + H^+ \tag{3.27}$$

$$K_{ZH} = \frac{\left[Me(OH)^0_Z\right] \cdot [H]^+}{\left[Me(OH)^+_{Z-1}\right]} \cdot \frac{f_{H^+}}{f_{Me(OH)^+_{z-1}}} = K_{H_2O} \cdot K_{Me(OH)^o_z} = K_{H_2O} \cdot \frac{\beta_{Me(OH)^o_z}}{\beta_{Me(OH)^+_{z-1}}} \tag{3.28}$$

where $K_{Me(OH)^0_z}$—stepwise stability constant of hydroxo $Me(OH)^0_Z$; $\beta_{Me(OH)^0_Z}$ and $\beta_{Me(OH)^+_{Z-1}}$—cumulative stability constants of corresponding hydroxocomplexes.

Using Eq. (3.28) acidity of a solution can be calculated, at which the hydrolysis of metal ions to form molecules $Me(OH)^0_Z$ is almost complete, that is 99 %:

$$[H^+]_{99\%} = K_{ZH} \cdot \frac{\left[Me(OH)^+_{Z-1}\right]}{\left[Me(OH)^0_Z\right]} \cdot \frac{f_{Me(OH)^+_{Z-1}}}{f_{Me(OH)^0_Z}} = K_{ZH} \cdot \frac{1}{99} \approx \frac{K_{ZH}}{100} \tag{3.29}$$

$$pH_{99\%} = -\lg[H^+]_{99\%}$$

where $f_{Me(OH)^+_{Z-1}} = f_{H^+}$ (see Table 3.1); $f_{Me(OH)^0_Z} = 1$.

Equation (3.29) implies that pH of the hydrolysis to form molecules $Me(OH)z$ does not depend on the activity coefficients of ions, i.e. water mineralization. The calculation results of $pH_{1\%}$ and $pH_{99\%}$ are given in Table 3.7. From numerous hydrolysis constants published in the literature [2, 20], those that correspond to the maximum extent to Eq. (3.25) were chosen. At the same time, there were used ion activity coefficients calculated by the equations in Table 3.1 for the minimum

Table 3.7 Dependence of beginning ($pH_{1\%}$) and almost complete ($pH_{99\%}$) hydrolysis of some metal cations on hydrolysis constants and water mineralization (t = 20–25 °C)

Ion	Hydrolysis constants				70 mg/L		500 mg/L		7800 mg/L		Dominating forms at pH 6–10 of surface water [13]
	K_{1H}	pK_{1H}	K_{ZH}	pK_{ZH}	$pH_{1\%}$	$pH_{99\%}$	$pH_{1\%}$	$pH_{99\%}$	$pH_{1\%}$	$pH_{99\%}$	
K^+	3.2×10^{-15}	14.5	–	–	12.5	–	12.5	–	12.5	–	K^+
Na^+	6.3×10^{-15}	14.2	–	–	12.2	–	12.2	–	12.2	–	Na^+
Ca^{2+}	1.6×10^{-13}	12.8	–	–	10.8	–	10.9	–	11.0	–	Ca^{2+}
Mg^{2+}	4.0×10^{-12}	11.4	–	–	9.4	–	9.5	–	9.6	–	Mg^{2+}
Mn^{2+}	2.5×10^{-11}	10.6	8.4×10^{-12}	11.1	8.6	11.5	8.7	11.5	8.8	11.5	Mn^{2+}, $MnOH^+$, $Mn(OH)_2^0$
Ni^{2+}	1.3×10^{-10}	9.9	3.8×10^{-11}	10.4	7.9	12.4	8.0	12.4	8.1	12.4	Ni^{2+}, $Ni(OH)_2^0$
Co^{2+}	2.5×10^{-10}	9.6	6.3×10^{-10}	9.2	7.6	11.2	7.7	11.2	7.8	11.2	Co^{2+}, $Co(OH)_2^0$
Fe^{2+}	3.2×10^{-10}	9.5	1.6×10^{-10}	9.8	7.5	11.8	7.6	11.8	7.7	11.8	Fe^{2+}, $FeOH^+$, $Fe(OH)_2^0$
Zn^{2+}	1.0×10^{-9}	9.0	7.6×10^{-10}	9.1	7.0	10	7.1	10	7.2	10	Zn^{2+}, $ZnOH^+$, $Zn(OH)_2^0$
Cd^{2+}	1.2×10^{-8}	7.9	1.2×10^{-8}	7.9	5.9	9.9	6.0	9.9	6.1	9.9	Cd^{2+} , $CdOH^+$
Cu^{2+}	2.2×10^{-7}	6.7	2.2×10^{-7}	6.7	4.7	8.7	4.8	8.7	4.9	8.7	Cu^{2+}, $CuOH^+$, $Cu(OH)_2^0$
Pb^{2+}	3.3×10^{-7}	6.5	1.1×10^{-11}	10.9	4.5	10.8	4.6	10.8	4.7	10.8	Pb^{2+}, $Pb\ OH^+$, $Pb(OH)_2^0$
Hg^{2+}	4.0×10^{-4}	3.4	2.5×10^{-3}	2.6	1.4	4.6	1.5	4.6	1.6	4.6	$Hg(OH)_2^0$
Al^{3+}	1×10^{-5}	5.0	2×10^{-7}	6.7	3.1	7.7	3.2	7.7	3.4	7.7	$Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$
Cr^{3+}	1×10^{-4}	4.0	9.1×10^{-9}	8.0	2.1	9.0	2.2	9.0	2.4	9.0	$CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, $Cr(OH)_4^-$
Fe^{3+}	6.3×10^{-3}	2.2	3.2×10^{-5}	4.5	0.3	6.5	0.4	6.5	0.6	6.5	$Fe(OH)_2^+$, $Fe(OH)_3^0$

(70 mg/L), medium (500 mg/L) and maximum (7800 mg/L) mineralization of surface water in Ukraine.

The data presented in Table 3.7. show that under conditions of surface water in Ukraine ($pH \leq 9.5$) hydrolysis of singly charged cations and calcium ions does not occur, magnesium ions hydrolyze for not more than 1 %, and mercury ions' (II) ability to hydrolysis is close to triply charged metal cations.

The increase in water mineralization from minimum to maximum increases the beginning of hydrolysis only by 0.2–0.3 *pH* units and does not affect the *pH* of complete hydrolysis.

The effect of temperature at the beginning of hydrolysis of metal ions is slightly higher. For example, given the hydrolysis constants presented in monograph [20], $pH_{1\%}$ hydrolysis of Fe^{3+} ions at different temperatures is as follows ($\mu = 0.145$):

t (°C)	0	10	25	35
pK_{1h}	2.96	2.74	2.49	2.39
$pH_{1\%}$	0.96	0.74	0.49	0.39

Thus, with increasing temperature from 0 to 25 °C the degree of hydrolysis increases, resulting in $pH_{1\%}$ decreasing by almost 0.6 units.

The degree of *h* and *pH* of hydrolysis of salts of weak bases and strong acids, which are salts of heavy metals, is calculated by equation [28]:

$$h = \frac{\left[MeOH^{(z-1)+}\right]}{C} = -\frac{K_{H_2O} \cdot \beta_{MeOH}}{2C} + \sqrt{\left(\frac{K_{H_2O} \cdot \beta_{MeOH}}{2C}\right)^2 + \frac{K_{H_2O} \cdot \beta_{MeOH}}{C}} \tag{3.30}$$

$$[H^+] = -\frac{K_{H_2O} \cdot \beta_{MeOH}}{2} + \sqrt{\left(\frac{K_{H_2O} \cdot \beta_{MeOH}}{2}\right)^2 + C \cdot K_{H_2O} \cdot \beta_{MeOH}} \tag{3.31}$$

$$pH = -\lg[H^+]$$

where $\left[MeOH^{(z-1)+}\right]$—concentration of hydrolyzed part of the salt (mol/L), C—total salt concentration (mol/L), K_{H_2O}—ionic product of water at certain temperature, β_{MeOH}—stability constant of metal hydroxo complex, which is the inverse of dissociation constant of a respective base and is related to hydrolysis constant by Eq. (3.25).

The well-known provisions follow from Eqs. (3.30), (3.31) and ratio (3.24) that the degree of hydrolysis increases with diluted solution, increasing temperature and decreasing dissociation constant of weak base $MeOH^{(z-1)+}$ (increasing hydrolysis constant); hydrolysis *pH* increases with dilution, lower temperature and increasing the dissociation constant of weak base (reducing hydrolysis constant).

Figure 3.11 shows examples of the influence of main factors—hydrolysis constants, concentration of metal ions, water temperature and mineralization on the degree of hydrolysis. It can be seen that the main factors affecting the degree of hydrolysis is hydrolysis constant and concentration of metal salt. Ions of iron (III) are almost completely hydrolyzed, mangan (II) ions are hardly hydrolyzed, and other heavy metal ions occupy an intermediate position according to pK_{1h} values. Effect of water temperature and mineralization (ionic strength) is much lower.

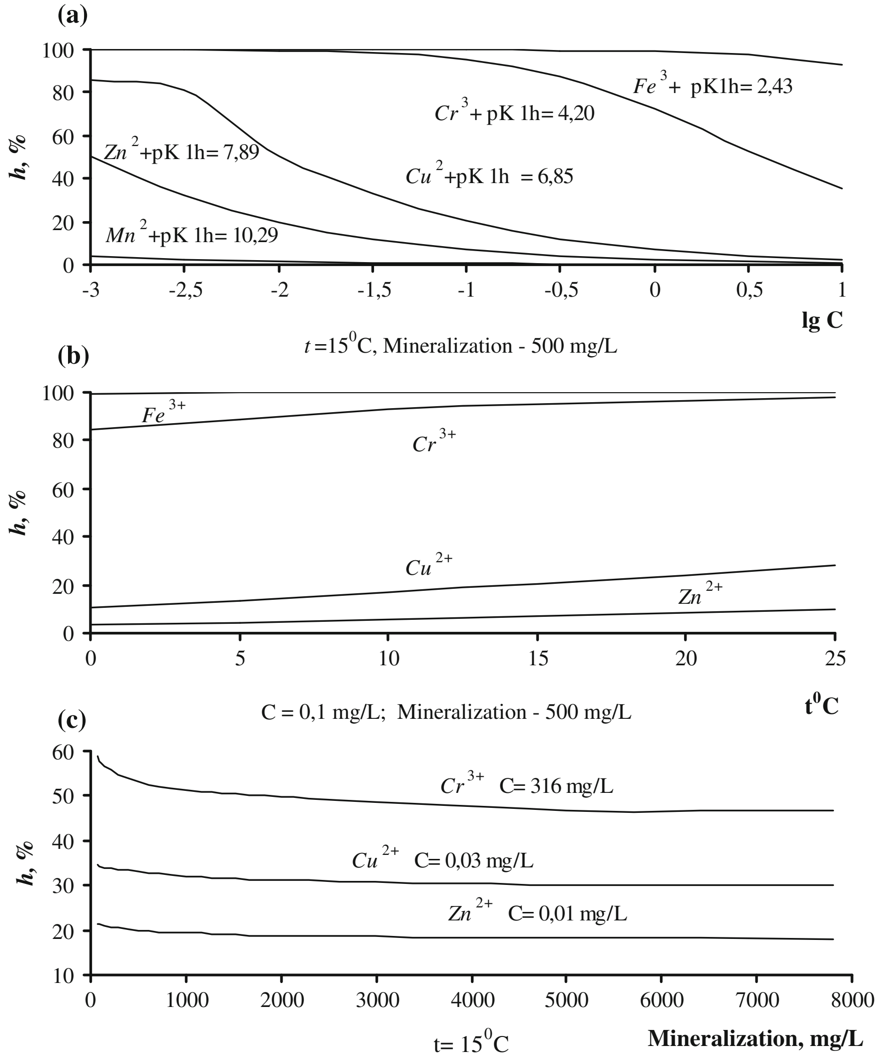


Fig. 3.11 Dependence of the degree of hydrolysis h (%) of some metals' ions on **a** their concentration C, mg/L, **b** temperature and **c** water mineralization

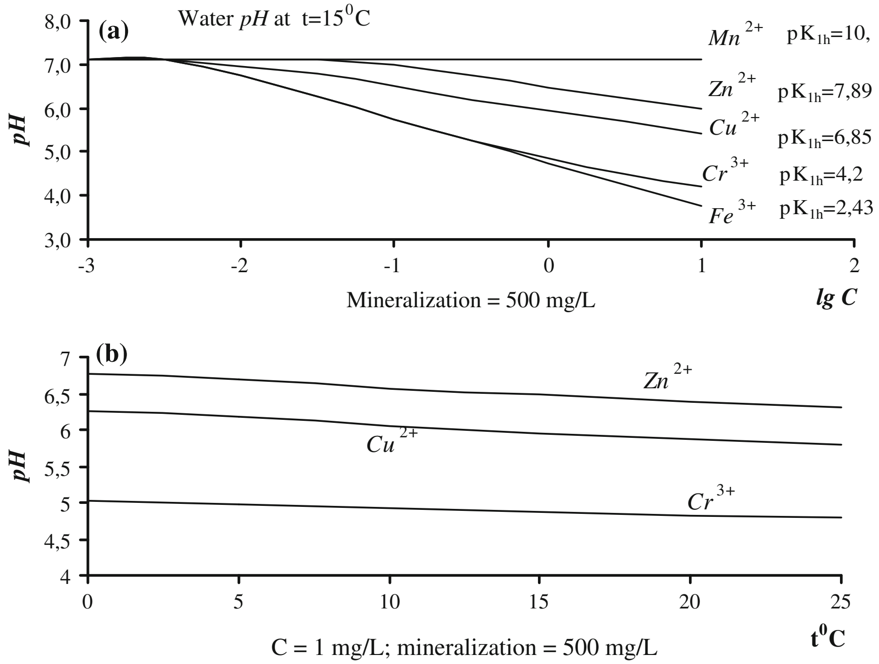


Fig. 3.12 Dependence of *pH* of hydrolysis of some metals' ions on their concentration (C, mg/L), hydrolysis constant (**a**) and water temperature (**b**)

Figure 3.12 shows the effect of hydrolysis constants, the concentration of metal ions and temperature on the *pH* of the hydrolysis. It can be seen that water *pH* is significantly affected by heavy metal ions at concentrations of more than 0.01–0.1 mg/L. However, it should be borne in mind that under the conditions of surface water heavy metal ions are largely combined into complex compounds (see Sect. 3.3), so their effect on the *pH* of water is much lower than indicated in Fig. 3.12.

In addition, the *pH* of surface water during hydrolysis of metal ions is greatly affected by the buffer capacity of water carbonate system (see Sect. 3.2.2).

Calculation of natural water *pH* with taking into account the hydrolysis of metal ions is fulfilled by Eq. (3.11b), where $[H^+]$—concentration of hydrogen ions, which is created as a result of hydrolysis of metal salt.

For example, the hydrolysis of iron salt with a concentration of 10 mg*Fe*/L (1.79×10^{-4} mol/L) by a conventional scheme $Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+$ creates concentration of hydrogen ions $3 \times 1.79 \times 10^{-4} = 5.37 \times 10^{-4}$ mol/L ($pH = 3.27$).

If the same amount of iron enters natural water with temperature 25 °C, mineralization of 500 mg/L $(pK'_{1H_2CO_3} = 6.27)$, *pH* 7.00, $C_{HCO_3^-}$ 100 mg/L $(1.64 \times 10^{-3}\,\text{mol/L})$ and respectively $C_{H_2CO_3}$ 3.05×10^{-4} mol/L, the acidity of such water, calculated by Eq. (3.11b), will drop to just *pH* 6.39 instead of 3.27 in pure water. With increase of $C_{HCO_3^-}$ to 500 mg/L (8.20 × 10^{-3} mol/L) and accordingly $C_{H_2CO_3}$ to 1.53 × 10^{-3} mol/L acidity of natural water drops even lower—to *pH* 6.84.

Thus, as mentioned above, the buffer capacity of a carbonate system of natural water is an important factor in stabilizing the *pH* at entering into water of H^+ or OH^- ions as a result of hydrological, physical, chemical or biological processes, as well as anthropogenous factor.

The final products of hydrolysis are soluble metal hydroxides, solubility of which depends mainly on the *pH* of water and only slightly on temperature and mineralization.

Figure 3.13 shows the results of calculations of the solubility of some metal hydroxides, depending on *pH* and mineralization (ionic strength) of water. The calculations were carried out using an equation that takes into account the formation in solutions, balanced with hydroxides residues, of cations Me^{z+}, $Me(OH)^{(Z-1)+}$, $Me(OH)_2^{(Z-2)+}$ and molecules $Me(OH)_z^0$, and in the case of amphoteric elements—anionic hydroxocomplexes $Me(OH)_{Z+1}^-$:

$$S(mol/L) = [Me^{z+}] + \left[MeOH^{(z-1)+}\right] + \left[Me(OH)_2^{(z-2)+}\right] + \left[Me(OH)_z^0\right] + \left[Me(OH)_{z+1}^-\right] = \\ = \frac{SP'_z}{[OH^-]^z} + \frac{SP'_{z-1}}{[OH^-]^{z-1}} + \frac{SP'_{z-2}}{[OH^-]^{z-2}} + SP'_z \cdot \beta'_z + SP'_z \cdot \beta'_{z+1} \cdot [OH^-] \tag{3.32}$$

where z = 2 or 3; P'—products of soluble hydroxide concentrations; β'—concentration stability constants of corresponding hydroxo complexes.

Solubility of iron hydroxide (III) is conditioned mainly by the presence in the solution of molecules of $Fe(OH)_3^0$ and does not dependent on *pH* and mineralization of water in the specified range. However, concentrations of iron (III) compounds in surface water [25] are much higher than the solubility of hydroxide; the reason for this is discussed in Sect. 3.3. Hydroxide of iron (II) precipitates only at $pH > 9$. Under these conditions, surface water are saturated with oxygen due to photosynthetic activity of aquatic organisms, having high value of E_h, therefore $Fe(OH)_2$ is oxidized to $Fe(OH)_3$. Thus, in natural aquatic ecosystems there are no conditions for the formation of a $Fe(OH)_2$ precipitate and the presence of *Fe* (II) compounds in the bottom sediments is due to their co-precipitation with $Fe(OH)_3$ and ion-exchange or molecular sorption on clay minerals (see Sect. 3.6). Similarly, mangan (II) hydroxide neither can be formed, because with an increase of E_h and *pH* is oxidized to insoluble mangan dioxide MnO_2 (see Sect. 3.4), which is a good collector for co-precipitation, in particular of mangan (II) compounds.

Table 3.8 presents *pH* intervals of minimum solubility of some metal hydroxides. $Me(OH)_z^0$ molecules are in equilibrium with hydroxides precipitates at the indicated *pH*, so the minimum solubility does not affect the mineralization (ionic strength) of water.

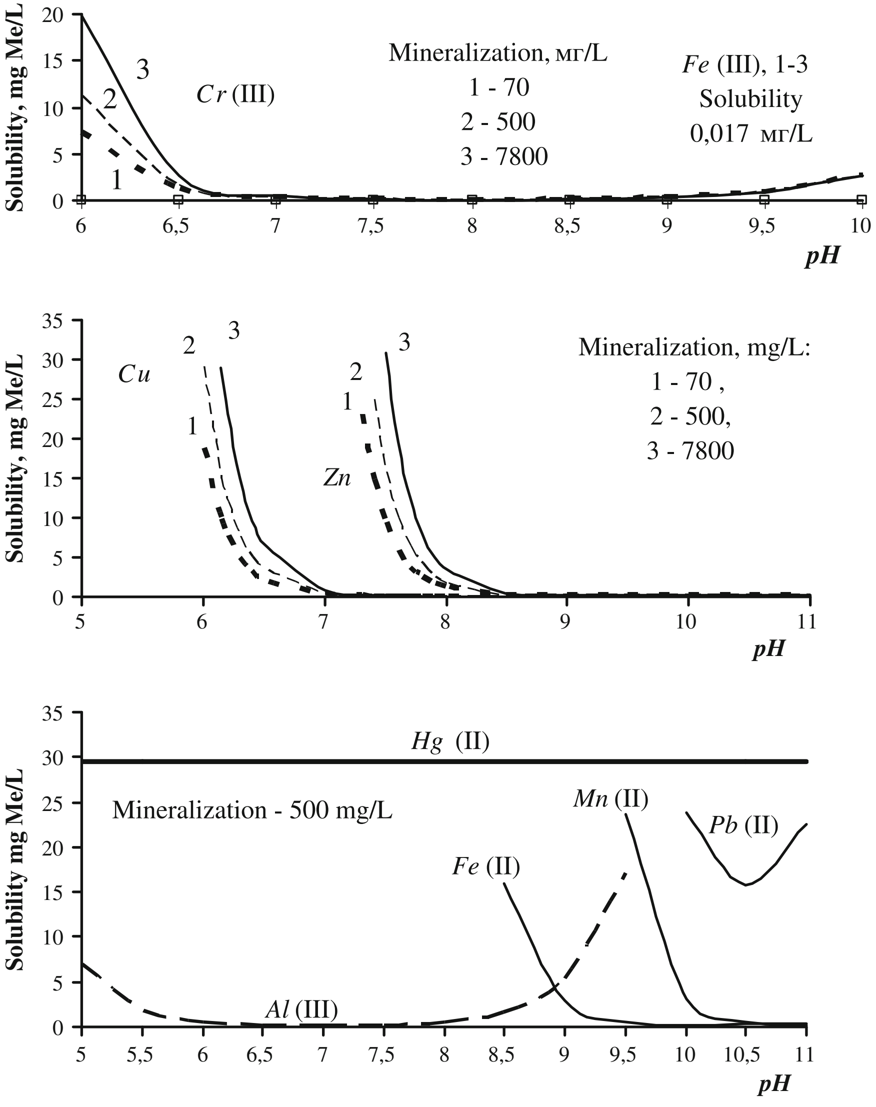


Fig. 3.13 Solubility of some metal hydroxides, depending on water *pH* and mineralization (t = 25 °C)

It is known that heavy metals, including their free hydrated ions have toxic effect on aquatic organisms. Therefore, the reduction of concentration of metal compounds due to their singling out into bottom phase or sorption on suspension and colloidal particles reduces their toxic effect.

Precipitation of hydroxides of chromium (III), copper (II), zinc (II), lead (II), mercury (II) and other divalent metals is unlikely, because in uncontaminated surface water concentrations of these elements tend to be smaller than the solubility of hydroxides (see Table 3.8), besides, they are bound in complex compounds with

Table 3.8 The minimum solubility of some metal hydroxides (t = 25 °C)

Hydroxide	Minimus solubility, mg Me/L	pH^a interval
$Fe(OH)_3$	0.017	≥ 5.0
$Cr(OH)_3$	0.10	7.5–8.5
$Al(OH)_3$	0.15	6.5–7.5
$Cu(OH)_2$	0.080	≥ 8.0
$Ni(OH)_2$	0.10	10.5–11.5
$Zn(OH)_2$	0.14	9.0–10.5
$Co(OH)_2$	0.16	10.5–12.0
$Mn(OH)_2$	0.20	≥ 11
$Fe(OH)_2$	0.30	≥ 10.5
$Cd(OH)_2$	1.3	≥ 12.5
$Pb(OH)_2$	17	10.2–10.8
$Hg(OH)_2$	30	≥ 4.5

[a] At smaller *pH* values the solubility increases due to the formation of hydroxocations, while at greater *pH* values—hydroxoanions in the case of amphoteric elements

organic substances present in natural water. Their accumulation in bottom sediments apparently is due to co-precipitation with such collectors as $Fe(OH)_3$ and MnO_2, and ion-exchange and molecular sorption on clay minerals and mineral and organo-mineral suspensions.

3.3 Complexation Processes

Among the dissolved forms of metals one can identify free hydrated ions, ion pairs (e.g. $CaHCO_3^+$, $MgHCO_3^+$, $CaSO_4^0$, $MgSO_4^0$ et al. [1, 8]), which are characterized by low stability and are formed mainly in highly mineralized water, and coordination compounds with well-defined structure and high values of stability constants (complex compounds of ρ- and d-elements).

Metal ions interact with inorganic and organic ligands in line with the following possible formulas (for notational simplicity water molecules in aqua complex and ions charges are not listed):

$$Me + nL \rightleftarrows MeLn, \tag{3.33}$$

$$Me(OH)x + nL \rightleftarrows MeLn + xOH, \tag{3.34}$$

$$Me(OH)x + nL \rightleftarrows Me(OH)xLn, \tag{3.35}$$

$$Me(OH)x + nL \rightleftarrows Me(OH)yLn + (x-y)OH \tag{3.36}$$

In natural water according to formula (3.33) complexes form ions Ca^{2+} and Mg^{2+}, for which at $pH < 10$ hydrolysis does not occur (see Table 3.7.). Other doubly charged cations form complex compounds, usually by formula (3.34), and triply charged cations—also by formula (3.35) or (3.36). For example, iron (III) ions form complex compounds $[Fe\mathrm{FA}]^{+}$, $[Fe(OH)\mathrm{FA}]^{0}$ and $[Fe(OH)_2\mathrm{FA}]^{-}$, where FA^{2-}—anion of fulvic acid [13]. Concentration stability constants of complex compounds that are related to thermodynamic constants by Eq. (3.2) include the concentration of all ions and molecules that make them up:

$$\beta_n^{'} = \frac{[MeL_n]}{[Me] \cdot [L]^n}\ \beta_{n,OH}^{'} = \frac{\left[Me(OH)_y L_n\right]}{[Me] \cdot [OH]^y [L]^n} \tag{3.37}$$

where $[Me]$—concentration of free (uncomplexed) metal cations; $[L]$—concentration of ligand anions or amine molecules in the case of amine complexes.

The same metal ion can at the same time form complex compounds with different ligands, which are present in natural water. The equation of a balance of all dissolved forms of metal is:

$$C_{Me} = [Me] + \sum_{1}^{n} [MeL_n] \tag{3.38}$$

Concentration or content ratio (%) of each form of metal is calculated by equation:

$$[Me] = \frac{C_{Me}(or\,100\,\%)}{1 + \sum_1^n \beta_n^{'} \cdot [L]^n};\ [MeL_n] = [Me] \cdot \beta_n^{'} \cdot [L]^n \tag{3.39}$$

Equations (3.37)–(3.39) refer to complexing of metal ions with individual ligands. To use these equations it is necessary to determine the concentration of each ligand in natural water, which is not always possible, especially in the case of numerous organic substances present in natural water (see Sect. 3.4). Therefore, to assess the proportion of complexed metal ions in natural water one can use *formal concentration equilibrium constants* $K_p^{'}$ derived on the basis of *collective ligand HhL concept*, which is the sum of all natural water complexing compounds [11, 12, 18]. It is found by determining the complexing ability (CA) of natural water by a particular metal, expressed in terms of its molar concentration.

Complex formation with collective ligand is expressed by a general formula:

$$Me + pH_hL \rightleftarrows ML_p + phH^{+} \tag{3.40}$$

In this formula, for notational simplicity charges of metal ion and complex compound are not indicated. The value of H_hL implies not a number of moles of the compound but, the number of active centers of collective ligand C_L. Therefore, figure p is not the number of ligands, but the average number of active centers of complexing compounds in natural water, with which one metal ion is bound. At the same time active centers may be partly bound with other metals. Thereby, Eq. (3.40) implies the possibility of competing reactions and reactions to form mixed-ligand and mixed-metal complexes.

In this regard, the equilibrium constant (3.40) depends on the quality of the complexing compounds, the presence of other metals and *pH* of natural water. Given the stability of all factors, except total concentration of complexing compounds, formal equilibrium constant (3.40) has the following expression:

$$K_p^{'} = \frac{[MeL_p]}{[Me] \cdot [H_hL]^p} = \frac{[MeL_p]}{[Me] \cdot C_L^p} \tag{3.41}$$

If the total concentration of active centers *CL*, that is CA of natural water, is much greater than the concentration of metal *CMe* in this natural water, then formal equilibrium constant at a given *pH* is calculated by formula:

$$K_p^{'} = \frac{C_{Me} - [Me]}{[Me] \cdot C_L^p} \tag{3.41.1}$$

where [*Me*]—concentration of uncomplexed metal ions, which is determined by potentiometric or kinetic method [19]. One can also use a cation exchange method [17]. The value of *p*, which can be a noninteger number, is read off from a graph by tangent of inclination to the horizontal axis of the straight line reflecting the equation:

$$\lg \frac{C_{Me} - [Me]}{[Me]} = f(C_L)^* \tag{3.42}$$

**CL* is changed by dilution of natural water with a solution of salts with the same ionic strength and total concentration of metal.

If $CL \approx CMe$ or $CL < CMe$, then $[HhL] = CL - p(CMe - [Me])$, and the Eq. (3.41) looks as follows:

$$K_p^{'} = \frac{C_{Me} - [Me]}{[Me] \cdot \{C_L - p(C_{Me} - [Me])\}^p} \tag{3.43}$$

In this case, the value of *p* is found by method of successive approximations by entering arbitrary values of *p* in the Eq. (3.43), in particular noninteger ones, and finding out with which of them $K_p^{'}$ appears to be most stable with changing C_L. It is this value of *p* which is valid for given natural water.

As an example, Table 3.9 shows the results of determination of *p* and $K_p^{'}$ of mangan (II) complexes in water of Dnipro river [12, 18].

It can be seen, that complexes with different composition and different stability were formed in the studied water in different seasons. In most cases complexed forms of mangan were dominating. With higher *pH* the value of $K_p^{'}$ and mangan complexity increase, indicating its binding to ligands, which are anions of weak acids.

Table 3.9 Formal equilibrium constants and the degree of binding of mangan (II) in complex compounds in the water of the Dnipro river

Date of water sampling (1976 y.)	*pH*	$C_{Mn} \times 10^7$ mol/L	$[Mn] \times 10^7$ mol/L	$C_L \times 10^6$ mol/L	p	K_p'	% complexed *Mn*(II)	
							Calculation by Eq. (3.41.1)	Experiment
10.05	6.0	8.3	4.4	2.4	1.3	1.1×10^7	34.9	28.9
	8.0[a]	7.8	2.7	3.2	1.3	1.4×10^7	65.0	65.4
	9.6	7.6	1.4	5.6	1.3	2.5×10^7	77.6	81.6
10.06	6.0	9.4	5.4	3.9	1.2	1.5×10^6	33.3	45.6
	7.9[a]	9.7	4.4	4.9	1.2	2.9×10^6	55.7	53.6
	9.6	9.0	1.4	10.4	1.2	5.7×10^6	85.7	84.2
10.08	6.0	26.6	19.5	5.4	1.6	6.8×10^7	20.7	26.7
	8.1[a]	24.2	16.6	7.6	1.6	8.0×10^7	33.9	31.4
	9.6	24.6	6.8	13.8	1.6	14.5×10^7	70.6	72.4
31.08	6.0	22.0	6.3	6.6	1.8	2.9×10^9	58.6	71.4
	8.2[a]	22.6	4.1	8.4	1.8	3.3×10^9	76.5	81.9
	9.6	22.5	1.9	14.8	1.8	6.8×10^9	93.3	91.6

[a] *pH* of natural water in Dnipro near Kyiv

The effect of temperature on equilibrium constants, including stability constants of complex compounds, is calculated by Van't Hoff's equation:

$$\lg K_x = \lg K_{CT} = -\frac{\Delta H_{CT}}{2.3 \cdot R}\left(\frac{1}{T_x} - \frac{1}{T_{CT}}\right) \tag{3.44}$$

where K_x and K_{CT}—equilibrium constants with x temperature and CT, respectively; T—temperature in degrees Kelvin ($T_{CT} = 298$ K); R—gas constant (8.31×10^{-3} kJ/mol); ΔH_{CT}—standard change of reaction enthalpy. It is calculated by the approximate equation $\Delta H_{CT} \approx -2.3\ RT_{CT}\ \lg = -5.69\ \lg\ K_{CT}$, conceding that the product of temperature by standard entropy change (TΔS) is much smaller than ΔH_{CT} and can be neglected.

3.3.1 Complexes with Inorganic Ligands

Anions of strong acids Among the anions of strong acids capable of forming complex compounds (ionic associates) with metal cations, SO_4^{2+} and Cl^- are present in natural water. The degree of binding in complex compounds of metals, which in natural water do not hydrolyze, $-Ca^{2+}$ and Mg^{2+}, do not depend on pH (Fig. 3.14a, example for Mg^{2+}), decreases with higher water mineralization and increases, but not in direct proportion, with higher ligand concentration (Fig. 3.14b).

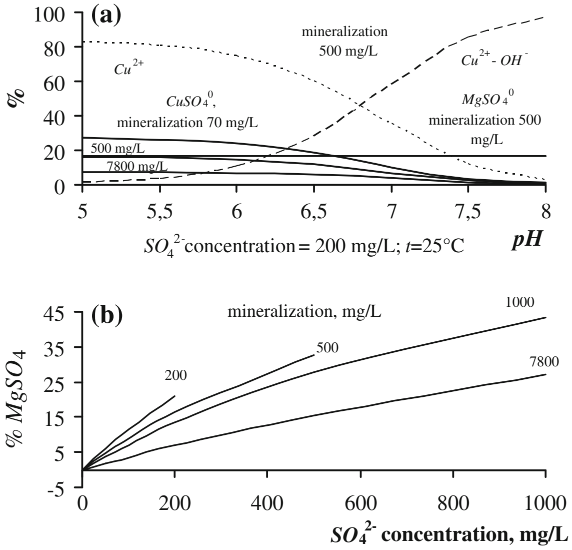


Fig. 3.14 **a** Influence of *pH*, water mineralization **b** ligand concentration on the formation of complexes with anions of strong acids of metals which do not hydrolyze in natural water (Mg^{2+}), and those which hydrolyze (Cu^{2+})

In the case of cations that hydrolyze at $pH \geq 6$—Mn^{2+}, Cu^{2+}, Zn^{2+} and others, growing pH leads to the destruction of complex compounds due to the formation of hydroxo complexes (Fig. 3.14a, example Cu^{2+}):

$$MeL_n^{z-ny} + xOH^- \rightleftarrows Me(OH)_x^{z-x} + nL^{y-} \tag{3.45}$$

Complexes with anions of strong acids are unstable (lgβ < 4, except mercury chloride complexes). When temperature increases their stability grows [9, 22].

Anions of weak acids Among the anions of weak inorganic acids, which can form complex compounds (ionic associates) with metal cations, in surface water are present CO_3^{2-} and HCO_3^- and in much lower concentrations PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$. With decreased water pH complex compounds decompose due to protonation of weak acid anions (Fig. 3.15a, b):

$$MeL_n^{z-ny} + nxH^+ \rightarrow Me^{z+} + nH_xL^{y-x} \tag{3.46}$$

Increased water pH contributes to the formation of complexes with metal cations, which are not hydrolyzed (Fig. 3.15a). In the case of cations that hydrolyze, higher pH contributes to a certain extent to complex formation due to increasing the share of anions, which are part of the complex. However, further increase in pH leads to destruction of complexes (Fig. 3.15b) due to hydrolysis of a metal ion by the Eq. (3.45).

Thus, to form complex compounds of heavy metals with anions of weak acids, including organic (see below), there is a certain optimum pH interval, which depends on the stability constants of metal complexes with ligand *L*y-and the corresponding hydroxo complexes.

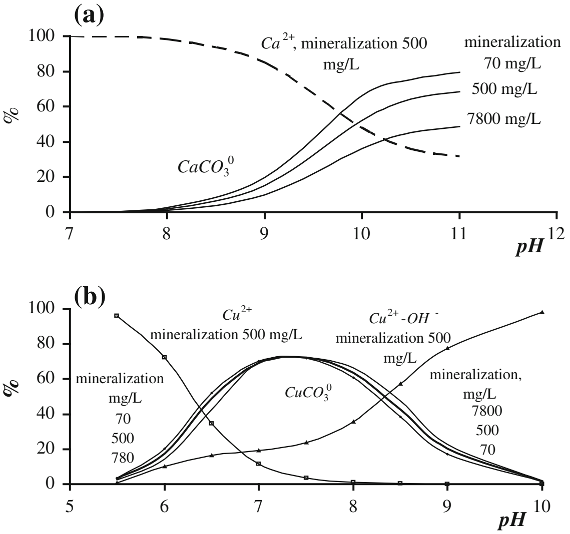


Fig. 3.15 Effect of *pH* and mineralization of water on complexation with anions of weak carbonic acid of metals, which in surface water are not hydrolyzed (*Ca*, **a**), and hydrolyzed (*Cu*, **b**)

Total concentration of carbonates 250 mg/L; t=25°C

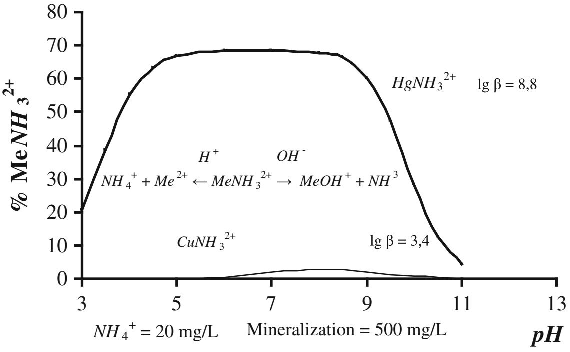


Fig. 3.16 Effect of *pH* and stability constants on the formation of amine complexes (t = 25 °C)

Ammonia Ammonia complexes of heavy metals are formed within a certain *pH* interval, depending on their stability constants and concentrations of NH_3 molecules. At lower *pH* the complexes are destroyed as a result of protonation of ammonia molecules, while at higher *pH*—due to hydrolysis of the central metal ion (Fig. 3.16).

3.3.2 Complexes with Organic Ligands

Anions of weak acids The structure of complex metal compounds includes, as a rule, unprotonated and sometimes protonated anions of weak organic acids, the relative proportion of which increases with increasing *pH*.

At low *pH* complex compounds decompose due to protonating of weak acid anions by the Eq. (3.46), and at higher *pH* are destroyed due to hydrolysis of metal ion by Eq. (3.45).

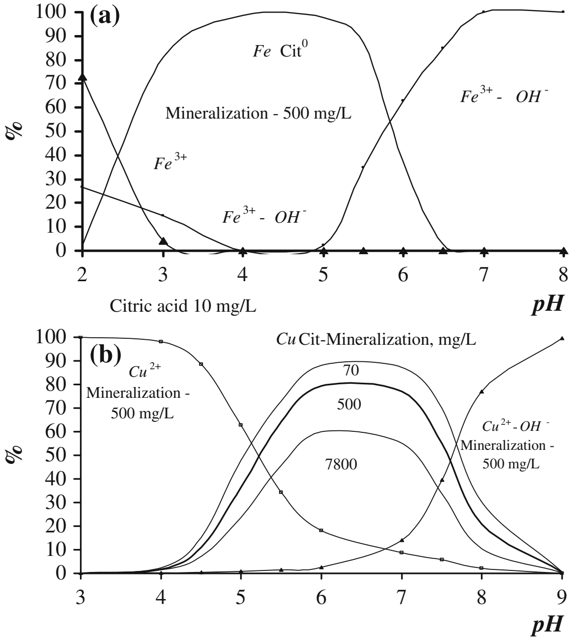
Effect of *pH* on complex metal compounds which do not hydrolyze in natural water, is similar to carbonate complexes.

Effect of *pH* on metal complexes that hydrolyze is shown in Fig. 3.17. Effect of ligand concentration is the same as in the case of complexes with anions of strong acids.

Effect of water mineralization on the formation of complexes with anions of weak acids is ambiguous. If only one compound is formed, e.g. $CaCO_3$ (see Fig. 3.15a), then with an increase of water mineralization the level of metal binding decreases. When several compounds are formed, for example $CuCO_3^0$, $CuOH^+$ and $Cu(OH)_2^0$ at $pH > 6$ (Fig. 3.15b), or $Cu\text{Cit}^-$, $CuOH^+$ and $Cu(OH)_2^0$ at $pH > 6$ (Fig. 3.17b), then increased water mineralization can hinder or facilitate the formation of complexes, depending on their stability constants and water *pH*.

Effect of water temperature on the formation of complex compounds is ambiguous. If $\lg\beta n < 4$, then with higher temperature stability of complexes increases, and when $\lg\beta n > 10$—decreases [9, 22]. Effect of temperature on the

Fig. 3.17 Effect of pH and mineralization of water on complex compounds of metal cations that hydrolyze **a** Fe, **b** Cu with anions of weak organic acids



stability of complexes with intermediate values of lgβ*n* depends on standard change of complexation reaction enthalpy.

Fulvic and humate complexes Humic substances are one of the most common organic weak acids in surface water. The content of soluble fulvic acids (FA) is in the range of 1–100 mg/L, of less soluble humic acids (HA)—within 0.01–30 mg/L [32]. The dissociation constants of FA and HA by carboxyl groups are close [33]. However, because the concentration of FA is much higher than the concentration of HA, surface water are dominated fulvic metal complexes.

Fulvic acids in aqueous solutions form associates, the average molecular weight of which increases with growing *pH* (Table 3.10).

Therefore the stability constants of metal fulvic complexes, identified at certain *pH* values, are *conditional*. They also depend on the source and method of separation of fulvic acids [12, 25].

Stability constants of fulvic complexes increase with higher *pH*, which is due to structural changes of humic substances (HS), when many of the surface functional groups are acting as additional binding centers. In addition, HS molecules have a number of functional groups, acidity of which depends on the neighboring groups and neutrality of a molecule as a whole.

It is known that the stability of complex compounds is affected by the nature of metal cation, in particular by its ionic potential (IP) (ratio z^2/r). For certain groups of metals that form complexes with predominantly ionic bonding, the relationship between IP and β*n* is quite clear. Therefore, it becomes possible to predict the stability constants by extrapolation.

Table 3.10 Values of average molecular weight $\overline{M}_W$ (Da) of fulvic acids depending on *pH* [34]: Within *pH* interval 4–11: $\overline{M}_W = 1350\ pH–4540$

pH	2–4	4.5	5.0	5.5	6.0	5.6	7.0	7.5	8	8.5	9	9.5	10
$\overline{M}_W$	≈300 monomer	1540	2210	2890	3560	4240	4910	5590	6260	6940	7610	8290	8960

Table 3.11 Dependence of conditional stability constants of fulvic complexes of some metals on *pH*

Metal	Conditional stability constants, lgβ1(c) at *pH*								A
	3	4	5	6	7	8	9	10	
Ca^{2+}	2.6	3.0	3.6[a]	4.3	5.1	6.1	7.2	8.4	2.1
Mn^{2+}	2.7–2.1[a]	3.1	3.7[a]	4.4	5.2	6.2	7.3	8.5	2.2
Zn^{2+}	2.5–2.2[a]	2.9–3.0[a]	3.5[a]	4.2	5.0	6.0–5.6[a]	7.1	8.3	2.0
Co^{2+}	3.2–2.9[a]	3.6	4.2[a]	4.9	5.7	6.7–7.0[a]	7.8	9.0	2.7
Ni^{2+}	3.2–3.1[a]	3.6–3.2[a]	4.2[a]	4.9	5.7	6.7–7.0[a]	7.8	9.0	2.7
Cd^{2+}	2.4–2.0[a]	2.9–3.1[a]	3.4[a]	4.1–3.7[a]	4.9	5.9	7.0	8.2	1.9
Cu^{2+}	5.0	5.4–5.5[a]	6.0[a]	6.7–6.1[a]	7.5	8.5	9.6	10.8	4.5
Fe^{2+}	3.4	4.1	4.7[a]	5.4	6.2	7.2	8.3	9.5	3.2
Fe^{3+}	6–0	6.4	7.0[a]	7.7	8.5	9.5	10.6	11.8	5.5
Fe^{3+}–HFA[b]	19.1	19.2	20.1[a]	20.8	21.6	22.6	23.7	24.9	18.6

Ionic strength $\mu = 0.1–0.05$

$\lg\beta1(c) = 0.0667\ pH^2 - 0.033\ pH + A$

[a] Experimental data for metal complexes with fulvic acids, extracted from surface water [25, 30]

[b] Hydrofulvic complexes

The paper [30] with the use of examples of ethylenediaminetetraacetate complexes and products of some metal hydroxides solubility shows that the same dependence is observed between *pMe*(*pMe* = –lg[Me^{z+}]) and IP at different *pH* values. This allows predict the stability constants of fulvic metal complexes which depend on *pH*, given the availability of at least one constant, determined experimentally at a certain *pH*. The equations for these calculations are shown in Table 3.11. Constants determined at *pH* = 5 [25, 30] were used as a basis.

It should be noted that in some cases the stability constants of fulvic metal complexes, defined by different authors [25], differ among themselves and from the calculated by the equation given in the Table 3.11. Perhaps this is due to the fact that for their definition were used fulvic acids of different origin, educed in different ways. Not only heavy metal ions in microgram concentrations are present in natural water, but also Ca^{2+} and Mg^{2+}, the concentration of which reaches dozens and hundreds of mg/L [25]. They can be competitive with heavy metal ions, binding HS in unstable complex compounds, when the concentration of the latter in surface water is only a few mg/L. The same competition can be created by Fe(III) ions present in unpolluted surface water at concentrations up to 10 mg/L and forming very stable hydrofulvic (humate) complexes.

Free concentration of humate ions (L^{2-}) in the presence of several metals can be calculated by balance equation:

$$\left[L^{2-}\right] = C_L - m[MeL] - 2m[MeL_2] = C_L - m\sum_{i=2}^{2} i[ML_i] \qquad (3.46.1)$$

Table 3.12 Effect of calcium and magnesium as well as iron (III) salt components, on fulvic complexing of iron, manganese and copper (model calculations)

Concentration (mg/L)			Share of fulvic acid (%)	Share of fulvic and hydroxofulvic complexes (%)				
Ca	*Mg*	*Fe*(III)		*Ca*	*Mg*	*Fe*(III)	*Cu*(II)	*Mn*(II)
–	–	–	99.1	–	–	–	87.1	4.3
100	–	–	11.6	0.7	–	–	54.2	1.3
100	20	–	11.4	0.7	0.2	–	53.6	1.3
100	20	0.2	8.5	0.5	0.2	98.7	46.4	1.1
100	20	0.5	4.6	0.4	0.1	97.6	31.7	1.0
100	20	1.0	0.9	0.2	0.1	81.0	4.7	0.7
100	20	1.5	0.6	0.2	–	56.3	1.4	0.5
100	20	2.0	0.3	0.1	–	42.5	0.2	0.1

C_{FA} = 10 mg/L (1 × 10^{-5} mol/L); $pH = 7$; C_{Cu} = 0.005 mg/L; C_{Mn} = 0.05 mg/L

where C_L—total concentration of humic substances (mol/L); m—number of metals; $i = 1$ or 2, because humate and fulvic complexes only have ratios 1:1 or 1:2.

The joint solution of balance equations (3.38), (3.39) and (3.46.1) allowed creating a formula of calculating the relative shares of all forms of coexisting metals with known values of their concentration and the total concentration of HS. Calculations are performed using TETRA complex, which is based on known thermodynamic model MINTEOQA 2. A detailed calculation algorithm is given in papers [23, 24].

As an example, Table 3.12 shows the results of model calculations of influence of macroconcentrations of Ca^{2+} and Mg^{2+} main ions and *Fe*(III) ions which form strong fulvic and hydroxofulvic complexes, on binding microconcentrations of Cu^{2+} and Mn^{2+} into corresponding complex compounds. Complex formation of tracer elements is significantly reduced in the presence of calcium and especially iron (III) due to their binding of fulvic ions. Thus, the increase of water mineralization and especially the content of iron (III) compounds increases toxic effect of heavy metals due to their displacement from fulvic (and other) complex compounds and, as a result—the relative content of uncomplexed toxic forms.

Figures 3.18, 3.19, 3.20 and 3.21 give examples of modeling some hydrochemical processes involving metal ions in real natural water based on their chemical composition. This modeling allows identifying the main physical and chemical processes that affect the form of migration of certain metals in the water of a natural water body.

Complexes with amines Patterns of formation of complex compounds of heavy metals with organic amines are the same as in the case of ammonia. Optimal conditions for their formation are shifted towards higher *pH* values because the dissociation constants of amines are higher than of ammonia (Table 3.6).

Fig. 3.18 Proportion of fulvic (FA) hydroxofulvic (HFA) and hydroxo complexes of **a** iron and **b** copper in some rivers of Ukraine

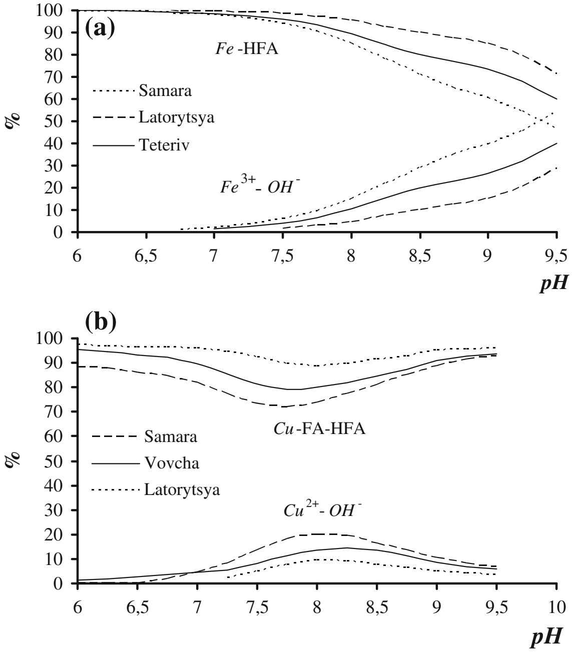


Fig. 3.19 Graph of coexisting forms of **a** nickel in the water of Uzh river and **b** lead in the water of Teteriv river

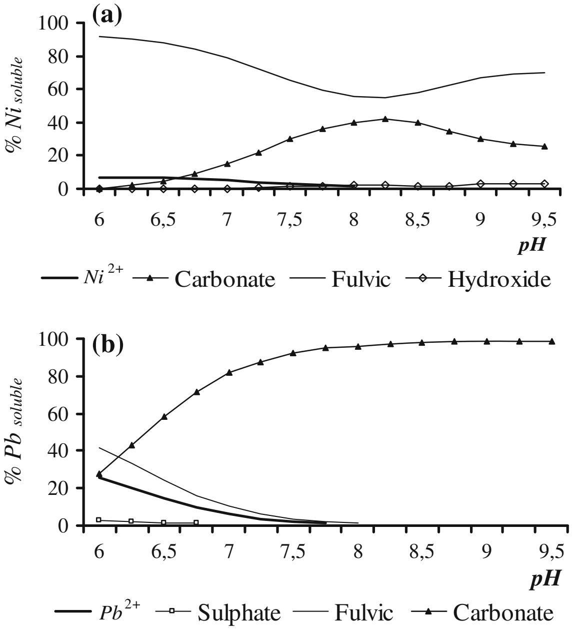
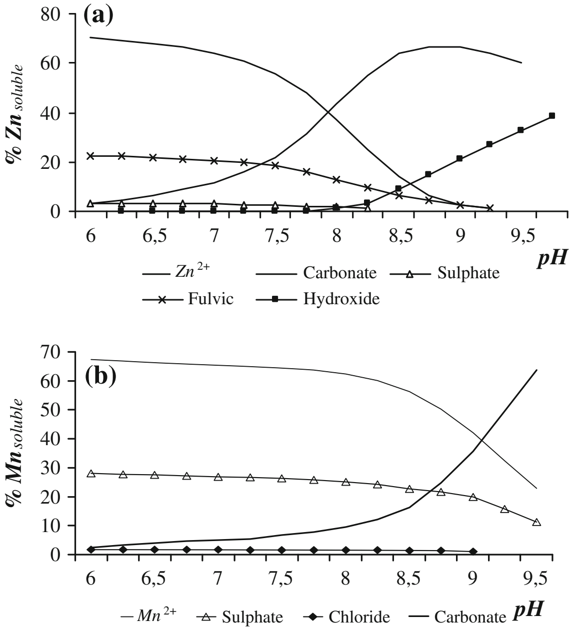


Fig. 3.20 Graph of coexisting forms of **a** zinc in the water of Latorytsya river and **b** manganese in the water of Vovcha river



3.3.3 Overview of Complexation Processes in Surface Water

To calculate the degree of binding of metal ions in complex compounds in natural water the following constants are used:

- stability concentration constant $\beta n'$ (see Eq. (3.37)), expressed through concentration of complex compounds and ions (molecules) that are part of it. Thereby molecular weight of a complex compound and a certain inorganic or organic ligand is constant;
- conditional stability constant $\beta' n(c)$ for systems in which the molecular weight of macroligand is not constant, such as fulvic acids, but is an average value of the sum of molecular weights of associates and depends in particular on the *pH* (see Table 3.11). In this case, the molecular weight of a complex compound is neither constant;
- formal equilibrium constant K'_p (see Eq. (3.41)), in which ligand concentration C_L is the total concentration of all complexed substances of natural water, i.e. concentration of so-called *collective ligand*. Obviously, constant K'_x belongs only to a body of water at the time of water sampling and may vary at different times of the year.

Equation (3.37) implies that the degree of involvement of metal ions in complexes, i.e. the ratio $[ML_n]/[M]$ depends not only on the value of the corresponding stability constant, but also on the concentration of ligand. Natural water most often

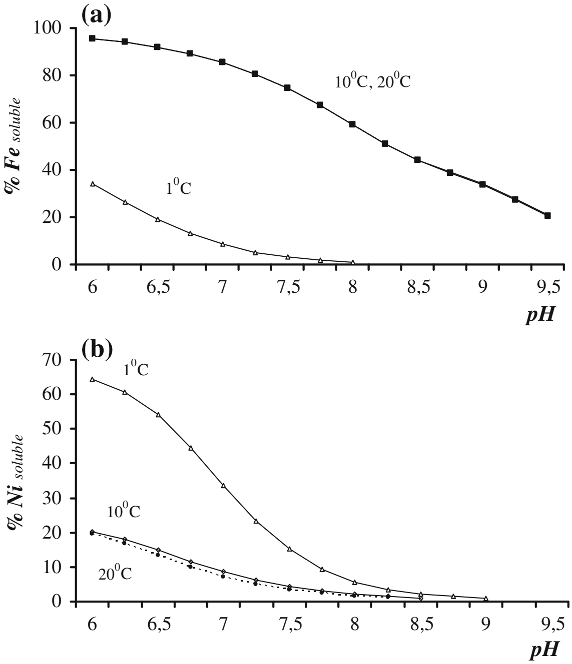


Fig. 3.21 Dependence of forming hydroxofulvic complex compounds of **a** iron and **b** nickel on water temperature of Siversky Donets river, city of Lysychansk

has complex compounds with ratio Me:L = 1:1 (except hydroxo complexes). Therefore, the relative tendency of metals to form complexes can be expressed by the product of β_1 [L]:

$$[MeL]/[Me] = \beta_1 \cdot [L] \tag{3.47}$$

where β_1—stability constant; [L]—concentration of ligand, which in the case of weak acids depends on *pH*. With [MeL]/[Me] < 1 concentration of complexed forms is less than 50 %, while with [MeL]/[Me] $\geq$ 1—equal to or greater than 50 %.

The results of calculations for complex metal compounds with some ligands are shown in Table 3.13. Calculations were performed considering the most typical minimum and maximum concentrations of ligands in surface water. Citric and glutamic acids were selected as representatives of hydroxycarboxylic and amino acids that form with metal ions most stable complexes.

In acidic medium at the minimum concentration of complexing agents chloride complexes of mercury, bicarbonate, carbonate and amino acid complexes of iron (III), as well as complexes of mercury and iron (III) with hydroxycarboxylic and fulvic acids can dominate in surface water, that is to reach more than 50 % of the gross content of dissolved forms of metals.

The proportion of complexed forms of metals, particularly with anions of weak acids, is significantly increased in alkaline medium with a maximum concentration of complexation agents. It is typical for most metals to form fulvic (FC) and carbonate complexes. Apart of them, mercury binds well in chloride complexes, iron

Table 3.13 Relative ability of metal ions to form complexes with some ligands in surface water

Metal	pH = 6, minimum concentration of ligands		pH = 9, maximum concentration of ligands	
	$\beta_1 \cdot [L] < 1,\ [ML] < 50\,\%$	$\beta_1 \cdot [L] \geq 1,\ [ML] \geq 50\,\%$	$\beta_1 \cdot [L] < 1,\ [ML] < 50\,\%$	$\beta_1 \cdot [L] \geq 1,\ [ML] \geq 50\,\%$
Ca^{2+}	$OH^- < \mathrm{Glut}^{2-} < CO_3^{2-} < \mathrm{FA}^{2-} < \mathrm{Cit}^{3-} \leq HCO_3^- < SO_4^{2-}$	–	$\mathrm{Glut}^{2-} < OH^- < HCO_3^- < \mathrm{FA}^{2-}$	$CO_3^{2-} < SO_4^{2-} \approx \mathrm{Cit}^{3-}$
Mg^{2+}	$\mathrm{Glut}^{2-} < OH^- < CO_3^{2-} < \mathrm{FA}^{2-} < \mathrm{Cit}^{3-} < HCO_3^- < SO_4^{2-}$	–	$\mathrm{Glut}^{2-} < OH^- < HCO_3^- < \mathrm{FA}^{2-} < \mathrm{Cit}^{3-}$	$CO_3^{2-} < SO_4^{2-}$
Mn^{2+}	$Cl^- \approx \mathrm{Glut}^{2-} < OH^- < \mathrm{Cit}^{3-} < CO_3^{2-} < SO_4^{2-} \approx HCO_3^- \approx \mathrm{FA}^{2-}$	–	$\mathrm{Glut}^{2-} < Cl^- < OH^- < \mathrm{Cit}^{3-} < HCO_3^-$	$SO_4^{2-} < CO_3^{2-} < \mathrm{FA}$
Co^{2+}	$Cl^- < OH^- < CO_3^{2-} < \mathrm{Glut}^{2-} < \mathrm{Cit}^{3-} < SO_4^{2-} < \mathrm{FA}^{2-} < HCO_3^-$	–	$Cl^- < \mathrm{Glut}^{2-} < OH^-$	$SO_4^{2-} < \mathrm{Cit}^{3-} < HCO_3^- < CO_3^{2-} < \mathrm{FA}^{2-}$
Ni^{2+}	$Cl^- < CO_3^{2-} < OH^- < SO_4^{2-} \approx \mathrm{Glut}^{2-} < HCO_3^{2-} < \mathrm{Cit}^{3-} < \mathrm{FA}^{2-}$	–	$Cl^- < \mathrm{Glut}^{2-} < HCO_3^- \leq OH^-$	$SO_4^{2-} < \mathrm{Cit}^{3-} < CO_3^{2-} < \mathrm{FA}^{2-}$
Fe^{2+}	$SO_4^{2-} < Cl^{2-} < CO_3^{2-} \approx \mathrm{Glut}^{2-} < \mathrm{Cit}^{3-} < OH^- < \mathrm{FA}^{2-} < HCO_3^-$	–	$\mathrm{Glut}^{2-} < SO_4^{2-} < Cl^-$	$\mathrm{Cit}^{3-} < OH^- \approx \mathrm{FA}^{2-} < HCO_3^- < CO_3^{2-}$
Cd^{2+}	$\mathrm{Glut}^{2-} < SO_4^{2-} \approx CO_3^{2-} \approx \mathrm{FA}^{2-} < Cl^- < \mathrm{Cit}^{3-} < OH^-$	–	$\mathrm{Glut}^{2-} < SO_4^{2-}$	$Cl^- < \mathrm{Cit}^{3-} \approx OH^- < CO_3^{2-} \approx \mathrm{FA}^{2-} CO_3^{2-}$
Zn^{2+}	$Cl^- < CO_3^{2-} < SO_4^{2-} \approx \mathrm{Cit}^{3-} \approx \mathrm{Glut}^{2-} \approx \mathrm{FA}^{2-} \leq HCO_3^- < OH^-$	–	$\mathrm{Glut}^{2-} < Cl^-$	$HCO_3^- < SO_4^{2-} < \mathrm{Cit}^{3-} < OH^- < CO_3^{2-} < \mathrm{FA}^{2-}$
Cu^{2+}	$Cl^- < SO_4^{2-} < CO_3^{2-} \approx HCO_3^- \approx \mathrm{Cit}^{3-} < OH^- < \mathrm{Glut}^{2-} \approx \mathrm{FA}^{2-}$	–	Cl^-	$SO_4^{2-} < HCO_3^- < \mathrm{Glut} < \mathrm{Cit}^{3-} < OH^- < CO_3^{2-} < \mathrm{FA}^{2-}$
Pb^{2+}	$\mathrm{Glut}^{2-} < Cl^- \approx \mathrm{Cit}^{3-} < SO_4^{2-} < CO_3^{2-} \approx \mathrm{FA}^{2-} < HCO_3^- < OH^-$	–	$\mathrm{Glut}^{2-} < Cl^-$	$SO_4^{2-} \simeq HCO_3^- \leq \mathrm{FA}^{2-} < \mathrm{Cit}^{3-} < OH^- < CO_3^{2-}$
$Hg^{2+\,*}$	$SO_4^{2-} < CO_3^{2-}$	$Cl^- < \mathrm{Cit}^{3-} < \mathrm{FA}^{2-} < OH^-$	SO_4^{2-}	$CO_3^{2-} < Cl^- < \mathrm{Cit}^{3-} < \mathrm{FA}^{2-} < OH^-$
$Fe^{3+\,*}$	$Cl^- < SO_4^{2-}$	$\mathrm{FA}^{2-} < HCO_3^- < CO_3^{2-} < \mathrm{Cit}^{3-} \approx \mathrm{Glut}^{2-} < OH^- < \mathrm{HFA}^{2-\,\mathrm{b}}$	Cl^-	$SO_4^{2-} < HCO_3^- < \mathrm{Glut}^{2-} < CO_3^{2-} \leq \mathrm{FA} < \mathrm{Cit}^{3-} < OH^- < \mathrm{HFA}^{2-\,\mathrm{b}}$

Concentration intervals of complexation substances (mg/L): chlorides (1–1000), sulfates (1–1000), carbonates (10–600), citric acid H_3Cit (0.01–10), glutamic acid H_2Glut (0.002–0.2), fulvic acids (FA) (1–100) [25, 33]

[a] Calculation was carried out using respectively β_2 and β_3 of dominant hydroxo complexes

[b] Hydroxofulvic iron complexes [*FeOHFA*]

(III) and mercury—into complexes with hydroxycarboxylic acids, and iron (III) mostly forms hydroxofulvic (HFC) complexes. Calcium and magnesium form mainly sulfate and carbonate complexes. Hydroxo complexes of metals except calcium and magnesium may be dominant in alkaline medium. Formation of chloride (except mercury) and amino acid (except iron and copper) complexes in conditions of surface water can be neglected.

Metal ions in their ability to form complexes with some ligands in surface water are arranged in the following series:

$$OH^- : Ca^{2+} < Mg^{2+} < Mn^{2+} < Co^{2+} < Ni^{2+} < Fe^{2+} < Cd^{2+} < Zn^{2+} < Cu^{2+} < Pb^{2+} < \boldsymbol{Hg}^{2+} < \boldsymbol{Fe}^{3+};$$

$$Cl^- : Co^{2+} < Mn^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+} < Fe^{2+} < Pb^{2+} < Fe^{3+} < Cd^{2+} < \boldsymbol{Hg}^{2+};$$

$$SO_4^{2-} : Fe^{2+} < Hg^{2+} < Cd^{2+} < Ca^{2+} \approx Mn^{2+} \approx Zn^{2+} \approx Ni^{2+} < Mg^{2+} \approx Cu^{2+} < Co^{2+} < Pb^{2+} < F3^{3+};$$

$$CO_3^{2-} : Ca^{2+} < Mg^{2+} < Fe^{2+} < Mn^{2+} \approx Co^{2+} < Ni^{2+} \approx Zn^{2+} < Cd^{2+} < Pb^{2+} < Cu^{2+} < Hg^{2+} < \boldsymbol{Fe}^{3+};$$

$$HCO_3^- : Ca^{2+} \approx Mg^{2+} < Mn^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+} \approx Pb^{2+} < Fe^{2+} \approx Co^{2+} < \boldsymbol{Fe}^{3+};$$

$$Cit^{3-} : Mn^{2+} < Mg^{2+} < Pb^{2+} < Fe^{2+} < Ca^{2+} < Co^{2+} \approx Zn^{2+} < Ni^{2+} \approx Cd^{2+} < Cu^{2+} < \boldsymbol{Hg}^{2+} < Fe^{3+};$$

$$Clut^{2-} : Ca^{2+} < Mg^{2+} < Mn^{2+} < Pb^{2+} \approx Fe^{2+} < Cd^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} < Cu^{2+} < \boldsymbol{Fe}^{3+};$$

$$\mathrm{FA}^{2-} : Mg^{2+} < Ca^{2+} < Cd^{2+} < Zn^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} \approx Ni^{2+} < Pb^{2+} < Cu^{2+} < \boldsymbol{Fe}^{3+}(\mathbf{FA}) < \boldsymbol{Hg}^{2+} <$$
$$< \boldsymbol{Fe}^{3+}(\mathbf{HFA})$$

These series do not always correspond to the respective stability constants of complex compounds, because they are based on the most common ligand concentrations in surface water.

Cation complexes, marked in bold, may dominate virtually at any surface water *pH*.

Effect of mineralization and water temperature on the complexation is described above.

Effect of complexation on the degree and pH of hydrolysis of metal ions. Binding of metals in complex compounds significantly reduces the concentration of free M^{z+} ions.

This leads to an increase in the degree of hydrolysis (see Fig. 3.11a) and *pH* of hydrolysis (see Fig. 3.12a). Thus, complexation neutralizes lower *pH* of water under the influence of heavy metals.

Effect of complexation on the solubility of slightly soluble compounds—see Sect. 3.5.2.

Molecular weights and charges of complex compounds. In most cases, macromolecular compounds [12] are truly dissolved forms of metals migration in surface water. Thereby, for Fe^{3+}, Cr^{3+}, Pb^{2+} and Cu^{2+} ions fraction of macromolecular complexes is usually more than half of their gross content, sometimes reaching 95–100 %. For Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+} ions fraction of macromolecular complex compounds is lower and is usually 20–70 %. Ions of Ca^{2+} and Mg^{2+} form a macromolecular complex compounds only in the water of high color, which contain significant amounts of HS.

Table 3.14 presents averaged data on the distribution of metal ions among complex compounds with different molecular weight. For Ca^{2+}, Mg^{2+} and Hg^{2+}

Table 3.14 Medium (in brackets—the most common) degree of binding of metal ions in complex compounds of different molecular weight, % [12]

Metal%	Molecular weight (kDa)			
	$\gtrsim 100$	100–10	10–1	$\lesssim 1$
Ca^{2+}	6.4 (4–8)	4.6 (4–5)	52.0 (40–55)	37.0 (25–40)
Mg^{2+}	No data	13.0 (5–15)	39.5 (30–45)	47.5 (35–50)
Mn^{2+}	15.1 (15–25)	26.3 (30–50)	31.0 (40–55)	27.6 (30–50)
Co^{2+}	No data	37.5 (35–60)	46.5 (55–70)	16.0 (20–30)
Ni^{2+}	No data	33.0 (25–35)	18.0 (15–20)	49.0 (30–60)
Cd^{2+}	25.7 (20–35)	22.7 (10–30)	14.0 (10–20)	37.6 (30–45)
Zn^{2+}	No data	27.5 (25–45)	39.0 (30–65)	33.5 (30–40)
Cu^{2+}	15.0 (10–30)	23.2 (20–40)	43.8 (40–80)	18.0 (10–30)
Pb^{2+}	36.7 (30–60)	30.6 (30–50)	15.2 (5–30)	17.5 (15–30)
Hg^{2+}	5.7 (5–10)	6.4 (5–10)	43.6 (35–75)	44.3 (40–80)
Fe^{3+}	29.0 (20–60)	32.7 (25–60)	25.3 (25–50)	13.0 (10–25)

ions it is characteristic to form complexes with low molecular weight less than 10 kDa. Fe^{2+} and Pb^{2+} ions, in contrast, bind predominantly into macromolecular complex compounds with a molecular weight of 10 kDa. Other metals fall in between.

Distribution of complex compounds according to their charge—anionic, cationic, neutral—can be illustrated by the Dnipro reservoirs [13]:

	Anionic	**Cationic**	**Neutral**
Organic substances	fulvic and humic acids, carboxylic and hydroxycarboxylic acids 50–78%	proteins, polypeptides, amines 1,5–3,5%	polyoses, reduced sugars, hydrocarbons 2,3–10%
Complex compounds	40–80%	6–15%	10–30%

Thus, the main form of migration of metals in surface water, except for calcium, magnesium and in part for manganese and lead are anionic complexes with HS and organic acids.

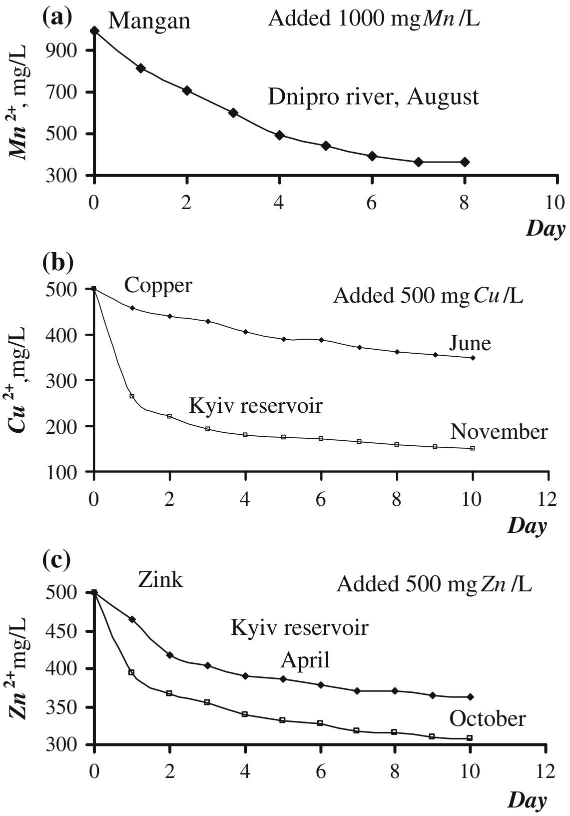


Fig. 3.22 Complexation kinetics for **a** mangan, **b** copper, **c** zink

Kinetics of complex formation. The rate of binding of metal ions in complex compounds depends on the nature of complexing agents, their concentration, water temperature, etc. For example, the binding of Mn^{2+}, $Cu^{2+}$and Zn^{2+} ions into complexes in water of the Dnipro and Desna rivers in different seasons takes place at different rate within a few days [11, 12] (Fig. 3.22).

The rate of complex formation also depends on the concentration of a metal. Thus, with copper concentration of 100 mg/L and 500 mg/L its binding into combined compounds in water of Kiev reservoir for about 50 % occurs within 6 and 1 day, respectively; binding of lead in water of Dnipro-Bug estuary occurs under similar conditions within 7 and 3 days, respectively. The same dependence of complex formation on the concentration of metal ions has also been established for Zn^{2+} and Cd^{2+} ions [10]. Ions of molybdenum (VI) are binding with low molecular weight ligands within several tens of minutes [13].

Thus, the rate of binding of metal ions depends on many factors and can not be definitely predicted. One can only note the trend of acceleration of complex formation with increasing concentration of metal ions, complexing ability of surface water and decreasing molecular weight ligands.

Table 3.15 Long-term averaged values of chemical components in the typical rivers of different physiographic zones in Ukraine (mg/L)

Zone	SO_4^{2-}	HCO_3^-	CO_3^{2-}	$Tart^{2-}$	FA
Carpathians	33.0	91.5	0.066	5	4.1
Forest	26.5	238	0.56	5	6.8
Forest-steppe	38.0	310	0.72	5	5.8
Steppe	233	46.5	1.08	5	4.3
Crimea, mountain	73.5	360	0.84	5	1.0

Modelling of the most common forms of migration of certain metals in the rivers of different geographical zones in Ukraine. The modeling is based on multi-year averaged values of chemical components in the most typical rivers of different physiographic zones in Ukraine (Table 3.15). Tartaric acid (H_2 Tart) was taken as a representative of organic acids, stability constants of complexes with metal ions and molecular weight of which are average among the most common organic acids in surface water. Fulvic acid concentrations (FA) typical for each natural zone were taken from the database of the Ukrainian Hydrometeorological Institute (UHMI).

As a result of the calculations (Table 3.16) the following key patterns have been identified:

- the main form of migration of **calcium** and **magnesium** are uncomplexed aquo-ions (75–90 %). Proportion of complexes with low molecular weight organic acids does not exceed 5–7 %. Proportion of sulphate and carbonate and hydrocarbon complexes increases in passing from forest (3–5 %) to the steppe (7–14 %) zone. Proportion of fulvic complexes does not exceed 6 % and decreases from forest (4–6 %) to mountainous zone (0.4–1 %);
- the most characteristic forms of **mangan** migration are uncomplexed ions (48–76 % in mountain rivers and about 30 % in other zones), carbonate and bicarbonate complexes (11–36 % in mountain rivers and 16–26 % with the increase from forest to steppe zones) and fulvic complexes (10–13 % in mountain rivers and 50–36 % with the decrease from forest to steppe zone). Proportion of sulfate complexes does not exceed 3–5 %, of complexes with organic acids—0.1–0.2 %;
- the most characteristic forms of **zink** migration are uncomplexed ions (25–60 % in mountain streams and 22–25 % in rivers of other zones), carbonate and bicarbonate complexes (15–43 % with an increase from forest to steppe zone and mountain rivers in Crimea). Share complexes with organic acids at the level of 2–3 %. Proportion of sulfate complexes does not exceed 4 % and increases from forest to steppe zone. Proportion of fulvic complexes does not exceed 25 % and decreases from steppe to forest zone (25–16 %) and mountain streams (4–5 %). Proportion of hydroxo complexes is 10–20 %;
- the main form of migration of **lead** are hydroxo complexes (44–47 %) and carbonate and hydrocarbonate compounds (35–50 %). Much lesser are proportions of sulfate (0.3–1.5 %) and fulvic (0.5–4 %) complexes. Proportion of uncomplexed forms does not exceed 4 %, except for the rivers of the Carpathians, where it reaches almost 20 %;

Table 3.16 Averaged data on migration forms of some metals in the surface water of different physiographic zones in Ukraine

Metal	Phisiographic zone	*pH*	Mineralization (mg/L)	Migration forms of metals (%)					
				Mez$^+$	$Me(OH)_x^{z-x}$	MeSO^{z-2}	MeCO_3^0 + MeHCO_3^+	MeTart^{z-2}	MeFA^{z-2} + MeOHFA^{z-3}
Ca^{2+}	Carpathians	7.2	205	87.6	–	3.2	1.8	7.0	0.4
	Forest	7.7	450	83.8	–	2.6	4.5	4.9	4.2
	Forest-steppe	7.7	675	79.9	–	6.0	5.5	4.7	3.9
	Steppe	7.9	863	75.9	–	11.4	6.5	3.5	2.7
	Crimea, mountain	7.9	446	82.7	–	5.1	6.6	4.9	0.7
Mg^{2+}	Carpathians	7.2	205	92.4	–	4.0	1.5	0.6	0.5
	Forest	7.7	450	86.6	–	3.1	3.8	0.4	6.1
	Forest-steppe	7.7	675	82.2	–	7.1	4.8	0.4	5.6
	Steppe	7.9	863	76.4	–	13.7	5.7	0.3	3.8
	Crimea, mountain	7.9	446	86.7	–	6.1	5.8	0.4	1.1
Mn^{2+}	Carpathians	7.2	205	76.1	0.1	2.6	11.2	0.2	9.9
	Forest	7.7	450	31.9	0.1	0.9	16.0	<0.1	51.1
	Forest-steppe	7.7	675	30.1	0.1	2.0	19.6	0.1	48.2
	Steppe	7.9	863	32.0	0.1	4.4	26.2	<0.1	35.8
	Crimea, mountain	7.9	446	47.8	0.2	2.6	36.3	0.1	12.9

(continued)

Table 3.16 (continued)

Metal	Phisiographic zone	*pH*	Mineralization (mg/L)	Migration forms of metals (%)					
				Mez$^+$	$Me(OH)_x^{z-x}$	MeSO^{z-2}	MeCO_3^0 + MeHCO_3^+	MeTart^{z-2}	MeFA^{z-2} + MeOHFA^{z-3}
Cu^{2+}	Carpathians	7.2	205	3.0	7.4	0.13	12.2	0.3	78.0
	Forest	7.7	450	0.3	2.3	<0.1	6.7	<0.1	90.7
	Forest-steppe	7.7	675	0.3	2.3	<0.1	8.7	<0.1	88.7
	Steppe	7.9	863	0.4	3.7	0.1	13.1	<0.1	82.8
	Crimea, mountain	7.9	446	0.9	9.8	0.1	36.7	<0.1	52.3
Zn^{2+}	Carpathians	7.2	205	58.6	8.8	2.5	15.2	2.1	4.9
	Forest	7.7	450	25.1	18.8	0.9	27.1	3.0	25.1
	Forest-steppe	7.7	675	23.2	17.4	2.0	33.2	2.8	22.5
	Steppe	7.9	863	21.9	19.1	3.7	37.3	2.1	15.8
	Crimea, mountain	7.9	446	25.9	22.6	1.8	43.2	3.1	4.4
Pb^{2+}	Carpathians	7.2	205	18.3	43.8	1.4	34.9	0.1	1.5
	Forest	7.7	450	3.9	46.8	0.3	44.9	0.2	3.9
	Forest-steppe	7.7	675	3.4	41.2	0.6	51.2	0.2	3.3

- **copper** is bound mainly in fulvic complexes (50–90 %), proportion of which decreased slightly from forest to steppe zone. Proportion of complexes with organic acids is negligible (<0.1 %) and only in the mountain rivers of the Carpathians it reaches 0.3 %. Proportion of carbonate and hydrocarbonate complexes increases from forest (7 %) to the steppe (13 %) zones, and in mountain rivers of Crimea it reaches almost 40 %. Proportion of hydroxo complexes does not exceed 10 %, of uncomplexed ions—3 %.
- **iron (III)** is bound in hydroxofulvic complexes by 99.5–99.9 % all natural zones, except Crimea mountain streams (98 %). Proportion of hydroxo complexes does not exceed 2 %. Uncomplexed Fe^{3+} ions, and sulfate, carbonate, and hydrocarbonate complexes with organic acids are virtually absent.

It should be noted that the distribution of metals among different forms in specific water bodies may differ from the results of model calculations presented in Table 3.16. This is because the mineralization and pH and concentration of chemical ingredients in a specific water body may differ significantly from the above averaged values. Therefore, the calculation results only indicate the trend of migration forms of metals in surface water according to geographical zones.

Effect of complex formation on the toxic effects of metal ions on hydrobionts

The most toxic forms of metals for aquatic organisms are, as is well-known, free aquo-cations, some oxo anions (e.g. CrO^{2-}) and organometallic compounds. Complex metal compounds, especially with natural ligands, are significantly less toxic or do not exhibit toxic properties at all. Detoxification of heavy metals is also observed in their interaction with metabolites of aquatic organisms. These processes are discussed in detail in Sect. 4.6 and in the monograph [12]. Based on numerous publications one can draw the following general conclusions:

- ions and compounds of heavy metals in lower oxidation degree (Sn^{2+}, Fe^{2+}, Cu^{+}, Hg^{+}, Cr^{3+}, etc.) are less toxic compared with higher degrees of oxidation (Sn^{4+}, Fe^{3+}, Cu^{2+}, Hg^{2+}, CrO_4, etc.);
- electroneutral forms, such as $Cu(OH)_2$ are more toxic than charged ones, because they easier penetrate the cell membrane;
- detoxification of heavy metal ions is increasing with hither concentration of complexing agents, stability and molecular weight of complex compounds.

It should be noted, however, that these patterns are varying depending on aquatic organisms of different nature and different environmental conditions (pH, Eh, $t°$, mineralization, water chemistry, etc.).

3.4 Redox Processes

Among the elements that can change the oxidation degree, in the surface water are present mainly nitrogen, sulfur, iron, mangan, chromium, copper, cobalt and mercury. In redox processes some organic compounds are also involved. The direction and completeness of redox processes are affected by redox potential Eh and *pH* of water, its temperature and mineralization (ionic strength), and the presence of complexing agents in the case of metal compounds.

Redox potential and water *pH* are greatly affected by dissolved oxygen: with an increase in its concentration Eh and *pH* are increased, and with a decrease—decreased (see Sect. 4.1).

Redox processes can occur by the following formulas, each of them corresponding to a particular expression of the Nernst equation:

A. ***a*** Oxidant + ne b Reductant

$$Eh = E_0 + \frac{RT}{nF} \ln \frac{a_{ox}^{a}}{a_{Red}^{b}}$$

$$\mathrm{Eh} = \mathrm{E}_0 + \frac{0.0591 + 0.002(t - 25^{\circ} C)}{n} lg \frac{[Ox]^{a} f_{Ox}^{a}}{[Red]^{\hat{a}} f_{Red}^{\hat{a}}}, \tag{3.48}$$

Note: *Ox*—Oxidant, *Red*—Reductant.

where *aOx*, [*Ox*], *fOx* and *aRed*, [*Red*], *fRed*—activity, concentration and activity coefficient of ions of oxidant and reductant, respectively; *R*—gas constant; *T*—solution absolute temperature (°C); *F* = 96,500 coulombs (Faraday); *n*—number of electrons involved in the redox reaction. Eh and E_0 values are expressed in volts.

B. $\boldsymbol{a}\ Ox + mH^{+} + ne \rightleftarrows \text{в}\ Red + qH_2O$

$$\mathrm{Eh} = \mathrm{E}_0 + \frac{0.0591 + 0.002(t - 25^{o} C)}{n}\ \mathrm{lg} \frac{[Ox]^{a} f_{Ox}^{a} [H^{+}]^{m} f_{H^{+}}^{m}}{[\mathrm{Red}]^{\text{в}} f_{\mathrm{Red}}^{\text{в}}} \tag{3.49}$$

C. $a\ Ox + q\ H_2O + ne \rightleftarrows \text{в}\ Red + m\ O^{-}$

$$\mathrm{Eh} = \mathrm{E}_0 + \frac{0.0591 + 0.002(t - 25^{\circ} C)}{n} lg \frac{[\mathrm{Ox}]^{a} f_{Ox}^{a}}{[\mathrm{Red}]^{\text{в}} f_{\mathrm{Red}}^{\text{в}} [OH^{-}]^{m} f_{OH^{-}}^{m}} \tag{3.50}$$

If complex compounds of oxidized *COx* and reduced *CRed* metal ions are present in natural water, their relative total content (%) is calculated by formulas:

$$\textbf{A}.\quad \frac{C_{Ox}}{C_{Red}} = \frac{1 + \sum_1^p \beta_{p(Ox)} [L]^p}{1 + \sum_1^q \beta_{q(Red)} [L]^q} \cdot 10^{\frac{(E_h - E_0)n}{0.0591 + 0.002(t - 25\,^{\circ}\mathrm{C})}}; \tag{3.51}$$

$$\textbf{B}.\quad \frac{C_{Ox}}{C_{Red}} = \frac{1 + \sum_1^p \beta_{p(Ox)} [L]^p}{1 + \sum_1^q \beta_{q(Red)} [L]^q} \cdot 10^{\frac{(E_h - E_0)n}{0.0591 + 0.002(t - 25\,^{\circ}\mathrm{C})} + mpH}; \tag{3.52}$$

$$\textbf{C}.\quad \frac{C_{Ox}}{C_{Red}} = \frac{1 + \sum_1^p \beta_{p(Ox)}[L]^p}{1 + \sum_1^q \beta_{q(Red)}[L]^q} \cdot 10^{\frac{(E_h - E_0)n}{0.0591 + 0.002(t - 25\,^\circ\mathrm{C})} + \frac{1}{m(14 - PH)}}; \tag{3.53}$$

$$\textbf{D}.\quad C_{Ox} = 100/(1 + \frac{1}{x}); C_{Red} = 100 - C_{Ox}; x = C_{Ox}/C_{Red}, \tag{3.54}$$

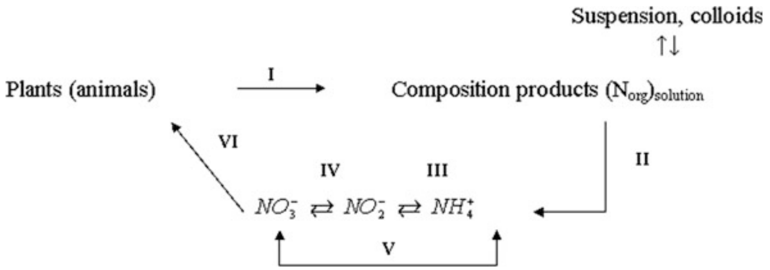
where $\beta p(Ox)$ and $\beta q(Red)$—respectively stability constants of complex compounds of oxidized and reduced metal ions with ligand (ligands) L; p and q—respectively the number of ligands that are part of complex compounds; Eh—redox potential of natural water (v), measured with platinum indicator electrode; E0—normal redox potential of the corresponding system.

Redox potential of a chemical system (Fe^{3+}–Fe^{2+}, NO_3^-–NH_4^+, SO_4^{2-}–S^{2-}etc.) depends on the normal capacity of E0, the ratio of activities of oxidized and reduced forms, as well as *pH* and temperature environment. However, different redox systems coexist in surface water, therefore calculating of water Eh on the basis of its chemical composition is impossible. At the same time, by measuring the Eh of natural water, which for surface water usually ranges from –0.100 to 0.700 V, and its *pH* and temperature, it is possible to calculate the relative content of oxidized and reduced forms of a particular ingredient for by Eqs. (3.48)–(3.54). Similar calculations enable simulate the impact of various factors on the redox state of the elements in natural water.

3.4.1 Nitrogen Compounds

NO_3^-, NO_2^- and NH_4^+ ions are inorganic forms of nitrogen which are present in surface water and are part of a variety of biochemical and physico-chemical processes. Toxic ammonia NH_3 molecules appear only in the water with high *pH*, temperature and the presence of ammonium (see Table 3.5 and Fig. 3.10). In organic compounds nitrogen is part of protein, amino acids, amines, amides, urea, metabolic products of aquatic organisms, etc. ("organic nitrogen" N_{org}).

Mutual transformation of some nitrogen compounds into other is a complex biochemical and physical-chemical process, which in general can be expressed by the following diagram:



Processes I, II and VI can not be described by certain mathematical relationships, so they can not be modeled. It should be noted, that at low *pH*, Eh and temperature *NH* ions, which are the first inorganic products of biochemical decomposition of aquatic organisms, accumulate in water. At high *pH*, Eh and temperature the proportion of NO_3^- ions increases, but their absolute concentration can be significantly decreased due to consumption by aquatic organisms in growing season. NO_2^- ions in natural water are unstable and depending on the *pH*, Eh, temperature and activity of water bacteria are easily oxidized to NO_3^- or reduced to NH_4^+. The presence of inert molecules N_2, that enter into surface water due to diffusion of air and denitrification during the interaction of nitrogen-free substances (starch, cellulose, etc.) with nitrites, can be neglected.

Preliminary calculations with taking into account the processes III and IV showed that at $pH < 8$ and $\mathrm{Eh} < 0.4\,\mathrm{V}$ the proportion of unstable NO_2^- ions can exceed the proportion of NO_3^- and NH_4^+ ions. This does not correspond to a real state of equilibrium in surface water, where the proportion of NO_2^- is always much lesser than the proportion of NO_3^- and NH_4^+. Therefore, close enough to the real conditions of natural water is modeling the process $NO_3^- \rightleftarrows NH_4^+$ by formula:

$$NO^{3^-} + 10H + 8e \rightleftarrows NH_4 + 3H_2O, \mathrm{E0} = +0.87\,\mathrm{V}. \tag{3.55}$$

Nernst equation for equilibrium (3.55) looks like:

$$Eh = 0.87 + \frac{0.0591 + 0.002(t - 25\,°\mathrm{C})}{8} \cdot \lg \frac{\left[NO_3^-\right] \cdot f_{NO_3^-} \cdot \left[H^+\right]^{10} \cdot f_{H^+}^{10}}{\left[NH_4^+\right] \cdot f_{NH_4^+}} \tag{3.56}$$

With equal concentrations of NO_3^- and NH_4^+ Eq. (3.56) looks like

$$Eh = 0.87 + \frac{0.0591 + 0.002(t - 25\,°\mathrm{C})}{8} \cdot \lg\left[H^+\right]^{10} \cdot f_{H^+}^{10} \tag{3.57}$$

Figure 3.23 shows the results of calculating the relationship between Eh and *pH* at different temperatures. Above the calculated curves is a zone of dominance of

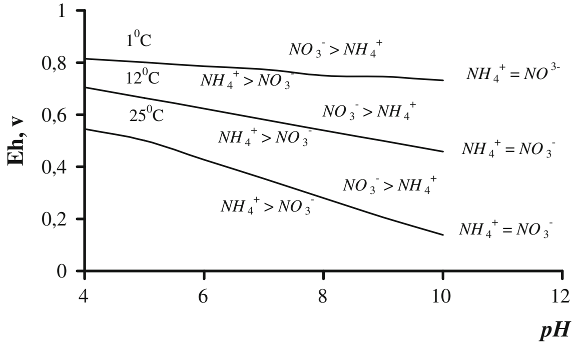


Fig. 3.23 NO_3^- and NH_4^+ domination zones depending on *pH*, Eh and water temperature

NO_3^- ions, below—of NH_4^+ ions. With higher pH and temperature NO_3^- dominance zone increases. This corresponds to the real state of surface water when in summer with high temperature an intensive photosynthesis with oxygen and absorption of carbon dioxide takes place, thereby increasing pH and consequently increasing NO_3^- dominance zone. Winter with low temperatures and decomposition of organic matter features increased content of carbon dioxide, resulting in reduced pH and increased area under the domination of NH_4^+. These processes are affected by mineralization (ionic strength) of water, but only through changes in the activity coefficient of H^+, ions, since the activity coefficients of NO_3^- and NH_4^+ are equal.

3.4.2 Sulfur Compounds

In surface water, depending on the Eh and pH, of the oxidation degree of sulfur is 2 (H_2S, organic compounds) and +6 (SO_4^{2-}). SO_4^{2-} ions are biologically unstable and in the absence of oxygen in pore water are reduced to hydrogen sulfide. In this case, the main role is played by sulfate-reducing bacteria, which are active in the presence of organic matter (reduction of sulfate):

$$2\mathrm{SO}_4^{2-} + 5C + 6H_2O \rightarrow 2H_2S + 2H_2 + CO_2 + 4HCO_3^-$$

Equilibrium state between sulfate-ions and hydrogen sulfide is expressed by following reaction equation.

$$SO_4^{2-} + 10H^+ + 8e \rightleftarrows H_2S + 4H_2O\, E_0 = +0.31\,\mathrm{V} \tag{3.58}$$

$$Eh = 0.31 + \frac{0.059 + 0.002(t - 25°\mathrm{C})}{8} \cdot \lg \frac{\left[SO_4^{2-}\right] \cdot f_{SO_4^{2-}} \cdot \left[H^+\right]^{10} \cdot f_{H^+}^{10}}{[H_2S]} \tag{3.59}$$

Eh and pH on the transition SO_4^{2-}–H_2S for 50 % can be calculated by equation $\left(\left[SO_4^{2-}\right] \cdot f_{SO_4^{2-}} / [H_2S] = 1\right)$:

$$Eh = 0.31 + \frac{0.059 + 0.002(t - 25\,°\mathrm{C})}{8} \cdot \lg\left[H^+\right]^{10} \cdot f_{H^+}^{10} \tag{3.60}$$

It follows from this equation that the areas of SO_4^{2-} and H_2S dominance depend not only on Eh, pH and t°, but also on mineralization (ionic strength) of water, which affects f_{H^+}.

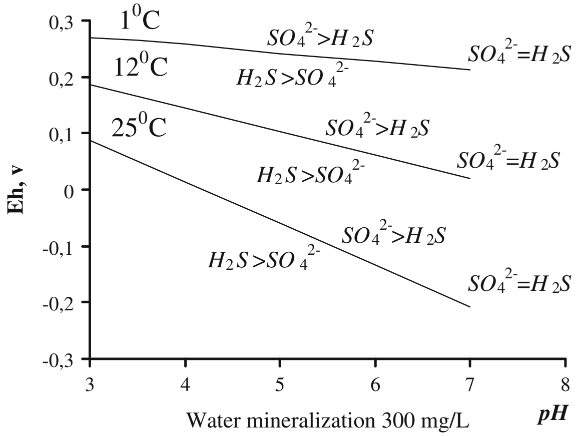


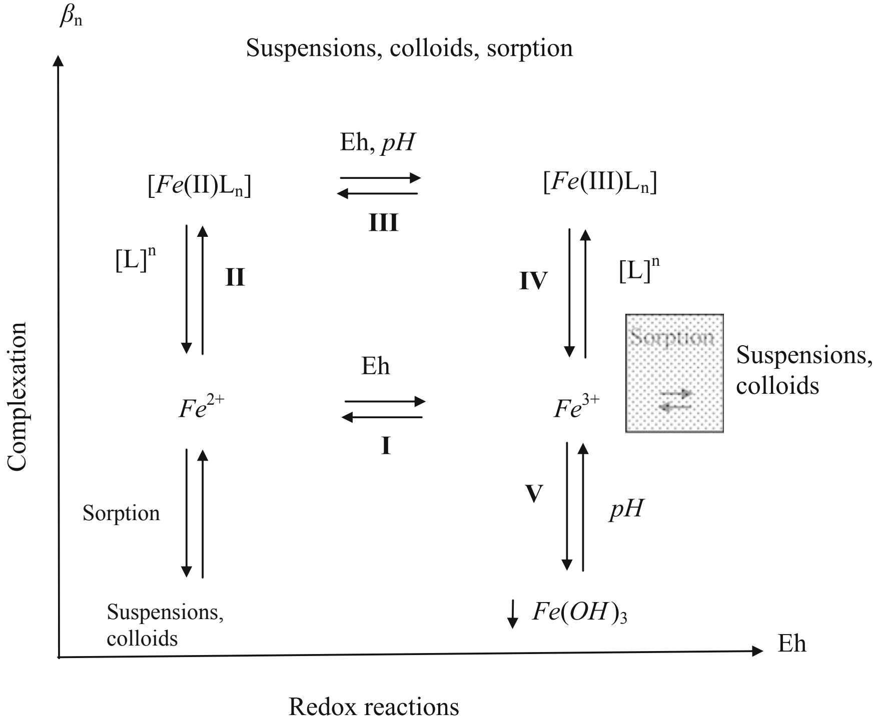
Fig. 3.24 SO_4^{2-} and H_2S domination zones depending on *pH*, Eh and water temperature

The results of calculations of the relationship between Eh and *pH* reveal (Fig. 3.24) that with hither temperature and *pH* of water SO_4^{2-} dominance zone increases and H_2S dominance zone decreases accordingly. Increasing water mineralization from 70 to 7800 mg/L extends the dominance zone of sulfate ions only by 0.0014 V.

3.4.3 Iron, Mangan, Chromium

Iron Depending on the redox potential of natural water iron exhibits oxidation degrees +2 and +3. Compounds of iron (III) are the most common. Iron (II) and its compounds are formed in water with low values of Eh and *pH* (e.g. hypolimnion water of eutrophic lakes, groundwater, etc.). Dissolved oxygen facilitates oxidation of *Fe* (II) to *Fe* (III). Oxidation of Fe^{2+} ions to Fe^{3+} occurs rapidly, within minutes, whereas the complexed with organic substances iron (II), mainly humic of nature, is oxidized to iron (III) slowly over several days. These processes can be represented by a general diagram (see below).

Hydroxo complexes and complex compounds of iron (II) and iron (III) are involved in this arrangement given the conditions of natural water. Relation I depends on Eh, *t*° and water mineralization and equations II–IV—on Eh, *pH*, concentration of complexed agents, stability constants of complex compounds, temperature and water mineralization. Relations IV and V depend on the solubility product of $Fe(OH)_3$, *pH*, concentration of complexing agents, stability constants of complex compounds and water mineralization.



Relations II and IV are calculated by Eq. (3.39); calculation of relation V is given in Sect. 3.5.

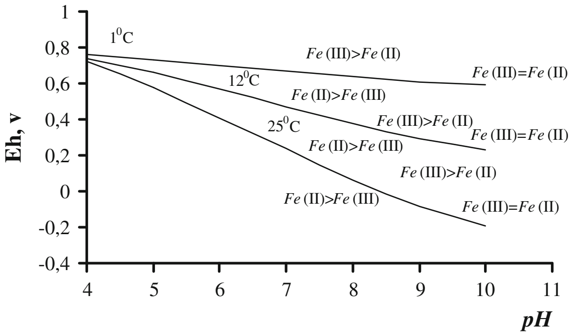
The relative total content of oxidized and reduced metal ions calculated by Eq. (3.51). For the system *Fe* (III)–*Fe* (II), under conditions of hydroxo complex formation, Eq. (3.51) will look like:

$$\frac{C_{Fe(III)}}{C_{Fe(II)}} = \frac{1 + \beta'_{FeOH^{2+}} \cdot [OH^-] + \beta'_{Fe(OH)_{2+}} \cdot [OH^-]^2 + \beta'_{Fe(OH)_3^0} \cdot [OH^-]^3}{1 + \beta'_{FeOH^+} \cdot [OH^-] + \beta'_{Fe(OH)_2^0} \cdot [OH^-]^2} \times 10^{\frac{Eh - 0.77}{0.0591 + 0.002(t - 25\,^{\circ}\mathrm{C})}} \tag{3.61}$$

where β'—concentration stability constants; 0.77—normal redox potential of the system Fe^{3+}–Fe^{2+} (v).

If $C_{Fe(III)} = C_{Fe(II)}$, then the relationship between Eh and *pH* can be calculated by the following equation obtained after taking logarithm of Eq. (3.61):

Fig. 3.25 *Fe*(III) and *Fe*(II) hydroxo complexes domination zones depending on *pH*, Eh and water temperature



$$\frac{C_{Fe(III)}}{C_{Fe(II)}} = \frac{1 + \beta'_{FeOH^{2+}} \cdot [OH^-] + \beta'_{Fe(OH)_{2+}} \cdot [OH^-]^2 + \beta'_{Fe(OH)_3^0} \cdot [OH^-]^3}{1 + \beta'_{FeOH^+} \cdot [OH^-] + \beta'_{Fe(OH)_2^0} \cdot [OH^-]^2} \times 10^{\frac{Eh-0.77}{0.0591+0.002(t-25\,^\circ\mathrm{C})}} \tag{3.62}$$

Figure 3.25 shows the results of calculations for different temperatures. The areas of iron (III) hydroxo complexes and iron (II) dominance (>50 %) are strongly influenced by water temperature. The increase in water mineralization from 70 to 7800 mg/dm^3 extends the dominance zone of *Fe* (III) compounds by 0.02–0.03 (V).

In the presence of other complexing agents—fulvic acids, organic acids, sulfates, carbonates, etc. proportion of iron (III) compounds increases and of iron (II) compounds is reduced because complex compounds of *Fe* (III) are more stable than the corresponding compounds of *Fe* (II).

Mangan In surface water mangan most often has oxidation degrees +2 (Mn^{2+}, complex and slightly soluble compounds sorbed on suspensions) and +4 (mostly suspensions and colloids MnO_2). Oxidation of *Mn* (II) to MnO_2 is a complex physico-chemical and microbiological process which occurs in several stages at different rates, depending on the *pH*, Eh, *t*° and dissolved oxygen concentration [12, 16]:

$$Mn(II) + O_2 \overset{Slowly}{\rightarrow} \downarrow MnO_2,$$

$$Mn(II) + \downarrow MnO_2 \overset{Rapidly}{\rightarrow} \downarrow Mn(II) \cdot MnO_2,$$

$$\downarrow Mn(II) \cdot MnO_2 + O_2 \overset{Slowly}{\rightarrow} 2 \downarrow MnO_2,$$

In the presence of complexing compounds the oxidation of *Mn* (II) to MnO_2 is slowed down.

Physico-chemical processes in surface water with compounds *Mn* (II) and *Mn* (IV) can be represented by the following diagram:

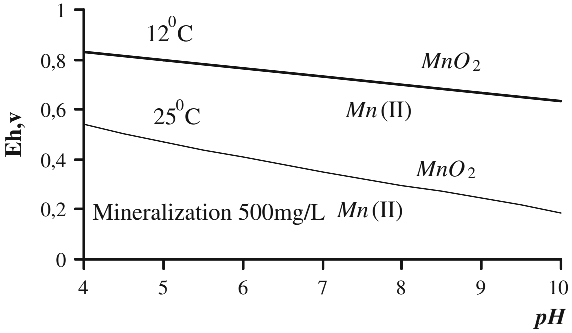
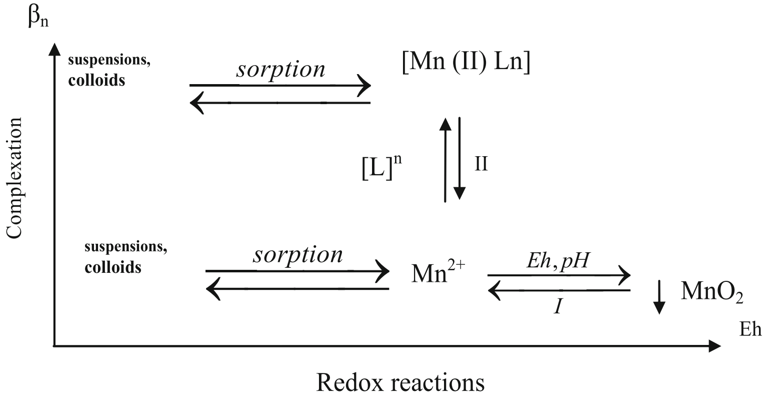


Fig. 3.26 *Mn*(II) and *Mn*(IV) compounds domination zones depending on *pH*, Eh and water temperature



Relation I is calculated by equation:

$$\downarrow MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2HO_2\; E_0 = +1.23\,\text{V},$$

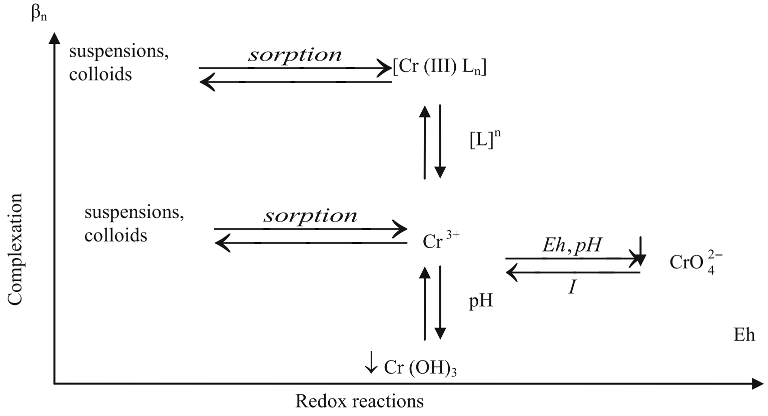
$$Eh = E_0 + \frac{0.059 + 0.002(t^\circ - 25\,^\circ\text{C})}{2} \cdot \lg \frac{[H^+]^4 \cdot f_{H^+}^4}{[Mn^{2+}] \cdot f_{Mn^{2+}}}$$

Taking into account that $[Mn^{2+}] = SP_{Mn(OH)_2}/[OH^-]^2$, we obtain equation

$$Eh = 1.23 + \frac{0.059 + 0.002(t^\circ - 25\,^\circ\text{C})}{2} \cdot \lg \frac{K_{H_2O}^2 \cdot [H^+]^2 \cdot f_{H^+}^2}{SP_{Mn(OH)_2}} \qquad (3.63)$$

Calculated by this equation dominance zones of MnO_2 and mangan (II) compounds, depending on the Eh and *pH*, are shown in Fig. 3.26. Mineralization of water has little effect on the relation I.

Chrome In surface water, chromium has oxidation degree +3 (Cr^{3+}, complex compounds, some slightly soluble compounds, sorbed on suspensions and colloids) and +6 (salts of chromic acid). The relationship between various chromium compounds can be represented by the following diagram:



Relation I is calculated by equation:

$$CrO_4^{2-}+8H^{+}+3e\rightleftarrows Cr^{3+}+4H_2O\quad E_0=+1.48\,\mathrm{V}$$

$$Eh=E_0+\frac{0.0591+0.002(t^\circ-25\,^\circ\mathrm{C})}{3}\cdot\lg\frac{\left[CrO_4^{2-}\right]\cdot\left[H^+\right]^8\cdot f_{CrO_4^{2-}}\cdot f_{H^+}^8}{\left[Cr^{3+}\right]\cdot f_{Cr^{3+}}}\quad E_0=1.48\,\mathrm{V}$$

Within pH interval 5–10 the solution is dominated by $HCrO_4^-$ and CrO_4^{2-} (see Fig. 3.9) and $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$ (see Table 3.7), therefore Eq. (3.52) for the system Cr (VI)–Cr (III) will look like:

$$\frac{C_{Cr(VI)}}{C_{Cr(III)}}=\frac{1+[H^+]/K_2'}{1+\sum_1^4\beta_n'\cdot[OH^-]^n}\cdot10^{\frac{(Eh-E_0)\cdot3}{0.0591+0.002(t-25\,^\circ\mathrm{C})}+8pH}\tag{3.64}$$

where K'_2—concentration constant of chromic acid dissociation; β'_n—concentration stability constants of chromium (III) hydroxo complexes.

By taking logarithm of Eq. (3.64) and assuming that C_{Cr} (VI) = C_{Cr} (III), we obtain the equation for calculating Cr (VI) dominance zones and hydroxo complexes of chromium (III) depending on the Eh and pH:

$$Eh=\left(\frac{E_0\cdot3}{0.0591+0.002(t-25\,^\circ\mathrm{C})}-\lg\frac{1+[H^+]/K_2'}{1+\sum_1^4\beta_n'\cdot[OH^-]^n}-8pH\right)\times\frac{0.0591+0.002(t-25\,^\circ\mathrm{C})}{3}\tag{3.65}$$

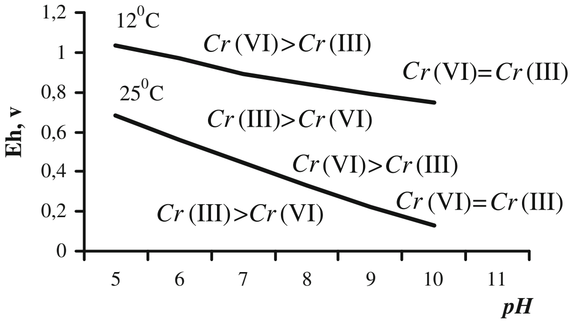


Fig. 3.27 *Cr*(VI) and *Cr*(III) domination zones depending on *pH*, Eh and water temperature

The calculation results are shown in Fig. 3.27. They are little dependent on mineralization (ionic strength) of water.

3.4.4 Organic Compounds

Redox reactions involving organic compounds are complex physical, chemical, biological and microbiological processes. Under the conditions of natural aquatic ecosystems a major role is played by microbiological processes affected by *pH*, Eh, temperature and presence of catalysts. Redox processes involving some specific organic pollutants of the environment are considered in the monograph [31] and with the involvement of humic substances—in Sect. 3.7.

3.5 Slightly Soluble Compounds

In natural aquatic ecosystems soluble compounds are formed by metal cations with charge $z \geq 2$ with anions of strong or weak acids, including ions OH^{-} (hydroxides, carbonates, phosphates, sulfides, sulfates, etc.). The main characteristic of the solubility of slightly soluble compounds is their solubility product:

$$\downarrow Me_nA_m \rightleftarrows nMe + mA$$

$$SP_{Me_nA_m} = a_{Me}^n \cdot a_A^m = [Me]^n \cdot [A]^m \cdot f_{Me}^n \cdot f_A^m \tag{3.66}$$

where a—ion activity; *f*—their activity coefficients (for notational simplicity charges of *Me* cation and *A* anion are not specified).

Using the product of solubility one can calculate concentration of metal ion, which is part of slightly soluble compounds. However, the solution contains its molecules whose concentration is calculated by the equation:

$$\left[Me_nA_m^0\right] = \beta_{Me_nA_m} \cdot SP_{Me_nA_m} \tag{3.67}$$

For example, the concentration of molecules of $Fe(OH)_3^0$, which do not depend on *pH*, is calculated by the equation:

$$\left[Fe(OH)_3^0\right] = \beta_{Fe(OH)_3^0} \cdot SP_{Fe(OH)_3}$$

If the stability constant of *MenAm* or *MeAm* complex is unknown, the molecular solubility of *MenAm* or *MeAm* precipitate is impossible to calculate. However, it should be noted that the more ionic is *Me–A* bond, the lower is the concentration of soluble compounds molecules, as salts with ionic bonding easily dissociate in aqueous solution.

3.5.1 Effect of pH on the Solubility of Slightly Soluble Compounds

Solubility of slightly soluble compounds, composed of anions of strong acids (sulphates, chlorides) and metal cations, which are not hydrolysed, does not dependent on *pH*. If the soluble compounds include anions of weak acids (CO_3^{2-}, PO_4^{3-}, S^{2-}, OH^- etc.) and metal cations that hydrolyze, then with lower *pH* their solubility increases, such as $CaCO_3$ (see Fig. 3.6), metal hydroxides (see Fig. 3.13) etc. due to protonation of acid anions or formation of water molecules. Increasing *pH* does not affect the solubility, except amphoteric hydroxides.

3.5.2 Influence of Complexation and Water Mineralization

Surface water always contains compounds, with anions of which metal cations are able to form complexes. This causes a change in the solubility of slightly soluble compounds. If anion (ligand) is not included in the slightly soluble compound, then the increase of its concentration, i.e. the ionic strength of the solution, leads to an increase in solubility due to reduced ion activity coefficients in Eq. (3.66). If an anion of ligand is part of slightly soluble compound, the increase of its concentration first leads to decrease in solubility, while further increase in the concentration increases solubility due to formation of the corresponding complex compound (e.g., anionic hydroxo complexes in case of amphoteric hydroxides of aluminum, chromium, lead—see Fig. 3.13).

3.5.3 General Pattern of Calculating Solubility of Slightly Soluble Compounds

Solubility S (mol/L) of a slightly soluble compound in the presence of ligands L is the sum of all forms of metal, which are in equilibrium (eq) with the solid phase:

$$S = [Me] + \sum_{1}^{n} [MeL_n] \tag{3.68}$$

The concentration of Me cations with known concentration of A anions, which are part of slightly soluble compounds $MeAm$, equals:

$$[Me] = SP'_{MeA_m}/[A]^m \tag{3.69}$$

Dissolution of a slightly soluble compound in the presence of ligands L occurs by the equation:

$$\begin{gathered} \downarrow MeA_m + nL \rightleftarrows MeL_n + mA \\ K_{eq} = \frac{[MeL_n] \cdot [A]^m}{[L]^n} \cdot \frac{[Me]}{[Me]} = SP'_{MeA_m} \cdot \beta'_{MeL_n} \\ [MeL_n] = SP'_{MeA_m} \cdot \beta'_{MeL_n} \cdot \frac{[L]^n}{[A]^m} \end{gathered} \tag{3.70}$$

By combining Eqs. (3.68)–(3.70), we obtain:

$$S(mol/L) = \frac{SP'_{MeA_m}}{[A]^m} \cdot \left(1 + \sum_{1}^{n} \beta'_{MeL_n} \cdot [L]^n\right) \tag{3.71}$$

$$S(mgMe/L) = S(mol/L) \cdot 1000 \cdot A_T \tag{3.72}$$

where A_T—atomic weight of a metal; PS' and β'—concentration values of the product of solubility and stability constant, which depend on mineralization (ionic strength) and water temperature.

As an example, Fig. 3.28 shows the results of calculating the solubility of $CaCO_3$ and $Fe\ (OH)_3$, depending on the pH in the presence of sulfonic acid (10 mg/L) and citric acid (1 mg/L) in natural water with a concentration of hydrocarbons 300 mg/L and mineralization of 500 mg/L. The selected agent concentrations are the most widespread in surface water [25, 32].

In both cases, fulvic acids affect the solubility of slightly soluble compounds in much stronger way than citric acid (representative of hydroxycarboxylic acids). In the case of calcium carbonate, at higher pH its solubility initially decreases due to the increase of CO_3^{2-}concentration. Citrate ions have little effect on this process. Formation of fulvic complexes increases the solubility of $CaCO_3$, especially at

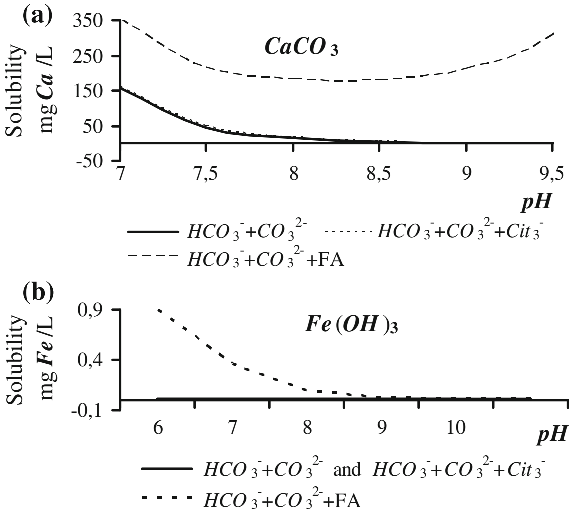


Fig. 3.28 Effect of complexation on the solubility of $CaCO_3$ **a** and $Fe(OH)_3$ **b** in natural water

$HCO_3^-+CO_3^{2-}$=300 mg/L, citric acid = 1 mg/L, fulvic acid (FA) =10 mg/L, t=25°C, mineralization 500 mg/L

$pH > 8$, due to an increase in their stability constants with increasing pH (see Table 3.11). The solubility of iron hydroxide (III) within pH interval 6–10 remains constant and equal to 0.017 mg*Fe*/L (see Fig. 3.13). Citrates with their concentration of 1 mg/dm^3 virtually have no effect on the solubility. Formation of hydroxo-fulvic complexes considerably increases the solubility of iron hydroxide, however, at higher pH, it is decreased and at $pH > 8$ fulvates with their concentration of 10 mg/dm^3 do not affect the solubility. It should be noted that in surface water concentration of *Fe* (III) is often much higher than calculated in the presence of fulvic acids. Perhaps iron (III) is bound with metabolites of aquatic organisms in complex compounds and is in the form of colloidal particles, which are not separated during filtering water through standard membrane filters with pore size of 0.45 µm. The monograph [12] presents data on migration of large proportion of iron (III) in surface water precisely in the form of negatively charged colloids, which are adsorbed on the surface of organic compounds, in particular of humic nature.

3.6 Sorption-Desorption Processes in "Water-Suspensions—Bottom Sediments" System

Sorption of chemical ingredients in surface water on organomineral suspensions and colloids is an important factor of their migration in aquatic ecosystems, and suspension sedimentation and coagulation of colloids—of their accumulation in the bottom sediments and water self-purification. Under certain conditions, adsorbed compounds may desorb, which leads to self-pollution of water.

Sorbents—suspensions, colloids, bottom sediments—are not homogeneous. They may contain a mixture of various clay minerals, manganese dioxide, hydroxide of iron (III), organic detritus, etc. Sorbates—metal ions, their complexes, organic matter, etc.—in the aqueous phase they can be in different forms (cations, anions, electroneutral low molecular weight and high molecular weight compounds). Thus, the distribution of chemical compounds in the "solid phase-natural water" system is a complex multifactorial physical and physico-chemical process, which comprises a mixture of sorbents and sorbates. Therefore it is not possible to be described by a particular equation, like Langmuir, Freundlich or Henry equations of adsorption isotherms, or by ion exchange constants that relate to a particular sorbent and sorbate. At the same time, for any aquatic ecosystem under certain conditions it is possible to establish the dependence experimentally, for example, between the total concentration of different forms of a chemical compound and its content in the bottom sediments and describe this relationship using most appropriate adsorption isotherm. This in itself formal isotherm is local in nature and cannot be used to predict the interfacial distribution of a given compound in other aquatic ecosystems.

3.6.1 Sorption of Metal Ions and Their Compounds

Clay minerals exhibit cation exchange properties, therefore uncomplexed hydrated cations Na^+, K^+, Ca^{2+}, Mg^{2+} and Mn^{2+}, which dominate in surface water, are sorbed mainly through cation exchange mechanism. Sorption of cations is electrostatic in nature and increases with an increase in their charge, and for ions with equal charges—with decreasing of hydration energy (increasing crystallochemical radius).

Sorption of heavy metals by different sorbents tends to increase with higher water pH (e.g. zinc and cadmium, Fig. 3.29). As for suspensions, sorption of metals increases with increased turbidity (Fig. 3.30). However, there is no a clear link between sorption and properties of heavy metals. One can only note that it mainly increases with increased oxidation degree of a metal and consequently the degree of hydrolysis, and hydroxoanions such as MoO_4^{2-}, are poorly sorbed. High sorption degree of vanadium is, apparently, due to its oxidation state +4.

One of the important quantitative indicators of adsorption capacity is the surface area of an adsorbent. Suspensions and bottom sediments have various grain sizes. For example, bottom sediments of the middle Danube are dominated by granules with a size >0.5 mm, and the Ukrainian part of the lower Danube—less than 0.01–0.005 mm [26].

The total surface area of suspended particles of varying dispersion in a certain volume of water can be calculated as follows, taking the form of a particle as a ball:

- mass of the particle $m = \frac{4}{3}\pi R^3 \rho$ (g),
- where R—radius of the particle (cm); ρ—particle density (g/mL);

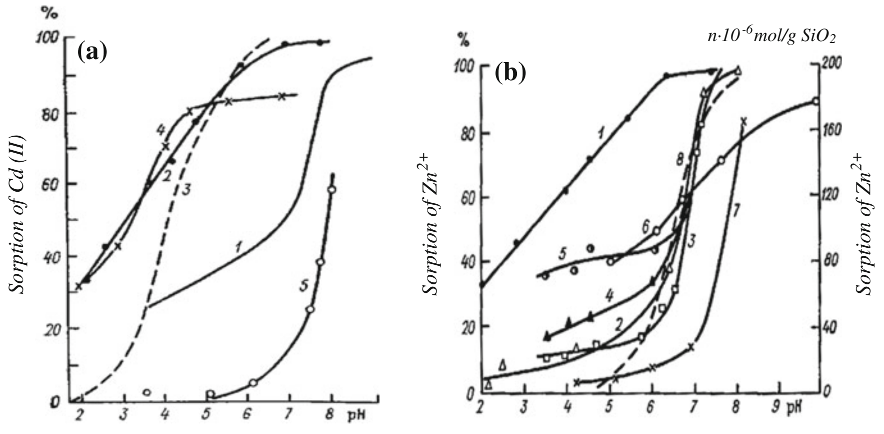
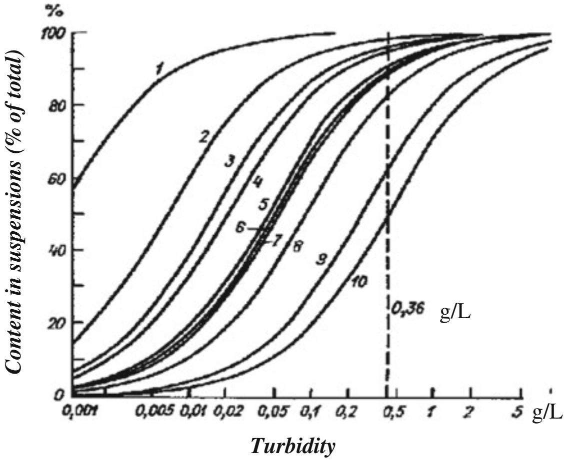


Fig. 3.29 Effect of *pH* on the degree of sorption of cadmium (II) **a** and zinc (II) **b** by various adsorbents [12]. **a** Cadmium (II). *1*—montmorillonite; *2*—mangan dioxide; *3*—river bottom sediments; *4*—suspension of humic acids; *5*—iron (III) hydroxide. **b** Zinc (II). *1*—mangan dioxide; *2*—SiO_2; *3*—montmorillonite (0.013 %); *4*—montmorillonite + fulvic acids; *5*—montmorillonite (0.023 %); *6*—cellulose; *7*—iron (III) hydroxide; *8*—bottom sediments of Maas river

Fig. 3.30 Content of elements in suspensions (% of total) depending on water turbidity [35]



- number of particles in a sample volume V(L) N = C V/m,
- where *C*—turbidity of water (g/L);
- surface of one particle $s = 4\pi R^2$ (cm^2);
- total surface of all particles in the sample volume V (density of particle ρ is taken as one).

The results of calculation of total area of suspended particles of varying dispersion in one cubic meter of water depending on the turbidity is given in Table 3.17, and in Fig. 3.31—graphically for turbidity of 10 mg/L. With decrease

Table 3.17 Surface area of different particle-size fractions of suspended particles (m^2 in 1 m^3 of water)

Size (R) of particle (mm)	Area S (m^2/m^3) at water turbidity C (mg/L)				
	1	2	5	10	20
0.001	3	6	15	30	60
0.002	1.5	3	7.5	15	30
0.003	1	2	5	10	20
0.004	0.75	1.5	3.75	7.5	15
0.005	0.6	1.2	3	6	12
0.01	0.3	0.6	1.5	3	6
0.05	0.06	0.12	0.3	0.6	1.2

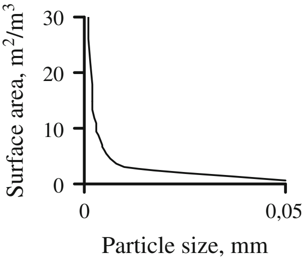


Fig. 3.31 Dependence of surface area on the size of suspended particles (water turbidity 10 mg/L, water volume 1 m^3)

of the size of suspended particles their area sharply increases, leading to growing adsorption of metal compounds. It can be seen from the example of bottom sediments of the Danube river (Fig. 3.32) that this relationship in general is true, although in some cases it fails. It obvious that distribution of metals between different factions of dispersion depends on the relative content of the latter.

$$S(\mathrm{m}^2/\mathrm{m}^3) = s \cdot N = 4\pi R^2 \cdot \frac{C \cdot V \cdot 10^3}{\frac{4}{3}\pi R^3 \cdot 10^4} = \frac{0.3 \cdot C \cdot V(\mathrm{m}^3)}{R} \tag{3.73}$$

where 10^4—factor for converting area from cm^2 to m^2; 10^3—factor for converting volume from cm^3 to m^3.

Sorption capacity of bottom sediments (suspensions) is also largely affected by the content of organic matter (Fig. 3.33). This effect is not quite clear, but it is evident that increasing the content of organic matter in a sorbent generally leads to an increase in the sorption of metals, apparently due to the formation of complex compounds on the surface of the sorbent.

In natural aquatic ecosystems upper layer of bottom sediments is saturated with water and formed largely by settling suspension. Therefore, the system "sorbent-water", in fact, consists not of two parts, but three—"Sorbent—pore water (sludge solution)—bottom layer of water." Sorption equilibrium is established when the concentration of sorbed ingredient in pore water Cp is equaled with its concentration in the bottom layer of water Cw. If water is contaminated, that is Cw > Cp, then due to diffusion the ingredient penetrates from the bottom layer of

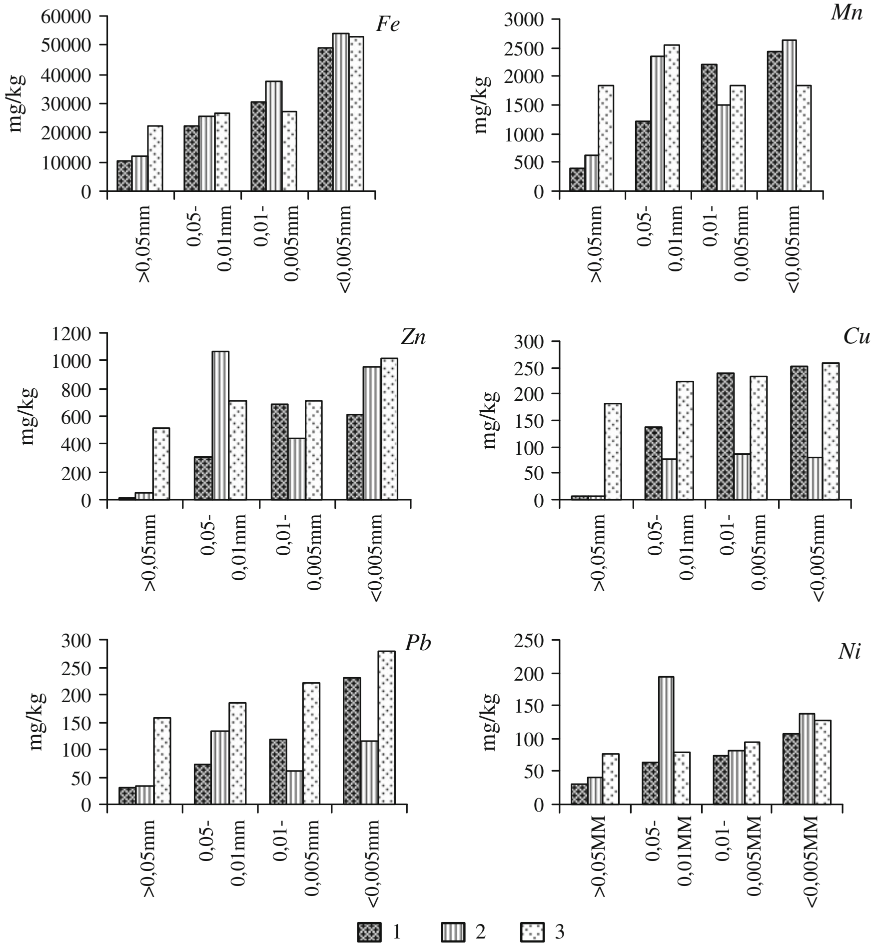


Fig. 3.32 Content of heavy metals in different particle size fractions of the Danube bottom sediments. *1*—Romanian segment (367th km); *2*—Bulgarian segment (788th km); *3*—Reservoir "Dzherdap" (945th km) [26]

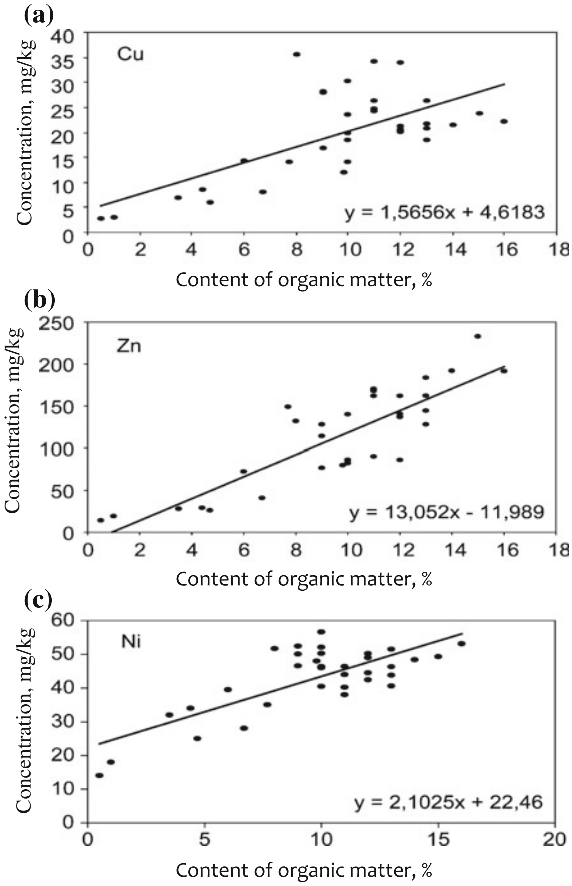
water into pore water and is sorbed on bottom sediments (a process of water "self-purification"). When Cp > Cw, then the sorbed ingredient diffuses from pore water into the bottom layer and then into the entire volume of water (a process of "self-pollution" of water). The speed of these processes depends on the molecular diffusion coefficient and the concentration gradient.

According to Fick's first law [29], diffusion flux (mass of displaced material) is:

$$y_M = -D_M \times S \times dt \times dc/dx \tag{3.74}$$

where *S*—cross-sectional area; D_M—molecular diffusion coefficient; *dt*—time; *dc/dx*—concentration gradient. Sign "–" in front of the equation means that the

Fig. 3.33 Empirical dependence of copper ($r = 0.66$) **a**, zinc ($r = 0.84$) **b** and nickel ($r = 0.77$) **c** content in bottom sediments of the Dnipro reservoirs on relative content of organic matter



substance concentration is changing from higher to lower. It is known that molecular diffusion coefficient of the substance is inversely proportional to the square root of its molecular mass (MM).

To estimate D_M values of heavy metal compounds dominating in surface water, an equation of D_M dependence on $\sqrt{\mathcal{MM}}$ [27] was created [27] based on the reference data [29]:

$$D_{\mathcal{M}} = 4.674 \cdot e^{-0.1912\sqrt{\mathcal{MM}}} \tag{3.75}$$

However, the rate of diffusion in pore water (sludge solution) is lower than that of pure water, because part of cross-sectional area is occupied by solid particles, which prevents diffusion.

To determine the molecular diffusion coefficient in pore water (*D*MP) one can use equation [6]:

$$D_{M\prod} = D_M \times n \times \lambda \qquad (3.76)$$

where *n*—porosity; λ—tortuosity coefficient.

Based on the porosity of clay and unconsolidated sediments of the seas, the value of which varies within 0.487–0.7 [3–5], it was assumed that the porosity $n = 0.6$.Tortuosity is interrelated with porosity by equation [6]:

$$\lambda = \frac{1 - (1 - n)^{\frac{2}{3}}}{n} \qquad (3.77)$$

At porosity $n = 0.6$ tortuosity $\lambda = 0.762$. According to Eq. (3.76) we obtain:

$$D_{M\prod} = D_M \times 0.457 \qquad (3.78)$$

Method for determining the molecular diffusion coefficients suggests considering the obtained results as estimates. In their determination temperature and mineralization of the water were not taken into account. An increase in temperature increases the rate of diffusion and increasing water mineralization reduces its speed due to electrostatic or other interaction of substances, which are diffusing with ions of salt composition in water.

As a result of calculations [27] there were obtained estimates of some heavy metals fluxes from bottom sediments into the bottom layer of water in Kyiv, Kaniv, Kremenchuk and Kakhovka reservoirs (Fig. 3.34). Calculations were performed for maximum, medium and minimum concentration gradients based on molecular diffusion coefficients of the prevailing forms of metals migration. Molecular weight of complex metal compounds with humic substances was determined experimentally.

Effluence of mangan is most likely from bottom sediments as Mn^{2+}, which in local areas of active sludge production can reach 230–300 mg/dm^2/day. Heavy inflows of mangan from bottom sediments into surface water were confirmed by numerous observations.

Probable inflows of other metals from bottom sediments in surface water are much lower and range within 0.1–1 mg/dm^2/day (zinc 0.5–10 mg/dm^2/day). Iron comes mainly in the form of hydroxofulvic complexes, zinc—of Zn^{2+} ions, copper—Cu^{2+}, $CuOH^+$ and $Cu(OH)_2^0$, lead—$PbCO_3^0$, cobalt—Co^{2+} and $CoHCO_3^+$, nickel—Ni^{2+} and $NiCO_3^0$, cadmium—Cd^{2+} and $CdCO_3^0$. It should be noted that extremely intense inflow of mangan is related to its concentration gradient, rather than molecular diffusion coefficient.

3.6.2 Sorption of Organic Compounds

Organic compounds can be present in surface water as anions and molecules (weak acids), cations and molecules (amines), depending on *pH,* or only as polar or

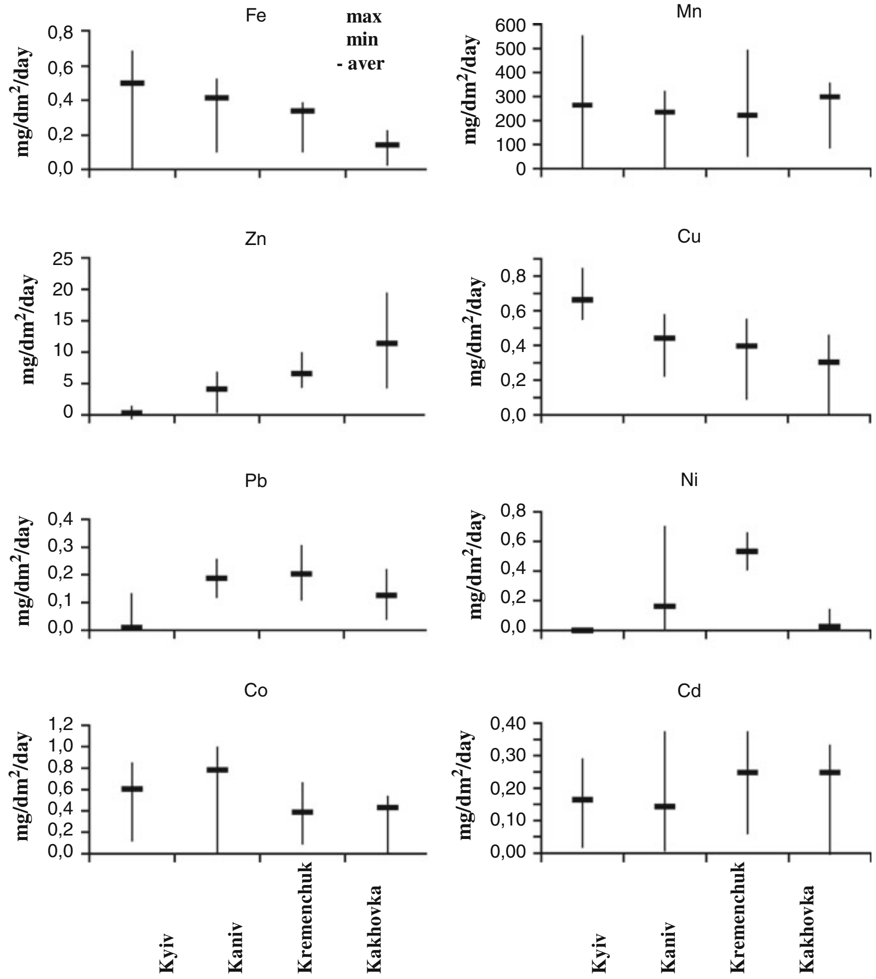


Fig. 3.34 Flux rating of iron, mangan, zinc, copper, lead, nickel, cobalt and cadmium from bottom sediments of Dnipro reservoirs due to molecular diffusion

non-polar molecules (aldehydes, ketones, alcohols, phenols, aliphatic and aromatic hydrocarbons, etc.). Depending on the form of the organic matter and surface properties of suspensions and bottom sediments, sorption occurs due to electrostatic, dispersion or dipole-dipole intermolecular interactions, including creation of hydrogen bonds in case of compounds containing electronegative atoms of nitrogen, oxygen, phosphorus, etc. It is also known that an increase in sorbate molecular weight contributes to its sorption (e.g. saturated hydrocarbons), which is associated with an increase in contact surface sorbate with the sorbent. However, sorption depends not only on the molecular weight of a sorbate, but on its structure as well. Multifactorial interaction within the “sorbate-sorbent” system in natural aquatic ecosystems does not allow one definitely predict the sorption rate of organic compounds. Even a priori assumption that the sorption increases with decreasing solubility of organic compounds in water is not always confirmed [31]. One can only suggest what organic compounds, similar to heavy metals (see previous section), are sorbed mainly on fine particles and molecular diffusion coefficients decrease with increasing molecular weight according to Eq. (3.75).

3.7 The Impact of Humic Substances on Surface Water Quality

Humus, which is the main and most reactive component of the soil profile, affects a wide range of processes in the hypergenesis zone and defines the conditions of inter-phase redistribution of mineral and organic substances, particularly in surface water ecosystems. Humic substances are largely responsible for the migration of biogenic elements, heavy metals, pesticides and other organic ecotoxicants, controlling their geochemical fluxes in the environment.

Among the processes which have an impact on surface water quality, which are significantly influenced by HS, the most important are:

- complexation of heavy metal ions, resulting in their detoxification;
- acid-base balance. Humic and fulvic acids are much stronger than carbonic acid, therefore their accumulation in surface water leads to acidification of water. For example, the *pH* of bog water with high content of humic substances is typically less than 4–5. At the same time, the system $H_2\mathrm{HS}$–$H\mathrm{HS}^-$–HS^{2-}, analogous to carbonate system, has buffering properties which contribute to stabilizing of water *pH* at a certain level;
- redox processes. Humic substances are able receive or donate electrons. After dissolved oxygen this is the second potential-setting surface water system, redox potential of which ranges within E0 = 0.5 V (FA) and +0.7 V (HA) [12, 25] (Fig. 3.35);

Humic substances have acidic properties, therefore their redox potential depends on the *pH* of water (see Fig. 3.35). Pronounced reducing properties have been found regarding vanadium (V), chromium (VI), mangan (IV), iron (III), mercury (II). Photochemical oxidation of humic substances by dissolved oxygen may reduce their content to almost zero, especially at low *pH*. Finally, due to reduced light penetration in the water column in the presence of colored humic substances, oxygen production by phytoplankton is significantly reduced;

Humic substances increase the solubility of slightly soluble compounds due to complex formation (see Sect. 3.5); for this reason, they increase the aggressiveness of surface water with respect to aluminosilicates and other species;

Macromolecular humic substances are well sorbed on hydroxides of ferrum, aluminum, organic-mineral suspensions. Thereby, toxic inorganic and organic compounds associated with them are removed from the aqueous phase.

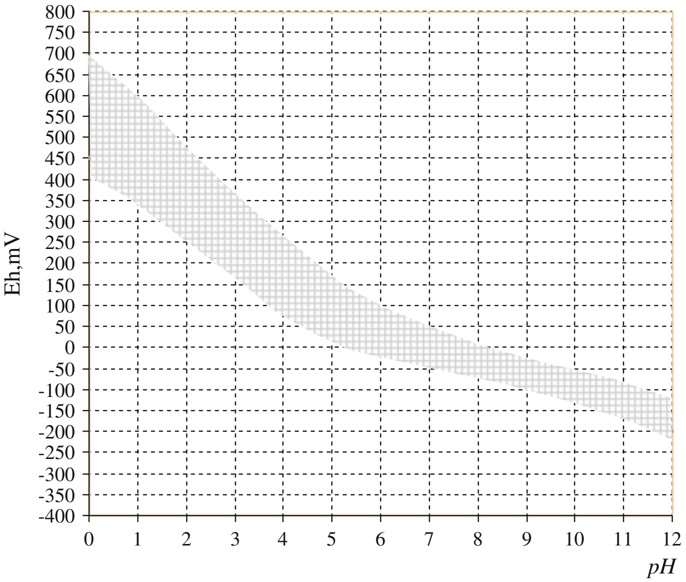


Fig. 3.35 Regions of stationary potential of humic acids redox system [14]

Addendum

Table 3.18 Ionic activity coefficients of inorganic compounds most common in natural waters at different values of ionic strength

Ions	Activity coefficients at the ionic strength μ							
	0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
NH_4^+, Ag^+	0.975	0.964	0.945	0.924	0.898	0.850	0.800	0.750
K^+, Cl^-, NO_2^-, NO_3^-	0.975	0.964	0.945	0.925	0.899	0.850	0.805	0.755
OH^-, F^-, HS^-	0.975	0.964	0.946	0.926	0.900	0.855	0.810	0.760
Na^+, $H_2PO_4^-$	0.975	0.964	0.947	0.928	0.902	0.860	0.820	0.775
SO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	0.903	0.867	0.803	0.740	0.660	0.545	0.445	0.355
Pb^{2+}, CO_3^{2-}, MoO_42^-	0.903	0.868	0.805	0.742	0.665	0.550	0.455	0.370
Ba^{2+}, Cd^{2+}, Hg^{2+}	0.903	0.868	0.805	0.744	0.670	0.555	0.465	0.380
Ca^{2+}, Cu^2+, Zn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}	0.905	0.870	0.809	0.749	0.675	0.570	0.485	0.405
Mg^{2+}	0.906	0.872	0.813	0.755	0.690	0.595	0.520	0.405
PO_4^{3-}	0.796	0.725	0.612	0.505	0.395	0.250	0.160	0.095
Fe^{3+}, Al^{3+}, Cr^{3+}	0.802	0.738	0.632	0.540	0.445	0.325	0.245	0.180

Table 3.19 H^+ ions activity coefficients at different ionic strength values

Ionic strength, μ	0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
Activity coefficient, fH^+	0.975	0.967	0.950	0.933	0.914	0.880	0.860	0.830
$-\lg fH^+ = p\,fH^+$	0.011	0.015	0.022	0.030	0.039	0.056	0.066	0.081

Table 3.20 HCO_3^- ions activity coefficients at different ionic strength values

Ionic strength, μ	f	Ionic strength, μ	f	Ionic strength, μ	f
0.001	0.97	0.008	0.91	0.035	0.83
0.002	0.96	0.009	0.91	0.040	0.83
0.003	0.95	0.010	0.90	0.045	0.82
0.004	0.93	0.015	0.88	0.050	0.81
0.005	0.93	0.020	0.87	0.060	0.80
0.006	0.92	0.025	0.85	0.080	0.79
0.007	0.92	0.030	0.84	0.100	0.78

Table 3.21 Ionic activity coefficients of some organic compounds most common in natural waters at different of ionic strength values

Ions	Activity coefficients at the ionic strength μ							
	0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
$HCOO^-$	0.975	0.964	0.946	0.926	0.900	0.855	0.810	0.760
CH_3COO^-, $NH_2CH_2COO^-$	0.975	0.964	0.947	0.928	0.902	0.860	0.820	0.775
$C_2O_4^{2-}$	0.903	0.867	0.804	0.741	0.662	0.550	0.450	0.360
$(CHOHCOO)_2^{2-}$, tartrate, Tart^{2-}	0.903	0.868	0.805	0.744	0.670	0.555	0.465	0.380
$C_6H_5O_7^{3-}$, citrate, Cit^{3-}	0.769	0.727	0.616	0.510	0.405	0.270	0.180	0.115
$C_6H_6O_7^{2-}$, hydrogen citrate, HCit^{2-}	0.903	0.867	0.804	0.741	0.662	0.550	0.450	0.360
$C_6H_7O_7^-$, dihydrogen citrate, H$_2$Cit$^-$	0.975	0.964	0.946	0.926	0.900	0.855	0.810	0.760
FA^{2-} fulvic acids and HA^{2-} humic acids (doubly charged anions' average activity coefficient)	0.903	0.867	0.804	0.742	0.665	0.552	0.455	0.370

Table 3.22 Ionic product of water at different temperatures $KH_2O = aH^+aOH^- = [H^+]\,[OH^-]\,f\,H^+\,f\,OH^-$; $aH^+ = aOH^- = \sqrt{K_{H_2O}}$

t (°C)	KH_2O, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}	t (°C)	KH_2O, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}
0	0.11	0.33	30	1.48	1.22
5	0.17	0.41	31	1.58	1.26
10	0.30	0.55	32	1.70	1.30
15	0.46	0.68	33	1.82	1.35
16	0.50	0.71	34	1.95	1.39
17	0.55	0.74	35	2.09	1.45
18	0.60	0.77	36	2.24	1.49
19	0.65	0.81	37	2.40	1.55
20	0.69	0.83	38	2.57	1.60
21	0.76	0.87	39	2.75	1.66
22	0.81	0.90	40	2.95	1.72
23	0.87	0.93	50	5.50	2.34
24	0.93	0.96	60	9.55	3.09
25	1.00	1.00	70	15.8	3.98

(continued)

Table 3.22 (continued)

t (°C)	KH_2O, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}	t (°C)	KH_2O, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}
26	1.10	1.05	80	25.1	5.01
27	1.17	1.08	90	38.0	6.16
28	1.29	1.14	100	55.0	7.41
29	1.38	1.17			

Table 3.23 Solubility product of slightly soluble compounds (t = 25 °C)[a]

Compound formula	*SP*	Compound formula	*SP*
$Al(OH)_3$ [Al^{3+}, $3OH^-$]	1×10^{-32}	[$Fe(OH)_2^+$, OH^-]	1×10^{-17}
[$AlOH^{2+}$, $2OH^-$]	1×10^{-23}	$FePO_4$	1.3×10^{-22}
[$Al(OH)_2^+$, $3OH^-$]	1.6×10^{-13}	FeS	5×10^{-18}
$AlPO_4$	5.8×10^{-19}	$Hg(OH)_2$ [Hg^{2+}, $2OH^-$]	3.0×10^{-26}
$CaCO_3$[a]	3.8×10^{-9}	[$HgOH^+$, OH^-]	6×10^{-16}
CaF_2	4.0×10^{-11}	HgS, red	4×10^{-53}
$Ca(HPO_4)$	2.7×10^{-7}	$Mg(OH)_2$ [Mg^{2+}, 2 OH^-]	7.1×10^{-12}
$CaSO_4$	2.5×10^{-5}	[$MgOH^+$, OH^-]	2.7×10^{-9}
$Cd(OH)_2$ [Cd^{2+}, $2OH^-$]	2.2×10^{-14}	$MgCO_3$	2.1×10^{-5}
[$CdOH^+$, OH^-]	2.6×10^{-8}	$MnCO_3$	1.8×10^{-11}
$CdCO_3$	1.0×10^{-12}	$Mn(OH)_2$ [Mn^{2+}, $2OH^-$]	1.9×10^{-13}
CdS	1.6×10^{-28}	[$MnOH^+$, OH^-]	1.5×10^{-9}
$CoCo_3$	1.05×10^{-10}	MnS	2.5×10^{-13}
$Co(OH)_2$ [Co^{2+}, $2OH^-$]	1.6×10^{-15}	$NiCO_3$	1.3×10^{-7}
[$CoOH^+$, OH^-]	4×10^{-11}	$Ni(OH)_2$ [Ni^{2+}, $2OH^-$]	2.0×10^{-15}
CoS, β	2×10^{-25}	[$NiOH^+$, OH^-]	1.7×10^{-10}
$Cr(OH)_3$ [Cr^{3+}, $3OH^-$]	6.3×10^{-31}	NiS, γ	2.0×10^{-26}
[$Cr(OH)^{2+}$, $2OH^-$]	7.9×10^{-21}	$PbCO_3$	7.5×10^{-14}
[$Cr(OH)_2^+$, OH^-]	4×10^{-13}	$Pb(OH)_2$ [Pb^{2+}, $2OH^-$]	7.9×10^{-16}
$CrPO_4$	1.0×10^{-17}	[$PbOH^+$, OH^-]	6.3×10^{-9}
$CuCO_3$	2.5×10^{-10}	$Pb_3(PO_4)_2$	7.9×10^{-43}
$Cu(OH)_2$ [Cu^{2+}, $2OH^-$]	2.2×10^{-20}	PbS	2.5×10^{-27}
[$CuOH^+$, OH^-]	2.2×10^{-13}	$PbSO_4$	1.6×10^{-8}
CuS	6.3×10^{-36}	$ZnCO_3$	1.5×10^{-11}
$FeCO_3$	3.5×10^{-11}	$Zn(OH)_2$ [Zn^{2+}, $2OH^-$]	1.2×10^{-17}
$Fe(OH)_2$ [Fe^{2+}, $2OH^-$]	8×10^{-16}	[$ZnOH^+$, OH^-]	3.0×10^{-13}
[$FeOH^+$, OH^-]	3×10^{-10}	ZnS	1.6×10^{-24}
$Fe(OH)_3$ [Fe^{3+}, $3OH^-$]	6.3×10^{-38}		
[$FeOH^{2+}$, $2OH^-$]	5×10^{-27}		

[a] Effect of water temperature on the solubility product of $CaCO_3$, see Table 3.29

Table 3.24 Standard redox potentials E_0 of some systems characteristic of natural waters (t = 25 °C)

Oxidant	+ne	Reductant	E0 (V)
$CrO_4^{2-} + 4H_2O$	+3e	$\downarrow Cr(OH)_3 + 5OH^-$	–0.13
$CrO_4^{2-} + 8H^+$	+3e	$Cr^{3+} + 4H_2O$	+1.48
Cu^{2+}	+e	Cu^+	+0.159
$\downarrow MnO_2 + 4H^+$	+2e	$Mn^{2+} + 2H_2O$	+1.23
Fe^{3+}	+e	Fe^{2+}	+0.771
$\downarrow Fe(OH)_3$	+e	$\downarrow Fe(OH)_2 + OH^-$	–0.56
$NO_3^- + H_2O$	+2e	$NO_2^- + 2OH^-$	+0.01
$NO_2^- + 6\ H_2O$	+6e	$NH_4OH + 7OH^-$	–0.15
$NO_3^- + 10H^+$	+8e	$NH_4+ + 3H_2O$	+0.87
$NO_3^- + 7H_2O$	+8e	$NH_4OH + 9OH^-$	–0.12
$SO_4^{2-} + 10H^+$	+8e	$H_2S\uparrow + 4H_2O$	+0.31

Table 3.25 Dissociation constants of acids most common in natural waters (t = 25 °C)[a]

Name		Formula	Ka	pKa
Amber	K_1	$HOOCCH_2CH_2COOH$	1.6×10^{-5}	4.80
	K_2		2.3×10^{-6}	5.64
Valeric (com.)		$CH_3(CH_2)_3COOH$	1.4×10^{-5}	4.85
Valeric (iso)		$(CH_3)_2CHCH_2COOH$	1.7×10^{-5}	4.77
Tartaric (H_2Tart)	K_1	$HOOCCH(OH)_xH(OH)$	1.3×10^{-3}	2.89
	K_2		3.0×10^{-5}	4.52
Carbonic	K_1	$CO_2+H_2O(H_2CO_3)$	4.3×10^{-7}	6.37
	K_2		4.7×10^{-11}	10.33
Glycolic		$CH_2(OH)COOH$	1.5×10^{-4}	3.82
Glutaric	K_1	$HOOC(CH_2)_3COOH$	4.6×10^{-5}	4.34
	K_2		5.4×10^{-6}	5.27
Gluconic		$CH_2OH(CHOH)_4COOH$	1.4×10^{-4}	3.85
Citric (H_3Cit)	K_1	$HOOCCH_2C(OH)\ (COOH)CH_2COOH$	7.4×10^{-4}	3.13
	K_2		2.2×10^{-5}	4.66
	K_3		4.0×10^{-7}	6.40

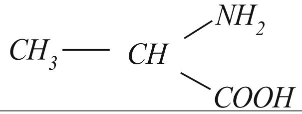
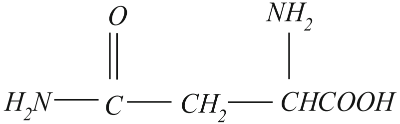
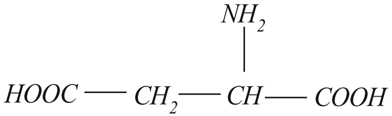
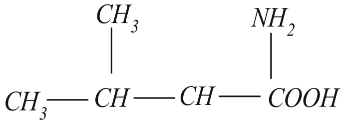
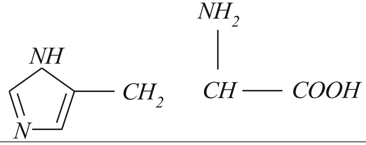
(continued)

Table 3.25 (continued)

Name		Formula	Ka	pKa
Malonic	K_1	$HOOCCH_2COOH$	4.2×10^{-2}	1.38
	K_2		2.1×10^{-6}	5.68
Butanoic (com.)		$CH_3CH_2CH_2COOH$	1.5×10^{-5}	4.82
Butanoic (iso)		$(CH_3)_2CHCOOH$	1.4×10^{-5}	4.85
Lactic		$CH_3CH(OH)COOH$	1.5×10^{-4}	3.82
Formic		$HCOOH$	1.8×10^{-4}	3.74
Acetic		CH_3COOH	1.74×10^{-5}	4.76
Propionic		CH_3CH_2COOH	1.35×10^{-5}	4.87
Hydrosulphuric	K_1	H_2S	1.0×10^{-7}	7.00
	K_2		2.5×10^{-13}	12.60
Silicic (orto)	K_1	H_4SiO_4	1.3×10^{-10}	9.9
	K_2		1.6×10^{-12}	11.8
	K_3		2.0×10^{-14}	13.7
Carbolic		C_6H_5OH	1.0×10^{-10}	10.0
Phosphorus (orto)	K_1	H_3PO_4	7.1×10^{-3}	2.15
	K_2		6.2×10^{-8}	7.21
	K_3		5.0×10^{-13}	12.3
Fluorhydric		HF	6.2×10^{-4}	3.21
Chromic	K_1	H_2CrO_4	1.6×10^{-1}	0.80
	K_2		3.2×10^{-7}	6.50
Oxalic	K_1	$H_2C_2O_4$	5.6×10^{-2}	1.25
	K_2		5.4×10^{-5}	4.27
Apple	K_1	$HOOCCH(OH)CH_2COOH$	3.5×10^{-4}	3.46
	K_2		8.9×10^{-6}	5.05

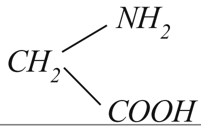
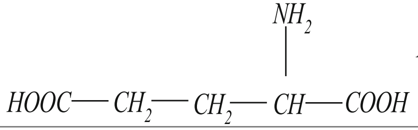
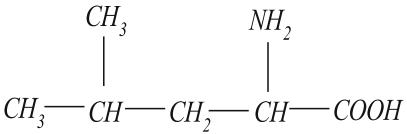
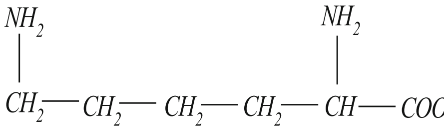
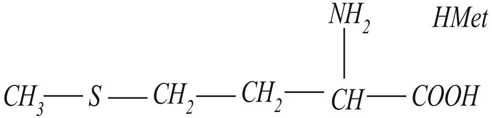
Humic and fulvic acids dissociation constants see Table 3.28

Table 3.26 Amino acids dissociation constants

Назва	Формула та позначення з урахуванням іонів H$^+$ карбоксильних груп	K$_a$	pK$_a$
α¯Alanine	K$_1$ K$_N$  *HAl*	4.57×10^{-3} 1.35×10^{-10}	2.34 9.87
Asparagine	K$_1$ K$_N$  $H_2N-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{NH_2}{\vert}}{C}HCOOH$ *HAsp*	5.96×10^{-3} 9.46×10^{-10}	2.22 9.02
Asparagine acid	K$_1$ K$_2$ K$_N$  $HOOC-CH_2-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ *H$_2$Asp*	8.51×10^{-3} 7.08×10^{-5} 4.27×10^{-11}	2.07 4.15 10.37
Valine	K$_1$ K$_N$  $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ *HVal*	4.79×10^{-3} 2.40×10^{-10}	2.32 9.20
Histidine	K$_{N1}$ K$_{N2}$  *HGis*	1.25×10^{-2} 6.10×10^{-7} 3.74×10^{-10}	1.90 6.21 9.43

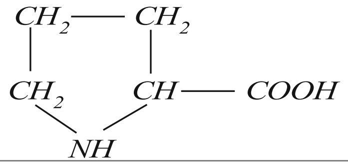
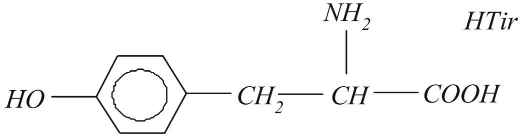
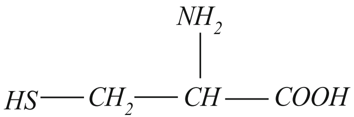
(continued)

Table 3.26 (continued)

Назва	Формула та позначення з урахуванням іонів H^+ карбоксильних груп	K_a	pK_a
Glycine (aminoacetic acid)	K_1  HGlic	4.47×10^{-3}	2.35
	K_N	1.66×10^{-10}	9.78
Glutaminic acid	K_1  $HOOC{-}CH_2{-}CH_2{-}CH(NH_2){-}COOH$ H_2Glut	3.16×10^{-3}	2.50
	K_2	2.06×10^{-5}	4.69
	K_N	4.68×10^{-11}	10.33
Leucine	K_1  $CH_3{-}CH(CH_3){-}CH_2{-}CH(NH_2){-}COOH$ HLeic	2.57×10^{-3}	2.59
	K_N	7.66×10^{-11}	10.12
Lysins	K_1  $CH_2(NH_2){-}CH_2{-}CH_2{-}CH_2{-}CH(NH_2){-}COOH$ HLiz	5.43×10^{-3}	2.26
	K_{N1}	4.43×10^{-10}	9.35
	K_{N2}	1.03×10^{-11}	10.99
Methionine	K_1  $CH_3{-}S{-}CH_2{-}CH_2{-}CH(NH_2){-}COOH$ HMet	5.19×10^{-3}	2.28
	K_N	3.06×10^{-10}	9.51

(continued)

Table 3.26 (continued)

Назва	Формула та позначення з урахуванням іонів H^+ карбоксильних груп		K_a	pK_a
Proline	K_1	 $HProl$	6.02×10^{-3}	2.22
	K_N		1.30×10^{-11}	10.89
Tyrosine	K_1		5.28×10^{-3}	2.28
	$K_{(HO-)}$		4.26×10^{-10}	9.37
	K_N		2.22×10^{-11}	10.65
Cysteine	K_1	 $HS-CH_2-\underset{}{\overset{NH_2}{\overset{\vert}{CH}}}-COOH$ H_2Cis	9.02×10^{-3}	2.04
	$K_{2(HS-)}$		2.93×10^{-9}	8.53
	K_N		2.83×10^{-11}	10.55

K_1, K_2—carboxy group ionization constants; K_N—amine group proton ionization constant
Almost exclusively carboxy groups dissociate in the natural waters ($pH \leq 10$)

Table 3.27 Dissociation constants of bases most common in natural waters (t = 25 °C)

Name	Formula	Kb	pKb
Ammonium hydroxide	$NH_3 + H_2O$ (NH_4OH)		
	25 °C	1.76×10^{-5}	4.75
	15 °C	3.65×10^{-5}	4.44
	5 °C	7.80×10^{-5}	4.11
Aniline	$C_6H_5NH_2 + H_2O$ ($C_6H_5NH_3OH$)	4.3×10^{-10}	9.37
Hydroxylamine	$NH_2OH + H_2O$ ($OHNH_3OH$)	8.9×10^{-9}	8.05
Diethylamine	$(C_2H_5)_2NH + H_2O$ [$(C_2H_5)_2NH_3OH$]	1.2×10^{-3}	2.92
Dimethylamine	$(CH_3)_2NH + H_2O$ [$(CH_3)_2NH_3OH$]	5.4×10^{-4}	3.27
Diphenylamine	$(C_6H_5)_2NH + H_2O$ [$(C_6H_5)_2NH_3OH$]	6.2×10^{-14}	13.21
Ethanolamine	$H_2NCH_2CH_2OH + H_2O$ ($HOH_3NCH_2CH_2OH$)	1.8×10^{-5}	4.74
Ethylamine	$CH_3CH_2NH_2 + H_2O$ ($CH_3CH_2NH_3OH$)	6.5×10^{-4}	3.19
Methylamine	$CH_3NH_2 + H_2O$ (CH_3NH_3OH)	4.6×10^{-3}	2.34
Urea	$CO(NH_2)_2 + H_2O$ ($CONH_2NH_3OH$)	1.5×10^{-14}	13.82
Trimethylamine	$(CH_3)_3N + H_2O$ [$(CH_3)_3NHOH$]	6.5×10^{-5}	4.19

Table 3.28 Humic and fulvic acid dissociation constants

Acids	Counter-ion	Carboxyl groups				Phenolic hydroxyl		References
		Ka(1)	pKa(1)	Ka(2)	pKa(2)	Ka	pKa	
Humic acids (peat extract)	Li^+	–	–	1.58×10^{-5}	4.80	5.62×10^{-10}	9.25	[1]
	Na^+	–	–	1.12×10^{-5}	4.95	3.39×10^{-10}	9.47	
	K^+	–	–	9.55×10^{-6}	5.02	5.75×10^{-10}	9.24	
Fulvic acids, molecular mass 300 Da (isolated from the waters of the Moscow River at different times)	Na^+	2.5×10^{-3}	2.62	4×10^{-5}– 6×10^{-6}	4.4– 5.2	2×10^{9}– 1×10^{9}	8.7– 9.0	[3]
	K^+							
Fulvic acids, eq. weight 90–160 Da	Na^+	2×10^{-3}	2.7	5×10^{-5}	4.3	–	–	[4]
Fulvic acids	Na^+	1.6×10^{-3}– 4×10^{-4}	2.8– 3.4	1.3×10^{-5}– 7.9×10^{-6}	4.9– 5.1	–	–	[2]

1. Lishtvan II., Kudritskiy NN, Tretinnik VYu (1976) Phisiko-khimicheskaya mekhanika humusovykh veshchestv (Physico-chemical mechanics of humic substances). Nauka i technika, Minsk
2. Reuter JH, Perdue EM (1977) Interaction of metals with organic matter. Geochim et cosmochim acta 41(2): 325–334
3. Varshal GM, Bugaevsky AA, Kholin YuYu. (1990) Modelirovanie ravnovesiy v rastvorakh fulvokislot prirodnykh vod (Modelling of equilibriums in fulvic acid solutions of natural waters). J Water Chem. Technology 12 (11): 979–986
4. Varshal GM, Koscheeva IYa, Sirotkina IS Velyuhanova TK, Intskirveli LL et al. (1979) Izuchenie organicheskikh veschestv poverkhnostnykh vod i ikh vzaimodeystviya s ionamy metallov (The study of surface water organic substances and their interaction with metal ions). Geochemistry 4: 598–607

Table 3.29 Carbonic acid dissociation constants and $CaCO_3$ solubility product depending on water temperature

Water t (°C)	K1 × 10^6	K2 × 10^{10}	SP × 10^9	Water t (°C)	K1 × 10^6	K2 × 10^{10}	SP × 10^9
0	0.26	0.23	5.50	16	0.38	0.38	4.44
2	0.28	0.25	5.37	18	0.39	0.40	4.31
4	0.29	0.27	5.24	20	0.40	0.42	4.17
5	0.30	0.28	5.18	22	0.42	0.44	4.04
6	0.31	0.29	5.11	24	0.43	0.46	3.90
8	0.32	0.30	4.98	25	0.43	0.47	3.84
10	0.34	0.32	4.84	26	0.44	0.48	3.77
12	0.35	0.34	4.71	28	0.44	0.50	3.64
14	0.37	0.36	4.57	30	0.45	0.51	3.51

Table 3.30 Stability constants of complex compounds most common in natural waters

Metal	Complex compound	β_n	Metal	Complex compound	β_n
Al^{3+}	$AlOH^{2+}$	$1.00 \cdot 10^{9}$	**Al^{3+}**	$AlGlic^{2+}$	$1.75 \cdot 10^{8}$
	$Al(OH)_2^+$	$7.94 \cdot 10^{17}$		$AlGlut^+$	$1.29 \cdot 10^{16}$
	$Al(OH)_3^0$	$1.58 \cdot 10^{25}$		$Al(Glut)_2^-$	$8.00 \cdot 10^{30}$
	$Al(OH)_4^-$	$2.00 \cdot 10^{33}$		$Al(Glut)_3^{3-}$	$4.40 \cdot 10^{39}$
	$AlSO_4^+$	$3.16 \cdot 10^{3}$	**Ca^{2+}**	$CaCO_3^0$	$1.58 \cdot 10^{3}$
	$Al(SO_4)_2^-$	$1.00 \cdot 10^{5}$		$CaHCO_3^+$	$1.82 \cdot 10^{1}$
	$AlPO_4^0$	$5.75 \cdot 10^{16}$		$CaSO_4^0$	$2.04 \cdot 10^{2}$
	AlF^{2+}	$1.26 \cdot 10^{7}$		$CaPO_4^-$	$2.88 \cdot 10^{6}$
	AlF_2^+	$9.55 \cdot 10^{11}$		$CaHPO_4^0$	$5.89 \cdot 10^{2}$
	AlF_3^0	$6.76 \cdot 10^{15}$		$CaH_2PO_4^+$	$2.57 \cdot 10^{1}$
	AlF_4^-	$3.39 \cdot 10^{18}$		$CaC_2O_4^0$	$4.57 \cdot 10^{1}$
	AlF_5^{2-}	$1.58 \cdot 10^{20}$		$Ca(C_2O_4)_2^{2-}$	$4.89 \cdot 10^{2}$
	AlF_6^{3-}	$4.68 \cdot 10^{20}$		$CaTart^0$	$9.55 \cdot 10^{2}$
	$AlC_2O_4^+$	$2.00 \cdot 10^{7}$		$Ca(Tart)_2^{2-}$	$1.02 \cdot 10^{9}$
	$Al(C_2O_4)_2^-$	$1.00 \cdot 10^{13}$		$CaCit^-$	$4.79 \cdot 10^{4}$
	$Al(C_2O_4)_3^{3-}$	$2.00 \cdot 10^{16}$		$CaHCit^0$	$1.12 \cdot 10^{3}$
	$AlCit^0$	$2.25 \cdot 10^{9}$		CaH_2Cit^+	$1.41 \cdot 10^{1}$
	$Al(Cit)_2^{3-}$	$9.55 \cdot 10^{14}$		$CaAl^+$	$1.74 \cdot 10^{1}$
	$AlHCit^+$	$1.10 \cdot 10^{12}$		$CaAsk^0$	$1.10 \cdot 10^{2}$
	$AlAsp^{2+}$	$1.21 \cdot 10^{7}$		$CaGlic^+$	$2.40 \cdot 10^{1}$
	$Al(Asp)_2^+$	$1.46 \cdot 10^{11}$		$CaGlut^0$	$7.41 \cdot 10^{1}$
	$AlAsk^+$	$2.23 \cdot 10^{17}$		$CaTir^+$	$3.02 \cdot 10^{1}$
	$Al(Ask)_2^-$	$1.56 \cdot 10^{32}$	**Cd**	$CdOH^+$	$1.20 \cdot 10^{6}$
	$Al(Ask)_3^{3-}$	$1.71 \cdot 10^{43}$		$Cd(OH)_2^0$	$5.01 \cdot 10^{8}$

(continued)

Table 3.30 (continued)

Cd	$CdCl^{+}$	$1.12 \cdot 10^{2}$	$CoHCO_3^{+}$	$1.00 \cdot 10^{3}$
	$CdSO_4^{0}$	$1.29 \cdot 10^{2}$	$CoSO_4^{0}$	$1.51 \cdot 10^{3}$
	$CdC_2O_4^{0}$	$1.00 \cdot 10^{4}$	$CoHPO_4^{0}$	$5.25 \cdot 10^{2}$
	$Cd(C_2O_4)_2^{2-}$	$5.89 \cdot 10^{5}$	$CoC_2O_4^{0}$	$5.01 \cdot 10^{5}$
	$CdCit^{-}$	$2.29 \cdot 10^{5}$	$Co(C_2O_4)_2^{2-}$	$6.31 \cdot 10^{6}$
	$CdHCit^{0}$	$1.58 \cdot 10^{2}$	$CoTart^{0}$	$1.20 \cdot 10^{3}$
	$CdAl^{+}$	$3.16 \cdot 10^{4}$	$CoCit^{-}$	$1.00 \cdot 10^{5}$
	$Cd(Al)_2^{0}$	$1.05 \cdot 10^{8}$	CoHCit0	$1.05 \cdot 10^{3}$
	$Cd(Asp)_2^{0}$	$1.16 \cdot 10^{7}$	$CoAl^{+}$	$6.61 \cdot 10^{4}$
	$CdAsk^{0}$	$6.46 \cdot 10^{4}$	$Co(Al)_2^{0}$	$3.02 \cdot 10^{8}$
	$Cd(Ask)_2^{2-}$	$1.38 \cdot 10^{8}$	CoAsp+	$1.12 \cdot 10^{5}$
	$CdGis^{+}$	$6.76 \cdot 10^{5}$	$Co(Asp)_2^{0}$	$5.14 \cdot 10^{8}$
	$Cd(Gis)_2^{0}$	$1.14 \cdot 10^{10}$	$CoAsk^{0}$	$2.19 \cdot 10^{6}$
	$CdGlic^{+}$	$6.31 \cdot 10^{4}$	$Co(Ask)_2^{2-}$	$1.11 \cdot 10^{11}$
	$Cd(Glic)_2^{0}$	$6.76 \cdot 10^{8}$	$CoGis^{+}$	$1.26 \cdot 10^{7}$
	$CdGlut^{0}$	$7.24 \cdot 10^{4}$	$Co(Gis)_2^{0}$	$5.04 \cdot 10^{12}$
	$Cd(Glut)_2^{2-}$	$1.20 \cdot 10^{8}$	$CoGlic^{+}$	$1.05 \cdot 10^{5}$
	$CdLeic^{+}$	$1.48 \cdot 10^{4}$	$Co(Glic)_2^{0}$	$9.77 \cdot 10^{8}$
	$Cd(Leic)_2^{0}$	$4.32 \cdot 10^{7}$	CoGlut0	$1.45 \cdot 10^{5}$
	$Cd(Liz)_2^{0}$	$9.89 \cdot 10^{5}$	$Co(Glut)_2^{2-}$	$9.28 \cdot 10^{8}$
	$CdMet^{+}$	$2.09 \cdot 10^{4}$	$CoLeic^{+}$	$4.68 \cdot 10^{4}$
	$CdProl^{+}$	$6.92 \cdot 10^{4}$	$Co(Leic)_2^{0}$	$2.15 \cdot 10^{8}$
	$Cd(Prol)_2^{0}$	$5.42 \cdot 10^{7}$	$CoLiz^{+}$	$4.34 \cdot 10^{3}$
	$Cd(Met)_2^{0}$	$1.53 \cdot 10^{7}$	$Co(Liz)_2^{0}$	$5.09 \cdot 10^{6}$
	$CdTir^{+}$	$1.37 \cdot 10^{3}$	$CoMet^{+}$	$3.63 \cdot 10^{4}$
	$Cd(Tir)_2$	$3.64 \cdot 10^{5}$	$Co(Met)_2^{0}$	$5.77 \cdot 10^{7}$
	$Cd(Cis)_2^{2-}$	$1.30 \cdot 10^{9}$	$CoProl^{+}$	$2.14 \cdot 10^{5}$
Co^{2+}	$CoOH^{+}$	$2.51 \cdot 10^{4}$	$CoTir^{+}$	$3.30 \cdot 10^{3}$
	$Co(OH)_2^{0}$	$1.58 \cdot 10^{9}$	$CoCis^{0}$	$8.90 \cdot 10^{8}$
	$CoCO_3^{0}$	$8.13 \cdot 10^{4}$	$Co(Cis)_2^{2-}$	$3.54 \cdot 10^{16}$

(continued)

Table 3.30 (continued)

Cr^{3+}	$CrOH^{2+}$	$1.26\cdot10^{10}$	**Cu^{2+}**	$Cr(Met)_2^+$	$5.58\cdot10^{13}$
	$Cr(OH)_2^+$	$6.31\cdot10^{17}$		$Cr(Met)_3^0$	$7.85\cdot10^{18}$
	$Cr(OH)_3^0$	$5.74\cdot10^{23}$		$CuOH^+$	$2.19\cdot10^{7}$
	$Cr(OH)_4^-$	$7.94\cdot10^{29}$		$Cu(OH)_2^0$	$5.01\cdot10^{13}$
	$CrSO_4^+$	$3.98\cdot10^{1}$		$Cu(OH)_3^-$	$2.63\cdot10^{14}$
	$CrHPO_4^+$	$2.82\cdot10^{9}$		$CuCO_3^0$	$5.89\cdot10^{6}$
	CrF^{2+}	$1.58\cdot10^{5}$		$Cu(CO3)_2^{2-}$	$1.02\cdot10^{10}$
	CrF_2^+	$3.47\cdot10^{8}$		$CuHCO_3^+$	$5.01\cdot10^{2}$
	CrF_3^0	$1.05\cdot10^{11}$		$CuCl^+$	$1.51\cdot10^{1}$
	$CrC_2O_4^+$	$2.19\cdot10^{5}$		$CuSO_4^0$	$2.29\cdot10^{2}$
	$Cr(C_2O_4)_2^-$	$3.24\cdot10^{10}$		$CuHPO_4^0$	$1.58\cdot10^{3}$
	$Cr(C_2O_4)_3^{3-}$	$2.75\cdot10^{15}$		$CuC_2O_4^0$	$5.01\cdot10^{6}$
	$CrAl^{2+}$	$1.00\cdot10^{9}$		$Cu(C_2O_4)_2^{2-}$	$2.00\cdot10^{10}$
	$Cr(Al)_2^+$	$6.82\cdot10^{16}$		CuTart0	$1.00\cdot10^{3}$
	$CrAsp^{2+}$	$1.42\cdot10^{8}$		$Cu(Tart)_2^{2-}$	$1.29\cdot10^{5}$
	$Cr(Asp)_2^+$	$1.34\cdot10^{14}$		$CuCit^-$	$7.94\cdot10^{5}$
	$Cr(Asp)_3^0$	$2.54\cdot10^{19}$		$CuHCit^0$	$2.64\cdot10^{3}$
	$CrVal^{2+}$	$5.66\cdot10^{8}$		CuH_2Cit^+	$1.82\cdot10^{2}$
	$Cr(Val)_2^+$	$2.84\cdot10^{15}$		$CuAl^+$	$3.24\cdot10^{8}$
	$Cr(Val)_3^0$	$1.01\cdot10^{21}$		$Cu(Al)_2^0$	$2.34\cdot10^{15}$
	$CrGlic^{2+}$	$7.12\cdot10^{8}$		$CuAsp^+$	$1.95\cdot10^{8}$
	$Cr(Glic)_2^+$	$3.58\cdot10^{15}$		$Cu(Asp)_2^0$	$5.14\cdot10^{14}$
	$Cr(Glic)_3^0$	$2.54\cdot10^{21}$		$CuAsk^0$	$2.63\cdot10^{9}$
	$CrLeic^{2+}$	$1.79\cdot10^{9}$		$Cu(Ask)_2^{2-}$	$5.34\cdot10^{16}$
	$Cr(Leic)_2^+$	$2.26\cdot10^{16}$		$CuVal^+$	$1.26\cdot10^{8}$
	$Cr(Lei)_3^0$	$2.54\cdot10^{22}$		$Cu(Val)_2^0$	$5.92\cdot10^{14}$
	$CrMet^{2+}$	$7.04\cdot10^{7}$		$CuGis^+$	$9.71\cdot10^{10}$

(continued)

Table 3.30 (continued)

Cu^{2+}	$Cu(Gis)_2^0$	$1.52 \cdot 10^{19}$		$Fe(Al)_2^0$	$3.65 \cdot 10^7$
	$CuGlic^+$	$4.17 \cdot 10^8$		$FeAsp^+$	$2.62 \cdot 10^3$
	$Cu(Glic)_2^0$	$3.89 \cdot 10^{15}$		$FeAsk^0$	$2.37 \cdot 10^4$
	$CuGlut^0$	$8.91 \cdot 10^7$		$Fe(Ask)_2^{2-}$	$7.15 \cdot 10^8$
	$Cu(Glut)_2^{2-}$	$8.09 \cdot 10^{14}$		$FeVal^+$	$2.56 \cdot 10^3$
	$CuLeic^+$	$1.17 \cdot 10^8$		$FeGis^+$	$1.66 \cdot 10^6$
	$Cu(Leic)_2^0$	$4.00 \cdot 10^{14}$		$Fe(Gis)_2^0$	$4.44 \cdot 10^{10}$
	$CuLiz^+$	$8.85 \cdot 10^7$		$FeGlic^+$	$3.02 \cdot 10^4$
	$Cu(Liz)_2^0$	$4.48 \cdot 10^{14}$		$Fe(Glic)_2^0$	$1.15 \cdot 10^8$
	$CuMet^+$	$2.04 \cdot 10^8$		$FeGlut^0$	$4.79 \cdot 10^4$
	$Cu(Met)_2^0$	$2.24 \cdot 10^{15}$		$Fe(Glut)_2^{2-}$	$1.82 \cdot 10^7$
	$CuProl^+$	$5.89 \cdot 10^8$		$FeLeic^+$	$2.74 \cdot 10^3$
	$Cu(Prol)_2^0$	$8.33 \cdot 10^{15}$		$FeLiz^+$	$4.79 \cdot 10^4$
	$CuTir^+$	$1.16 \cdot 10^8$		$FeMet^+$	$1.81 \cdot 10^3$
	$Cu(Tir)_2^0$	$1.17 \cdot 10^{15}$		$Fe(Met)_2^0$	$9.17 \cdot 10^6$
	$CuCis_2^{2-}$	$1.56 \cdot 10^{16}$		$FeProl^+$	$1.22 \cdot 10^4$
Fe^{2+}	$FeOH^+$	$3.63 \cdot 10^5$		$Fe(Prol)_2^0$	$4.84 \cdot 10^8$
	$Fe(OH)_2^0$	$5.89 \cdot 10^9$		FeGis	$3.02 \cdot 10^4$
	$FeCO_3^0$	$5.37 \cdot 10^4$		$Fe(Gis)_2^0$	$1.15 \cdot 10^8$
	$FeHCO_3^+$	$\sim 1 \cdot 10^3$		$Fe(Cis)_2^{2-}$	$5.89 \cdot 10^{11}$
	$FeSO_4^0$	$1.58 \cdot 10^2$	**Fe^{3+}**	$FeOH^{2+}$	$7.41 \cdot 10^{11}$
	$FeHPO_4^0$	$1.58 \cdot 10^7$		$Fe(OH)_2^+$	$1.48 \cdot 10^{21}$
	$FeH_2PO_4^+$	$5.01 \cdot 10^2$		$Fe(OH)_3^0$	$4.68 \cdot 10^{30}$
	$FeC_2O_4^0$	$1.12 \cdot 10^3$		$FeCO_3^+$	$5.23 \cdot 10^9$
	$Fe(C_2O_4)_2^{2-}$	$3.31 \cdot 10^4$		$FeHCO_3^{2+}$	$1.00 \cdot 10^5$
	$FeCit^-$	$2.51 \cdot 10^4$		$FeCl^{2+}$	$2.81 \cdot 10^1$
	$FeHCit^0$	$1.32 \cdot 10^2$		$FeCl_2^+$	$1.26 \cdot 10^2$
	$FeAl^+$	$3.61 \cdot 10^3$		$FeSO_4^+$	$1.10 \cdot 10^4$

(continued)

Table 3.30 (continued)

Fe^{3+}	$Fe(SO_4)_2^-$	$2.40\cdot10^5$	**Hg^{2+}**	$HgCl^+$	$5.01\cdot10^6$
	$FeHPO_4^+$	$5.62\cdot10^9$		$HgCl_2^0$	$1.70\cdot10^{13}$
	$FeH_2PO_4^{2+}$	$3.16\cdot10^3$		$HgCl_3^-$	$1.70\cdot10^{14}$
	FeF^{2+}	$1.10\cdot10^6$		$HgCl_4^{2-}$	$1.66\cdot10^{15}$
	FeF_2^+	$5.50\cdot10^{10}$		$HgSO_4^0$	$2.19\cdot10^1$
	FeF_3^0	$5.50\cdot10^{13}$		$Hg(SO_4)_2^{2-}$	$2.75\cdot10^2$
	FeF_4^-	$5.50\cdot10^{15}$		$HgCit^-$	$7.94\cdot10^{10}$
	$FeC_2O_4^+$	$2.51\cdot10^9$		$Hg(Al)_2^0$	$8.11\cdot10^{18}$
	$Fe(C_2O_4)_2^-$	$1.58\cdot10^{16}$		$Hg(Gis)_2^0$	$2.92\cdot10^{21}$
	$Fe(C_2O_4)_3^{3-}$	$1.58\cdot10^{20}$		$Hg(HGis)^{2+}$	$3.75\cdot10^{18}$
	$FeTart^+$	$3.09\cdot10^7$		$Hg(HGis)_2^{2+}$	$1.84\cdot10^{15}$
	$Fe(Tart)_2^-$	$7.24\cdot10^{11}$		$HgGlic^+$	$3.99\cdot10^{10}$
	$FeCit^0$	$2.51\cdot10^{11}$		$Hg(Glic)_2^0$	$4.49\cdot10^{19}$
	$FeHCit^+$	$2.00\cdot10^6$		$HgMet^+$	$9.12\cdot10^6$
	$FeAl^{2+}$	$1.02\cdot10^{11}$		$Hg(Met)_2^0$	$1.28\cdot10^{12}$
	$FeAsp^{2+}$	$4.24\cdot10^8$		$Hg(Prol)_2^0$	$5.83\cdot10^{20}$
	$FeAsk^+$	$2.85\cdot10^{11}$		$Hg(Tir)_2^0$	$1.75\cdot10^{17}$
	$FeVal^{2+}$	$4.24\cdot10^9$		$HgCis^0$	$5.62\cdot10^{14}$
	$FeGis^{2+}$	$5.34\cdot10^4$		$Hg(Cis)_2^{2-}$	$3.53\cdot10^{20}$
	$FeGlic^{2+}$	$1.07\cdot10^{10}$	**Mg^{2+}**	$MgCO_3^0$	$2.51\cdot10^3$
	$FeGlut^+$	$1.43\cdot10^{12}$		$MgHCO_3^+$	$1.45\cdot10^1$
	$FeLeic^{2+}$	$8.46\cdot10^9$		$MgSO_4^0$	$2.29\cdot10^2$
	$FeMet^{2+}$	$1.34\cdot10^9$		$MgHPO_4^0$	$7.59\cdot10^2$
	$FeProl^+$	$1.10\cdot10^{10}$		$MgH_2PO_4^+$	$1.48\cdot10^1$
	$Fe(Cis)_3^{3-}$	$1.26\cdot10^{32}$		$MgC_2O_4^0$	$3.55\cdot10^2$
Hg^{2+}	$HgOH^+$	$2.00\cdot10^{10}$		$Mg(C_2O_4)_2^{2-}$	$2.40\cdot10^4$
	$Hg(OH)_2^0$	$5.01\cdot10^{21}$		$MgTart^0$	$8.13\cdot10^1$
	$HgCO_3^0$	$3.24\cdot10^7$		$MgCit^-$	$9.12\cdot10^3$

(continued)

Table 3.30 (continued)

Mg^{2+}	$MgHCit^0$	$6.92\cdot10^1$	**Mn^{2+}**	$MnProl^+$	$6.03\cdot10^3$
	$MgAl^+$	$9.12\cdot10^1$		$MnTir^+$	$6.52\cdot10^1$
	$Mg(Asp)_2^0$	$1.79\cdot10^4$		$Mn(Tir)_2^0$	$9.94\cdot10^3$
	$MgAsk^0$	$7.41\cdot10^2$		$MnCis^0$	$1.00\cdot10^5$
	MgGlic	$4.27\cdot10^2$	**Ni^{2+}**	$NiOH^+$	$9.33\cdot10^4$
	$MgGlut^0$	$2.19\cdot10^2$		$Ni(OH)_2^0$	$3.55\cdot10^8$
Mn^{2+}	$MnOH^+$	$7.94\cdot10^3$		$NiCO_3^0$	$2.34\cdot10^5$
	$Mn(OH)_2^0$	$6.68\cdot10^6$		$NiHCO_3^+$	$5.01\cdot10^3$
	$Mn(OH)_3^-$	$2\cdot10^8$		$NiSO_4^0$	$2.09\cdot10^2$
	$MnCO_3^0$	$7.94\cdot10^4$		$Ni(SO_4)_2^{2-}$	$1.58\cdot10^3$
	$MnHCO_3^+$	$8.91\cdot10^1$		$NiHPO_4^0$	$1.20\cdot10^2$
	$MnSO_4^0$	$1.86\cdot10^2$		$NiC_2O_4^0$	$2.00\cdot10^5$
	$MnHPO_4^0$	$3.80\cdot10^2$		$Ni(C_2O_4)_2^{2-}$	$3.24\cdot10^6$
	$MnC_2O_4^0$	$6.61\cdot10^3$		$NiTart^0$	$4.07\cdot10^3$
	$MnTart^0$	$2.75\cdot10^1$		$Ni(Tart)_2^0$	$2.63\cdot10^5$
	$MnCit^-$	$5.25\cdot10^3$		$NiCit^-$	$2.51\cdot10^5$
	$MnHCit^0$	$1.20\cdot10^2$		$NiHCit^0$	$2.00\cdot10^3$
	$MnAl^+$	$1.05\cdot10^3$		$NiAl^+$	$9.12\cdot10^5$
	$Mn(Asp)_2^0$	$5.78\cdot10^4$		$Ni(Al)_2^0$	$4.57\cdot10^{10}$
	$MnAsk^0$	$1.83\cdot10^4$		$NiAsp^+$	$1.23\cdot10^6$
	$MnVal^+$	$1.05\cdot10^3$		$Ni(Asp)_2^0$	$3.90\cdot10^{10}$
	$Mn(Val)_2^0$	$6.64\cdot10^5$		$NiAsk^0$	$1.20\cdot10^7$
	$MnGis^+$	$1.05\cdot10^4$		$Ni(Ask)_2^{2-}$	$2.70\cdot10^{12}$
	$MnGlic^+$	$2.34\cdot10^3$		$NiVal^+$	$7.41\cdot10^5$
	$Mn(Glic)_2^0$	$15.78\cdot10^5$		$Ni(Val)_2^0$	$1.45\cdot10^{10}$
	$MnGlut^0$	$2.51\cdot10^3$		$NiGis^+$	$7.41\cdot10^8$
	$MnLeic^+$	$9.12\cdot10^2$		$Ni(Gis)_2^0$	$6.06\cdot10^{15}$
	$Mn(Leic)_2^0$	$5.15\cdot10^5$		$NiGlic^+$	$1.51\cdot10^6$
	$MnLiz^+$	$1.48\cdot10^2$		$Ni(Glic)_2^0$	$1.38\cdot10^{11}$
	$MnMet^+$	$1.62\cdot10^3$		$NiGlut^0$	$6.92\cdot10^5$
	$Mn(Met)_2^0$	$1.59\cdot10^5$		$Ni(Glut)_2^{2-}$	$3.37\cdot10^9$

(continued)

Table 3.30 (continued)

Ni^{2+}	$NiLeic^{+}$	$1.27\cdot10^{6}$	**Pb^{2+}**	$PbHCit^{0}$	$5.25\cdot10^{5}$
	$Ni(Leic)_2^{0}$	$7.78\cdot10^{10}$		$PbAl^{+}$	$1.00\cdot10^{5}$
	$Ni(Leic)_3^{-}$	$4.00\cdot10^{15}$		$Pb(Al)_2^{0}$	$1.74\cdot10^{8}$
	$NiLiz^{+}$	$3.07\cdot10^{5}$		$PbAsp^{+}$	$2.37\cdot10^{4}$
	$Ni(Liz)_2^{0}$	$1.06\cdot10^{9}$		$Pb(Asp)_2^{0}$	$1.80\cdot10^{6}$
	$Ni(Liz)_3^{-}$	$1.01\cdot10^{11}$		$PbAsk^{0}$	$7.90\cdot10^{5}$
	$NiMet^{+}$	$4.27\cdot10^{5}$		$Pb(Ask)_2^{0}$	$2.55\cdot10^{7}$
	$Ni(Met)_2^{0}$	$2.96\cdot10^{10}$		$PbVal^{+}$	$1.09\cdot10^{4}$
	$NiProl^{+}$	$3.89\cdot10^{6}$		$Pb(Val)_2^{0}$	$8.64\cdot10^{9}$
	$Ni(Prol)_2^{0}$	$8.15\cdot10^{11}$		$PbGis^{+}$	$1.87\cdot10^{7}$
	$NiTir^{+}$	$2.16\cdot10^{5}$		$PbGlic^{+}$	$5.95\cdot10^{5}$
	$Ni(Tir)_2^{0}$	$5.85\cdot10^{9}$		$Pb(Glic)_2^{0}$	$7.24\cdot10^{8}$
	$NiCis^{0}$	$6.86\cdot10^{9}$		$PbGlut^{0}$	$4.32\cdot10^{4}$
	$Ni(Cis)_2^{2-}$	$9.91\cdot10^{20}$		$Pb(Glut)_2^{2-}$	$1.80\cdot10^{6}$
Pb^{2+}	$PbOH^{+}$	$3.31\cdot10^{7}$		$PbMet^{+}$	$6.60\cdot10^{4}$
	$Pb(OH)_2^{0}$	$3.47\cdot10^{10}$		$Pb(Met)_2^{0}$	$1.95\cdot10^{9}$
	$Pb(OH)_3^{-}$	$8.91\cdot10^{13}$		$PbTir^{+}$	$3.07\cdot10^{4}$
	$PbCO_3^{0}$	$2.51\cdot10^{6}$		$Pb(Tir)_2^{0}$	$1.15\cdot10^{9}$
	$Pb(CO_3)_2^{2-}$	$1.23\cdot10^{9}$		$PbCis^{0}$	$8.73\cdot10^{11}$
	$PbHCO_3^{+}$	$5.32\cdot10^{2}$	**Zn^{2+}**	$ZnOH^{+}$	$2.04\cdot10^{6}$
	$Pb(HCO_3)_2^{0}$	$5.89\cdot10^{4}$		$Zn(OH)_2^{0}$	$1.55\cdot10^{11}$
	$Pb(HCO_3)_3^{-}$	$1.55\cdot10^{5}$		$Zn(OH)_3^{-}$	$2.04\cdot10^{14}$
	$PbCl^{+}$	$4.14\cdot10^{1}$		$ZnCO_3^{0}$	$2.00\cdot10^{5}$
	$PbCl_2^{0}$	$2.75\cdot10^{2}$		$ZnHCO_3^{+}$	$1.26\cdot10^{2}$
	$PbSO_4^{0}$	$4.17\cdot10^{2}$		$ZnSO_4^{0}$	$2.19\cdot10^{2}$
	$Pb(SO_4)_2^{2-}$	$2.95\cdot10^{3}$		$ZnHPO_4^{0}$	$2.51\cdot10^{2}$
	$PbC_2O_4^{0}$	$7.94\cdot10^{4}$		$ZnC_2O_4^{0}$	$7.08\cdot10^{4}$
	$Pb(C_2O_4)_2^{2-}$	$3.47\cdot10^{6}$		$Zn(C_2O_4)_2^{2-}$	$3.55\cdot10^{7}$
	$PbTart^{0}$	$8.32\cdot10^{2}$		$ZnTart^{0}$	$2.04\cdot10^{3}$
	$PbCit^{-}$	$3.16\cdot10^{6}$		$Zn(Tart)_2^{2-}$	$1.45\cdot10^{5}$

(continued)

Table 3.30 (continued)

Zn^{2+}	$ZnCit^-$	$9.55 \cdot 10^4$	$ZnGlut^0$	$3.55 \cdot 10^5$
	$ZnHCit^0$	$9.55 \cdot 10^2$	$Zn(Glut)_2^{2-}$	$9.28 \cdot 10^9$
	$ZnAl^+$	$1.62 \cdot 10^5$	$ZnLeic^+$	$1.23 \cdot 10^5$
	$Zn(Al)_2^0$	$3.47 \cdot 10^9$	$Zn(Leic)_2^0$	$1.56 \cdot 10^9$
	$Zn(Asp)_2^0$	$9.17 \cdot 10^8$	$Zn(Liz)_2^0$	$7.28 \cdot 10^7$
	$ZnAsk^0$	$1.91 \cdot 10^6$	$ZnMet^+$	$6.46 \cdot 10^4$
	$Zn(Ask)_2^{2-}$	$9.69 \cdot 10^{10}$	$Zn(Met)_2^0$	$6.52 \cdot 10^8$
	$ZnVal^+$	$1.51 \cdot 10^5$	$ZnProl^+$	$6.31 \cdot 10^5$
	$Zn(Val)_2^0$	$2.30 \cdot 10^9$	$ZnTir^+$	$2.91 \cdot 10^4$
	$ZnGis^+$	$1.13 \cdot 10^7$	$Zn(Tir)_2^0$	$5.71 \cdot 10^8$
	$Zn(Cis)_2^0$	$9.02 \cdot 10^{12}$	$ZnCis^0$	$3.02 \cdot 10^9$
	$ZnGlic^+$	$3.31 \cdot 10^5$	$Zn(Cis)_2^{2-}$	$1.48 \cdot 10^{18}$
	$Zn(Glic)_2^0$	$9.12 \cdot 10^5$		

Table 3.31 Conditional stability constants of fulvic (FA) and humate (HA) metal complexes

Metal	Expression of a constant	*β*	*pH*	Ionic strength μ	Other conditions	References
Al(III)	[AlFA]/[Al] · [FA]	4.68×10^4	4.0	0.1	FA isolated from water	[6]
		2.88×10^6	5.0	0.1		[6]
Au(III)	[AuFA]/[Au^{3+}] · [FA^{2-}]	2.57×10^6	3.5	0.1	FA isolated from water	[26]
		5.62×10^8	5.8	0.1		[26]
		8.91×10^9	7.5	0.1		[26]
Ca(II)	[CaFA]/[Ca^{2+}] · [FA^{2-}]	4.37×10^3	5.0	0.1	FA isolated from water	[26]
		1.00×10^3	5.0	0.05	FA isolated from soil	[9]
	[CaFA]/[Ca^{2+}] · [FA]	1.32×10^3	5.0	0.1	–	[22]
Cd(II)	[CdFA]/[Cd^{2+}] · [HFA^-]	1.38×10^3	4.0	0.1	FA isolated from water	[18]
		3.02×10^3	5.0	0.1		[18]
		4.79×10^3	6.0	0.1		[18]
	[CdFA]/[Cd^{2+}] · [HFA^-]	8.13×10^3	7.0	0.1	FA isolated from water	[18]
		1.20×10^4	8.0	0.1		[18]
	[CdFA]/[Cd^{2+}] · [HFA^-]	1.70×10^3	4.0	0.1	FA isolated from soil	[18]
		6.31×10^3	5.0	0.1		[18]
		1.20×10^4	6.0	0.1		[18]
		2.09×10^4	7.0	0.1		[18]
		4.27×10^4	8.0	0.1		[18]
	[CdFA]/[Cd^{2+}] · [H_xFA^-]	2.0×10^5	5.7	0.01	FA isolated from soil	[2]
		4.0×10^5	6.7	0.01		[2]
		1.0×10^6	7.7	0.01		[2]

(continued)

Table 3.31 (continued)

Metal	Expression of a constant	*β*	*pH*	Ionic strength μ	Other conditions	References
	$[CdFA]/[Cd^{2+}] \cdot [FA]$	1.10×10^3	5.0	0.1	–	[22]
	$[CdHA]/[Cd^{2+}] \cdot [HA^{2-}]$	$(0.2–1.0) \times 10^4$	4.0–6.0	0.1	HA isolated from soil	[20]
	$[CdHA^{(m-n)-}]/[Cd^{n+}] \cdot [HAm-]$	1.10×10^5	6.8	0.1	HA isolated from soil	[10]
Co(II)	$[CoFA]/[Co^{2+}] \cdot [FA^{2-}]$	5.0×10^3	6.0	0.1	FA isolated from soil	[16]
	$[CoFA]/[Co] \cdot [FA]$	9.33×10^6	7.6	0.01	FA isolated from water	[14]
Cr(III)	$[CrFA]/[Cr(OH)^{2+}] \cdot [FA^{2-}]$	6.3×10^5	4.8	0.1	FA isolated from peat soil	[13]
		1.6×10^5	4.8	0.1	FA isolated from forest soil	[13]
Cu(II)	$[CuFA]/[Cu^{2+}] \cdot [FA^{2-}]$	5.0×10^3	5.0	0.05	FA isolated from soil	[9]
		1.0×10^5	6.0	0.1		[16]
		5.50×10^5	7.5	0.1	FA isolated from water	[26]
	$[CuFA^+]/[Cu^{2+}] \cdot [FA^-]$	7.9×10^5	3.9	0.1	Aqueous acetone extract from peat	[23]
Cu(II)	$\left[Cu(FA)_2^0\right] / \left[Cu^{2+}\right] \cdot [FA^-]_2$	4.0×10^{12}	3.9	0.1		[23]
		1.3×10^{13}	3.9	0.1	Ammonium hydroxide extract from peat	[23]
	$[Cu(FA)]/[Cu^{2+}] \cdot [FA]$	2.75×10^5	4.8	0.1	Aqueous extract from peat soil	[13]
		7.76×10^4	4.8	0.1	Aqueous extract from forest soil	[13]
		3.72×10^2	4.0	0.1	FA isolated from soil	[1]
		8.51×10^3	5.5	0.1		[1]
		3.2×10^5	4.0	0.1	FA isolated from water	[3]
	$[Cu(FA)]/[Cu^{2+}] \cdot [FA]$	1.0×10^6	5.0	0.1	FA isolated from water	[3]
	$[Cu(FA)]/[Cu] \cdot [FA]$	1.3×10^6	6.0	0.1	FA isolated from soil	[3]
		4.0×10^5	4.0	0.1		[3]
		1.0×10^6	5.0	0.1	FA isolated from soil	[3]
		2.0×10^6	6.0	0.1		[3]
		4.79×10^4	5.0	0.1		[17]
	$[CuHA^0)]/[Cu^{2+}] \cdot [HA^{2-}]$	1.03×10^5	6.0	0.1	FA of lake waters	[17]
		2.82×10^5	7.0	0.1		[17]
		5.0×10^5	7.0	–		[21]
		6.3×10^7	7.6	0.01		[24]
		$(0.4–1.0) \times 10^7$	8.0	0.01	FA isolated from bottom sediments	[11]
		6.3×10^7	6.8	–	HA commercial formulation	[7]
	$\left[Cu(HA)_2^{2-}\right] / [Cu^{2+}] \cdot \left[HA^{2-}\right]^2$	6.3×10^{16}	6.8	–	HA of lake waters	[7]
	$[CuHA)]/[Cu] \cdot [HA]$	1.0×10^6	7.0	–		[21]
	$[CuHA^{(m-n)-}]/[Cu^{n+}] \cdot [HA^{m-}]$	$(0.3–6.3) \times 10^9$	8.0	0.02	HA of river and lake waters	[15]
		1.6×10^6	6.8	0.1	HA isolated from soil	[10]

(continued)

Table 3.31 (continued)

Metal	Expression of a constant	*β*	*pH*	Ionic strength μ	Other conditions	References
Fe(II)	$[FeFA]/[Fe^{2+}] \cdot [FA^{2-}]$	4.68×10^4	5.0	0.1	FA isolated from water	[26]
Fe(III)	$[FeFA]/[Fe^{3+}] \cdot [FA^{2-}]$	1.41×10^7	5.0	0.1		[26]
	$[Fe(FA)2]/[Fe^{3+}] \cdot [FA^{2-}]^2$	3.16×10^{12}	5.0	0.1		[12]
	$[FeFAOH]/[Fe^{3+}] \cdot [FA^{2-}] \cdot [OH^-]$	1.3×10^{20}	5.0	0.1		[12]
	$[FeFA(OH)^{2-}]/[Fe^{3+}] \cdot [FA^{2-}] \cdot [OH^-]^2$	3.2×10^{30}	5.0	0.1		[12]
Hg(II)	$[HgFA]/[Hg^{2+}] \cdot [FA^{2-}]$	1.70×10^{11}	6.4	0.1	FA isolated from water	[26]
		$(1.3–2.5) \times 10^{11}$	6.5	0.1		[25]
	$[HgFA]/[Hg] \cdot [FA]$	7.24×10^4	3.0	0.1	FA isolated from soil	[5]
		1.22×10^5	4.0	0.1		[5]
Mg(II)	$[MgFA]/[Mg^{2+}] \cdot [FA^{2-}]$	6.3×10^2	5.0	0.05	FA isolated from soil	[9]
	$[MgFA]/[Mg^{2+}] \cdot [FA]$	5.0×10^2	5.0	0.1	–	[22]
	$[MgFA]/[Mg^{2+}] \cdot [FA^{2-}]$	7.1×10^3	8.0	0.1	–	[22]
Mn(II)	$[MnFA]/[Mn^{2+}] \cdot [FA^{2-}]$	5.0×10^3	5.0	0.05	FA isolated from soil	[9]
	$[MnFA]/[Mn] \cdot [FA]$	4.0×10^3	6.0	0.1		[16]
		1.0×10^3	4.62–4.68	0.01	FA isolated from bottom sediments	[11]
Ni(II)	$[NiFA]/[Ni^{2+}] \cdot [FA^{2-}]$	$(1.4–1.6) \times 10^7$	4.0–6.5	0.05	FA isolated from soil	[9]
	$[NiFA^{2-x}]/[Ni^{2+}] \cdot [FAx-]$	6.3×10^3	5.7–6.5	0.05	Ammonium hydroxide extract from peat	[8]
	$[NiFA]/[Ni^{2+}] \cdot [FA]$	1.55×10^3	4.0	0.1	FA isolated from soil	[1]
		1.70×10^3	5.5	0.1		[1]
		2.24×10^4	4.0–5.0	0.1		[5]
		6.46×10^3	5.0	0.1	–	[22]
	$[NiFA]/[Ni] \cdot [FA]$	$(0.5–1.3) \times 10^7$	6.5–7.6	0.01	FA isolated from water	[14]
	$[NiHA)]/[Ni] \cdot [HA]$	9.55×10^4	8.0	0.02	HA isolated from peat	[15]
		$(1.4–1.8) \times 10^5$	8.0	0.02	HA isolated from water	[15]
Pb(II)	$[PbFA^0]/[Pb^{2+}] \cdot [FA]$	1.66×10^4	5.0	0.1	–	[22]
	$[Pb(FA)_2]/[Pb^{2+}] \cdot [FA]^2$	6.92×10^6	5.0	0.1	–	[22]
	$[PbFA]/[Pb^{2+}] \cdot [FA]$	$(0.5–1.3) \times 10^5$	5.0–6.0	–	–	[19]
	$[Pb(FA)_2]/[Pb^{2+}] \cdot [FA]^2$	$(0.2–1.3) \times 10^{10}$	5.0–6.0	–	–	[19]
	$[PbFA]/[Pb^{2+}] \cdot [FA]$	1.3×10^5	6.0	–	–	[4]
	$[Pb(FA)_2]/[Pb^{2+}] \cdot [FA]^2$	5.0×10^9	6.0	–	–	[4]
	$[PbHA^0)]/[Pb^{2+}] \cdot [HA^{2-}]$	1.3×10^6	6.8	–	Commercial formulation	[7]
	$\left[Pb(HA)_2^{2-}\right] \Big/ \left[Pb^{2+}\right] \cdot \left[HA^{2-}\right]^2$	6.3×10^{14}	6.8	–		[7]
	$[PbHA^{(m-n)-}]/[Pb^{n+}] \cdot [HA^{m-}]$	2.82×10^6	6.8	0.1	HA isolated from soil	[10]
Sb(III)	$[SbFA]/[Sb^{3+}] \cdot [FA^{2-}]$	8.71×10^7	5.8	0.1	FA isolated from water	[26]
Sr(II)	$[SrFA]/[Sr^{2+}] \cdot [FA^{2-}]$	3.72×10^3	5.0	0.1	FA isolated from water	[26]
Zn(II)	$[ZnFA]/[Zn^{2+}] \cdot [FA^{2-}]$	2.0×10^2	5.0	0.05	FA isolated from soil	[9]

(continued)

Table 3.31 (continued)

Metal	Expression of a constant	β	*pH*	Ionic strength μ	Other conditions	References
	$[ZnFA]/[Zn^{2+}] \cdot [FA]$	2.82×10^3	5.0	0.1	–	[22]
		9.77×10^2	4.0	0.1	FA isolated from soil	[1]
		1.45×10^4	5.5	0.1		[1]
	$[ZnFA]/[Zn] \cdot [FA]$	$(1.1–2.6) \times 10^5$	8.0	0.02	FA isolated from water	[15]
		$(4.7–6.3) \times 10^5$	8.0	0.01	FA isolated from bottom sediments	[11]
	$[ZnHA]/[Zn^{2+}] \cdot [HA^{2-}]$	$(0.4–5.1) \times 10^4$	4.0–6.0	0.1	HA isolated from soil	[20]
	$[ZnHA^{(m-n)-}]/[Zn^{n+}] \cdot [HA^{m-}]$	1.0×10^5	6.8	0.1		[10]

Expressions of constants are presented according to the original literature. Sign "–" means that the origin of FA and HA is not specified

1. Adhikari M. Hazra GC (1972) Stability constants of Cu^{2+}. Ni^{2+} and Zn^{2+} fulvic acid metal complexes. J Indian Chem Soc 49(10): 947–951
2. Brady B. Pagenkopf GK (1978) Cadmium complexation by soil fulvic acid. Can J Chem 56(17): 331–233
3. Bresnahan WT. Grant CL. Weber JH (1978) Stability Constants of the Complexation of Copper (II) Ions with Water and Soil Fulvic Acids Measured by an Ion Selective Electrode. Anal Chem 50(12): 1675–1679
4. Buble Y. Greter F-L (1979) Voltammetric study of humic and fulvic substances. Part II: Mechanism of reaction of the fulvic complexes on the mercury electrode. J Elektroanal Chem 101(2): 231–25
5. Cheam V. Gamble DS (1974) Metal-fulvic chelation equilibrium in aqueos $NaNO_3$ solution. *Hg*(II). *Cd*(II) and *Cu*(II) fulvate complexes. Can J Soil Sci 54(4): 413–418
6. Elkins KM. Nelson DJ (2002) Spectroscopic approaches to the study of the interaction of aluminium with humic substances. Coordination Chemistry Reviews 228: 205–225
7. Ernst R. Allen HE. Mancy KH (1975) Characterization of trace metal species and measurement of trace metal stability constants by electrochemical techniques. Water Res 9(11): 969–979
8. Goncharova TO. Kolosov IV. Kaplin VT (1978) Hydroliz i kompleksoobrazovanie ionov Ni^{2+} v rastvorakh fulvokisloy (Hydrolysis and complexing Ni^{2+} ions in fulvic acids solutions). Hydrochemical materials 71: 64–71
9. Goncharova TO. Kolosov IV. Kaplin VT (1989) O formakh nakhozhdenia metallov v poverkhnostnykh vodakh (Coexisting forms of metals in surface water). Hydrochemical materials (77): 16–26
10. Guy RD. Chakrabarty CL (1976) Studies of metal-organik interaction in model system pertaining to natural waters. Can J Chem 54(16): 2600–2611
11. Hirata Sh. (1981) Stability constants for the complexes of transition—metal ions with fulvic and humic acids in sediments measumered by gel filtration. Talanta 28(11): 809–815
12. Intskirveli LN (1975) Issledovanie i opredelenie form zheleza v pryrodnykh vodakh (The study and determination of iron forms in natural water). Dissertation. Vernadsky Institute of Geochemistry and Analytical chemistry of Russian Academy of Sciences
13. Kraync M. Stupar J. Milicev S (1995) Characterization of chromium and copper complexes with fulvic acidc isolated from soils Slovenia. Sci Total Environ 159: 23–31
14. Lee J (1983) Complexation analysis of fresh water by equilibrium diafiltration. Water Res 17(5): 501–510
15. Mantoura RFC. Riley JP (1975) The use of gel filtration in the study of metal binding by humic acids related compounds. Analyt Chem Acta 78(1): 193–200
16. Ryan DK. Thompson CP. Weber JH (1983) Comparison of Mn^{2+}. Co^{2+} and Cu^{2+} binding to fulvic acid as measured by fluorescence quenching. Can J Chem 61(7): 1505–1509
17. Ryan DK. Weber JH (1982) Fluorescence Quenching Titration for Determination of Complexing Capacities and Stability Constants of Fulvic Acid. Anal Chem 54(6): 986–990
18. Saar RA. Weber JH (1979) Complexation of cadmium (II) with water—and soil—derived fulvic acids: effect of *pH* and fulvic acid concentration. Canadian J Chem 57(11): 1263–1268
19. Saar RA. Weber JH (1980) Lead (II)—fulvic acid complexes. Conditional stability constants solubility and implications for lead (II) mobility. Environ Sci Technol 14(7): 877–880
20. Saha SK. Dutta SL. Chakravarti SK (1979) Polagrographic study of metal–humic acid interaction. Determination of stability constants of *Cd*- and *Zn*-humic acid complexes at different *pH*. J Indian Chem Soc 56(11): 1128–1134
21. Shuman MS. Cromer JL (1979) Copper association with aquatic fulvic and humic acid. Estimation of conditional formation constants with a titrimetic anodic stripping voltammetry procedure. Environ Sci Technol 13(5): 543–545
22. Sposito G (1981) Trace metals in contaminated waters. Environ Sci Technol 15(14): 396–403
23. Tokareva GI. Kolosova IV. Goncharova TO (1983) Vzaimodeystvie ionov Cu(II) s hyminovymi kislotami i razlichnymi tractsiyami fulvokislot (Interaction of Cu^{2+} ions with humic acids and fulvic acids different factions). Hydrochemical materials (58): 88–101
24. Van der Berg CMG. Kramer JR (1979) Determination of complexing capacities of ligands in natural waters and conditional stability constants of the copper complexes by means of manganes dioxide. Analyt Chim Acta 106(1): 113–120
25. Varshal GM. Buachidze NS (1983) Issledovanie sosushchestvuyushchikh form rtuti (II) v poverkhnostnych vodakh (Study coexisting forms of mercury (II) in surface water). Anal Chem J 38(12): 2155–2167
26. Varshal GM. Velukhanova TK. Koshcheeva IYa at all (1983) Izuchenie khimicheskikh form elementov v poverkhnostnykh vodakh (Study of chemical forms of elements in surface water). Ana Chem J 38(9): 1590–1600

Table 3.32 Dependence of normal oxygen concentration (C_0) in water upon temperature

Temperature (°C)	Normal oxygen concentration C_0, mg O_2/L									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	14.65	14.61	14.57	14.53	14.49	14.45	14.41	14.37	14.33	14.29
1	14.25	14.21	14.17	14.13	14.09	14.05	14.02	13.98	13.94	13.90
2	13.86	13.82	13.79	13.75	13.71	13.68	13.64	13.60	13.56	13.53
3	13.49	13.46	13.42	13.38	13.35	13.31	13.28	13.24	13.20	13.17
4	13.13	13.10	13.06	13.03	13.00	12.96	12.93	12.89	12.86	12.82
5	12.79	12.76	12.72	12.69	12.66	12.52	12.59	12.56	12.53	12.49
6	12.46	12.43	12.40	12.36	12.33	12.30	12.27	12.24	12.21	12.18
7	12.14	12.11	12.08	12.05	12.02	11.99	11.96	11.93	11.90	11.87
8	11.84	11.81	11.78	11.75	11.72	11.70	11.67	11.64	11.61	11.58
9	11.55	11.52	11.49	11.47	11.44	11.41	11.38	11.35	11.33	11.30
10	11.27	11.24	11.22	11.19	11.16	11.14	11.11	11.08	11.06	11.03
11	11.00	10.98	10.95	10.93	10.90	10.87	10.85	10.82	10.80	10.77
12	10.75	10.72	10.70	10.67	10.65	10.62	10.60	10.57	10.55	10.52
13	10.50	10.48	10.45	10.43	10.40	10.38	10.36	10.33	10.31	10.28
14	10.26	10.24	10.22	10.19	10.17	10.15	10.12	10.10	10.08	10.06
15	10.03	10.01	10.09	9.97	9.95	9.92	9.90	9.88	9.86	9.84
16	9.82	9.79	9.77	9.75	9.73	9.71	9.69	9.67	9.65	9.63
17	9.61	9.58	9.56	9.54	9.52	9.50	9.48	9.46	9.44	9.42
18	9.40	9.38	9.36	9.34	9.32	9.30	9.29	9.27	9.25	9.23
19	9.21	9.19	9.17	9.15	9.13	9.12	9.10	9.08	9.06	9.04
20	9.02	9.00	8.98	8.97	8.95	8.93	8.91	8.90	8.88	8.86
21	8.84	8.82	8.81	8.79	8.77	8.75	8.74	8.72	8.70	8.68
22	8.67	8.65	8.63	8.62	8.60	8.58	8.56	8.55	8.53	8.52

(continued)

Table 3.32 (continued)

Temperature (°C)	Normal oxygen concentration C_0, mg O_2/L									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
23	8.50	8.48	8.46	8.45	8.43	8.42	8.40	8.38	8.37	8.35
24	8.33	8.32	8.30	8.29	8.27	8.25	8.24	8.22	8.21	8.19
25	8.18	8.16	8.14	8.13	8.11	8.11	8.08	8.07	8.05	8.04
26	8.02	8.01	7.99	7.98	7.96	7.95	7.93	7.92	7.90	7.89
27	7.87	7.86	7.84	7.83	7.81	7.80	7.78	7.77	7.75	7.74
28	7.72	7.71	7.69	7.68	7.66	7.65	7.64	7.62	7.61	7.59
29	7.58	7.56	7.55	7.54	7.52	7.51	7.49	7.48	7.47	7.45
30	7.44	7.42	7.41	7.40	7.38	7.37	7.35	7.34	7.32	7.31

Atmospheric pressure 760 Mmhg; O_2 (%) = Cx × 100 × 760/C0 × p; Cx—oxygen concentration found experimentally. mg O_2/L; p—atmospheric pressure during water sampling. Mmhg

References

1. Alekin OA (1970) Osnovy gidrokhimii (Principles of hydrochemistry). Hydrometeoizdat, Leningrad
2. Baes ICF, Mesmer RE (1986) The hydrolysis of cationis. Willey, New York
3. Driver J (1985) Geokhimiya prirodnykh vod (Natural water geochemistry). Mir. Moscow
4. Gorev LN (1996) Osnovy modelyuvannya v gidroekologii (Fundamentals of modeling in hydroecology). Lyibid, Kiev
5. Gorev LN, Peleshenko VI (1979) Hydrochimicheskoe ravnovesie (Hydrochemical balances). KGU Press, Kiev
6. Gorev LN, Peleshenko VI (1985) Metodika gidrokhimicheskikh issledovaniy (Hydrochemical survey technique). Vyischa shcola, Kyiv
7. Intskirveli LN (1975) Issledovanie i opredelenie form zheleza v pryrodnykh vodakh (The study and determination of iron forms in natural water). Dissertation. Vernadsky Institute of Geochemistry and Analytical chemistry of Russian Academy of Sciences
8. Khilchevsky V, Osadchy V, Kurylo S (2012) Osnovy hydrokhimii (Principles of hydrochemistry). Nika-Center, Kyiv
9. Kraynov SR, Shvets VM (1992) Gidrogeokhimiya (Hydrogeochemistry). Nedra, Moscow
10. Larson TE, Buswell AM (1942) Calcium Carbonate Saturation Index and Alralinity interpretation. J Am Water Work Assoc 34(11):1667–1684
11. Linnik PN (2003) Complexation as the worst important factor in the fate and transport of heavy metals in the Dnieper Water bodies. Anal Bional Crem 37:405–412
12. Linnik PN, Nabivanets BI (1986) Formy migratsii metallov v presnykh poverkhnostnykh vodakh (Metal migration forms in fresh surface water). Hydromteoizdat, Leningrad
13. Linnik PN, Vasilchuk TA, Linnik RP, Ignatenko II (2007) Sosuschestvuyuschie formy tyazhyolykh metallov v poverkhnostnykh vodakh Ukrainy i rol organicheskikh veschestv v ikh migratsii (Coexisting heavy metal forms in surface water of Ukraine and the role of organic substances in their migration. Methods and objects of chemical analysis), vol 2, no 2, pp 130–145
14. Loginov LF (1992) Rol guminovykh kislot v formirovanii okislitelno-vosstanovitelnykh usloviy v prirodnykh protsessakh (The role of humic acids in the redox condition formation in natural processes). Soil Sci 1:72–75
15. Lure YuYu (1979) Spravochnik po analiticheskoy khimii (The handbook of analytical chemistry). Chemistry. Moscow
16. Morgan II (1967) Chemical equilibrium and kinetic properties of manganese in natural waters. In: Principles and applications of water chemistry. New York
17. Nabivanets BY, Kalabina LV (1977) Novy metod issledovaniya protsessov kompleleksoobrazovaniya ionov metallov v prirodnykh vodakh (The new method of study of metal ion complexation processes in natural water). Vestnik of Kiev polytech. in-te. Ser Chem Mach Technol 14:90–94
18. Nabivanets BY, Linnik PN (1978) Metodika issledovaniya kompleksoobrazovahiya margantsa v prirodnykh vodakh (The survey technique of manganese complexation in natural water). Water conservancy problems. Kharkov. 9:23–29
19. Nabivanets BY, Osadchy VI, Osadcha NM, Nabivanets YuB (2007) Analitychna khimiya poverkhnevykh vod (Analytical chemistry of surface water). Nauk dumka, Kyiv
20. Nazarenko VA, Antonovich VP, Nevskaya EM (1979) Gidroliz ionov metallov v razbavlrnnykh rastvorakh (Hydrolysis of metal ions in dilute solutions). Atomizdat, Moscow
21. Nikanorov AM (1989) Gidrokhimiya (Hydrochemistry). Hydrometeoizdat, Leningrad
22. Orlovsky VM, Maksimovich NP, Yakimchuk LN, Golovan DI (1983) Vliyaniya povysheniy temperatury na khimichesky sostav vody v usloviyakh modelirovaniya (Rising temperature impacts on chemical water composition in modeling conditions). Hydrochem Works Probl Chem Study Methods 88:103–109

23. Osadchy V, Osadcha N, Nabyvanets Yu (2003) Modelling of trace metal migration forms in water of the Dnieper reservoirs). Ekologija Vilnous 2:63–67
24. Osadchy VI, Krinichny VV, Osadcha NM (1998) Formy migratsii vazhkykh metaliv. rozchinenykh u void Dniprovskykh vodoskhovysch (Patterns of migration of heavy metals dissolved in water of the Dnieper reservoirs). Collect Stud UkrNDGMI 246:105–119
25. Osadchy VI, Nabivanets BY, Osadcha NM, Nabivanets YuB (2008) Gidrokhimichny dovidnyk (Hydrochemical handbook). Nika Centre. Kyiv
26. Osadchy VI, Peleshenko VI, Savitsky VN, Kirnichny VV, GrebenVV, Godun OS (1993) Raspredelenie tyazhyolykh metallov v vode. vzveshennykh veschestvakh i donnykh otlozheniyakh Dunaya (Heavy metal distribution in the water. Suspended substances and bottom sediments of the Danube). Water Resour 20(4):445–461
27. Osadchy VI, Voitsehovich OV, Milyukin MV et al (1997) Otsinka suchasnogo rivnya khimichnogo zabrudnennya vody ta donnykh vidkladiv dniprovskikh vodoskhovysch (Modern level assessment of chemical pollution of the Dnieper's reservoir water and bottom sediments). Final scientific report on the contract with IDRC. Canada, 1995–1997. Ukr. NDGMI Derzhkomitet of Ukraine. Kyiv. Registration 93-09505-92-10-4
28. Pyatnitsky IV (1978) Teoreticheskie osnovy analiticheskoy khimii (Theoretical fundamentals of analytical chemistry). Vyischa shkola, Kyiv
29. Spravochnik khimika (Cnemist handbook) (1964) Chemistry, vol 3. Leningrad
30. Supatashvili GD, Maharadze GA (1988) Formy nakhozhdeniya elementov v prirodnykh vodakh i ikh zavisimost ot ionnykh potentsialov (Metal occurrence forms in natural water and their dependence on ionic potential. Marine sediment chemical analysis). Collection of studies of P.L. Shirshov Oceanology inst of AN USSR. Nauka. Moscow
31. Tinsli I, Senyavin MM (ed) (1982) Povedenie khimicheskikh zagryazniteley v okruzhayuschey srede (Behavior of chemical environmental pollutants). Mir. Moscow
32. Varshal GM, Koscheeva IYa, Sirotkina IS, Velyuhanova TK, Intskirveli LL et al (1979) Izuchenie organicheskikh veschestv poverkhnostnykh vod i ikh vzaimodeystviya s ionamy metallov (The study of surface water organic substances and their interaction with metal ions). Geochemistry 4:598–607
33. Varshal GM, Velyuhanova TK, Koscheeva IYa et al (1983) Izuchenie khimicheskikh form elementov v poverkhnostnykh vodakh (Chemical element form study in surface water). J Anal Chem 38(9): 1590–1600
34. Varshal GM, Velyuhanova TK, Koscheeva IYa et al (1988) Kompleksoobrazovanie blagorodnykh metallov s fulvokislotami prirodnykh vod i geokhemicheskaya rol etikh protsessov (Cmplexation of precious metals with natural water fulvic acids and the geochemical role of these processes). Collection of sci. works of GEOChI AN USSR Analytical chemistry of rare elrments. Nauka. Moscow, pp 112–146
35. Volkov II (1975) Khimicheskie elementy v rechnom stoke i formy ikh postupleniya v more (na primere rek Chernomorskogo basseina) (River runoff chemical elements and their forms of input into the sea (the case of the Black Sea basin). The problems of lithology and geochemistry of sedimentary rocks and ores. Nauka. Moscow, pp 85–113

Chapter 4
Biological Processes. Effects of Hydrobionts on Surface Water Quality

Biological processes Among the various processes forming water quality characteristics in surface water objects an important role is played by biological processes. Water quality characteristic in a reservoir is affected by the biological factor in different ways, including physico-mechanical effect, which is accounted for the very presence of organisms in the water column, and chemical effect, which includes both metabolic, or lifetime, function and post-mortal effect (Table 4.1).

Photosynthetic hydrobionts, which are the primary source of energy in the biotic cycle of water bodies with slow water exchange, and non-photosynthetic microorganisms (fungi, yeast, actinomycetes), which are critical to the decomposition of complex organic biopolymers, have most significant effect on water quality [135].

Effects of hydrobionts of different trophic levels have been established for a number of water quality targets, which are graphically presented in Fig. 4.1. Undoubtedly, the contribution of each group of hydrobionts to the process of formation of water properties essentially differs and is subject to a significant change depending on the physiographic, hydrological and chemical characteristics of a water body, time of year and weather conditions, hydro-biological regime and biological characteristics of hydrobionts themselves. Algal plankton and periphyton, higher aquatic plants, bacteria, fungi, yeasts and actinomycetes, pnytobenthos organisms, out of fauna representatives—filter-feeding organisms, protozoa, in some cases—herbivorous fish substantially contribute to the formation of water quality. Each of these groups of hydrobionts affects water quality both, directly—by changing water quality parameters (e.g. dissolved oxygen concentrations, *pH*, concentrations of mineral and organic components, complexing ability, transparency and color, heating of water surface film etc.), and indirectly—through the function of other organisms [135].

The production and decomposition of organic substances are critical for any aquatic ecosystem. This is accounted for the fact that the processes of primary production, respiration and mineralization may cause considerable changes in the concentration of dissolved oxygen and carbon dioxide, they can change the *pH* and

V. Osadchyy et al., *Processes Determining Surface Water Chemistry*,
DOI 10.1007/978-3-319-42159-9_4

Table 4.1 Summary data on hydrobionts' effects on surface water quality [135]

Effect description	Group of hydrobionts
Physico-mechanical effect	
Change of water color (Physical effect)	Phytoplankton
Reduced transparency and increased turbidity of water (physical effect)	Bacterioplankton, phytoplankton, zooplankton
Deterioration of light penetration into water column due to the formation of surface films and suspensions (physical and mechanical effects)	Phytoplankton, mainly blue–green algae—activators of water "bloom"
Change of spectral distribution of solar radiation penetrating the water due to scattering and absorption of light rays (physical effect)	Phytoplankton, mainly the species of algae causing water "bloom" (blue–green, diatoms, dinophytes, green)
Heating of water surface film and lower layers below it (physical effect)	Blue–green algae—activators of water "bloom"
Vertical and horizontal movements of organic and inorganic substances (physico-mechanical effects)	Plankton organisms
Change of water viscosity (local physical effect)	Blue–green algae, which are characterized by enhancement of mucus formation from polysaccharides, produced exogenously
Change of water surface tension (local physical effect)	Planktonic organisms producing biopolymers
Metabolic or functional effect	
Release of oxygen and absorption of CO_2	Photosynthetic organisms—plankton, periphyton, benthos algae, submersed and semi-submersed macrophytes
Absorption of oxygen and release of CO_2	All hydrobionts
Change of water pH—alkalizing in the light, acidification in the dark	Photosynthetic hydrobionts
Absorption of biogenic elements from the water	Photosynthetic hydrobionts
Absorption of dissolved organic substances from the water	All hydrobionts
Release into water column of nitrogen, phosphorus and other biogenic elements from bottom sediment	Macrophytes, algae
Secretion of dissolved organic compounds, including aromatic, from cells (exometabolites), fecal discharge	All hydrobionts, animal organisms
Release of biologically active compounds, including with pronounced toxic effects	Algae, higher aquatic plants, aquatic fungi
Metal complexing	Algae forming exogenous mucous sheaths, degradable in the water and having high ion-exchange and adsorption capacity

(continued)

Table 4.1 (continued)

Effect description	Group of hydrobionts
Reutilization of bottom sediment phosphorus	Blue–green algae, characterized by a pronounced ability to daily vertical migration, a dominant component of algocenoses in eutrophic water bodies
Release of extracellular enzymes (e.g. alkaline phosphatase, etc.)	Algae
Release of nitrites, amines and other nitrogen compounds contributing to the formation of carcinogenic substances (e.g. nitrosamines)	Algae
Enrichment of water with nitrogen compounds through fixing free air nitrogen	Blue–green algae, bacteria, some fungi
Accumulation of biogenic and trace elements in cells, their transport by water currents and release into the water during cellular breakdown	All hydrobionts
Post-mortem effect	
Cellular debris of dead hydrobionts	All organisms
Autolysis of living cells	All hydrobionts
Input into the water of cyanophages during decomposition of cells	After breakdown of blue–green algae cells
Products of bacterial and fungal transformation of organic compounds of hydrobiont cells, including gases, that are removed from the water	All hydrobionts after death
Increased oxygen loss to oxidation of organic substances	All hydrobionts after death due to bacterial transformation

redox potential (Eh) of a system and, as a consequence, lead to the transformation of many chemical components.

Biological processes involve complex cycles and interactions that can be described as an inorganic (thermodynamically stable)—organic (thermodynamically unstable) matter cycle [31]. Photosynthesis and respiration play crucial roles in the biological processes. During the photosynthesis there occurs transition from stable state to unstable one. Respiration or breathing is a process during which heterotrophic organisms (bacteria, fungi, animals) use thermodynamic instability to derive energy for growth by oxidating organic matter and returning it to the inorganic form as thermodynamically stable.

Numerous microorganisms found in aquatic ecosystems can decompose various organic substances. At the same time, any naturally occurring organic compound is easily oxidized by certain species of microorganisms. It should be noted that even pesticides and plastics, which were not common in the biosphere in the recent past, experience, albeit slow, decomposition by microorganisms in the aquatic medium [109].

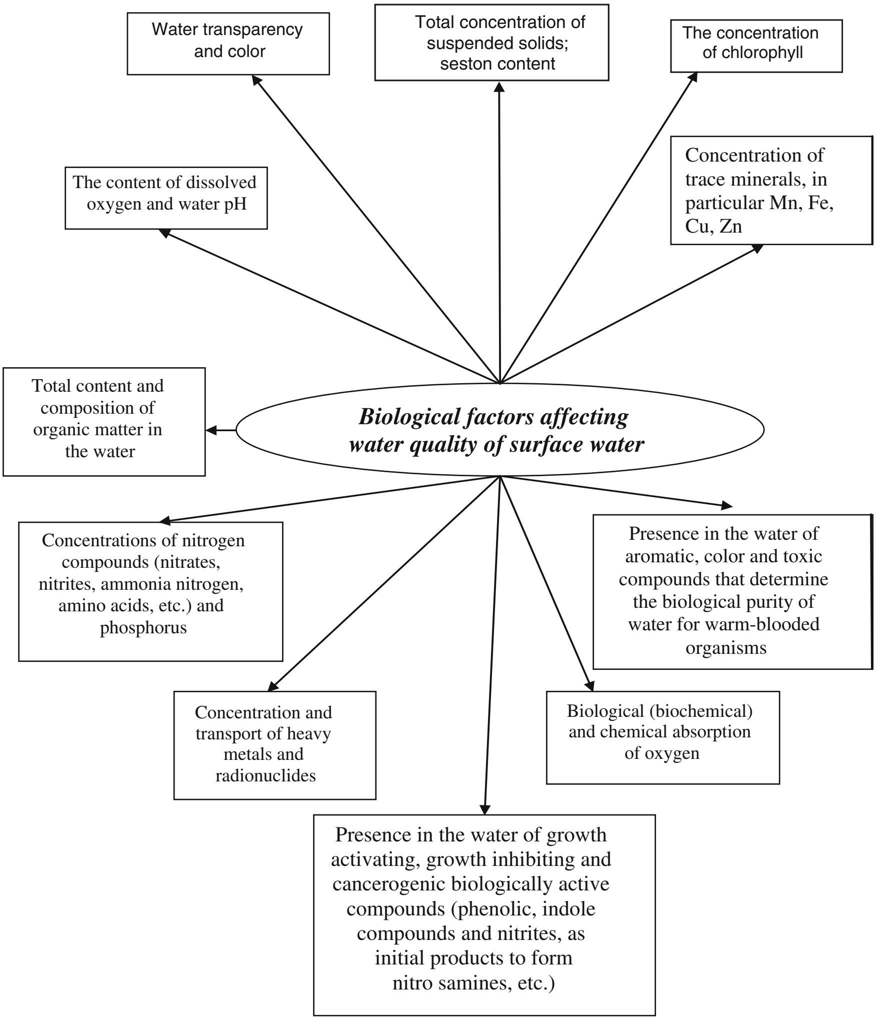


Fig. 4.1 Effects of hydrobionts on water quality of surface water objects [135]

At least three types of heterotrophic bacteria are involved in the process of recycling of organic compounds in aqueous medium:

- free-swimming bacterioplankton with well-developed locomotor system that are able to effectively consume organic compounds;
- stalked bacteria attached at the interface between liquid and solid or gaseous phases;
- bacteria forming colonies or aggregates to absorb organic matter.

Effects of hydrobionts on surface water quality Eutrophication of surface water bodies and intensive development of phytoplankton have caused their biological contamination and led to deterioration of the quality of natural water. This deterioration is due not only to growing water turbidity and its color, but also to a change in the chemical composition of the water as a result of its enrichment with lifetime excreta and decay products of dying phytoplankton, which significantly affect the composition of dissolved organic matter.

Biological contamination of water due to intensified reproduction of blue–green, diatom, dinophytes and other types of algae resulting in its "bloom" can significantly affect its quality, since the water medium is enriched with metabolites of high biological activity, including toxins [32, 119].

A crucial role in determining water quality and biological productivity of reservoirs is played by photosynthetic hydrobionts (phytoplankton, higher aquatic plants, epiphyton) and bacteria.

The contribution of phytoplankton to the processes affecting water quality and ecological condition of the reservoirs depends on the quality and quantity parameters of its biomass (Table 4.2) [98].

Intensive reproduction of blue–green algae (water "bloom") causes a water body biological contamination and deterioration of water quality, particularly in the areas of piled-up masses of algae and decomposition of their biomass. It is during this period that a sharp increase in bacterial water pollution and accumulation of highly toxic substances, dangerous not only for aquatic but also for warm-blooded organisms, occurs.

Table 4.2 Water "bloom" intensity gradation scale using the case study of Dnipro reservoirs [98]

Degree (gradation) of "Bloom"	Range of concentrations (g/m^3, green weight)	Environmental and sanitary-biological characteristics
I	Up to 1.0	Initial "bloom". Environmentally harmless concentrations
II	1–40 (50)	Optimal concentrations not leading to biological self-contamination, but neither providing a sufficient level of primary production to maintain fish productivity of reservoirs
III	50–250	Concentrations causing deterioration of water quality, but being acceptable for maintaining fish productivity of reservoirs
IV	250–500	Environmentally hazardous concentrations causing significant biological contamination, fish kill phenomena
V	>500	Piled-up concentrations causing heavy contamination of water masses and coastal areas. Environmentally hazardous, toxic, totally unacceptable

4.1 Effects of Hydrobionts on Water *pH*, Concentration of Dissolved Oxygen and Redox Potential

The *pH* values of surface natural water vary widely. However, in most cases they vary within the range from 5 to 9.

Natural water contains a variety of substances with different chemical properties and differ not only in the concentration of hydrogen ions, but also in buffer power. Water containing acids and their salts feature high buffer capacity, which inhibits sudden changes in the concentration of hydrogen ions. Water with high concentrations of dissolved substances, unlike water with their low content, feature a strong buffer effect. If there are no carbonates in the water, an increase or decrease of free carbon dioxide leads to a corresponding increase or decrease in carbonic acid and changes in the concentration of hydrogen ions. In the presence of higher concentrations of carbonates in the water, an increase or decrease in CO_2 concentration leads to an immediate restoring of the initial equilibrium, due to which the concentration of hydrogen ions usually remains the same. This mechanism works only within a certain range of concentrations that cause buffer effect. The effect of acidic or basic substances entering surface water on the *pH* depends on their buffer capacity. Soft water feature weak buffer action, therefore the concentration of hydrogen ions in them can vary dramatically with the input of the above substances. Hard water are characterized by high buffer values and are therefore resistant to substances that can change water *pH*.

Aquatic organisms change the *pH* of the aquatic medium in the course of their life [109]. This is due to the discharge of metabolic products into the medium or to selective removal of substances from it. For example, microorganisms involved in the oxidation of hydrocarbons to acids by using enzymes, can reduce the *pH* of the medium even by two units. However, *pH* may also rise as a result of bacteria activity. This usually happens during isolation of ammonia in the process of deamination of amino acids and other nitrogen-containing compounds.

On the other hand, the organisms that develop by using ammonia reduce the *pH* of their habitat by removing ammonium ions, and organisms that develop by using nitrates increase the *pH* by removing nitrate ions (probably due to the increased concentration of NH_4^+ ions) [109].

The *pH* of surface water bodies with slow water exchange (reservoirs, lakes, estuaries) undergoes significant changes during the active development of phytoplankton. This is especially true of the surface layer of water.

For instance, the *pH* values of water in the Dnipro reservoirs vary widely—from 6.7 to 9.7 [20]. The maximum *pH* values of water are observed in the summer due to the process of photosynthesis, which accounts for the assimilation of dissolved carbon dioxide. Its content in the surface layer of water is sharply reduced down, up to its complete loss. With that, the *pH* of water increases to 8.8–9.7. It should be noted that in the Kremenchuk and Kakhovka reservoirs water *pH* values in summer reach even 9.7–10.0. In summer, organic matter decomposition is intensitied in the bottom layers of water, accompanied by the accumulation of CO_2 to 5–10 and even

20–45 mg/L. The *pH* under these conditions is reduced to 7.4. A vertical stratification of *pH* variables occurs, which is most characteristic for middle and near-dam portions of the reservoirs. The difference in *pH* between the surface and bottom layers is usually 1.0–1.5 units.

Water *pH* in the Dnipro-Bug estuary is 7.4–9.2, having the lowest values in the Eastern portion, and the highest—in the central and western portions. Elevated *pH* of the water is due to the intense process of photosynthesis [20]. Water "bloom" of blue–green algae in summer causes sharp fluctuations of this indicator. Important in this case is the algae physiological condition and location of "bloom" spots on the estuary water surface. Given sea surge wave when the water column is divided into two layers, the surface layer features an increased *pH* and no carbon dioxide. In the bottom layers, conversely, the *pH* decreases to 7.4, and in anaerobic zones—even to 6.0. The concentration of CO_2 in this case is 20 mg/L [138]. In the area of shallow estuary water in the thickets of higher water plants the *pH* varies depending on the density of plants, their species composition and intensity of water exchange—from 9.2 to 6.0 [138].

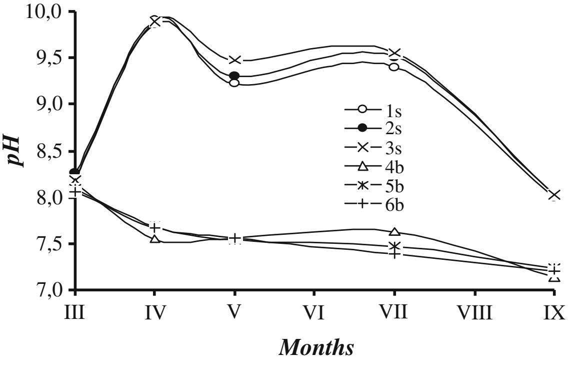
Lake Telbin belonging to the system of small reservoirs in the city of Kyiv can be a typical example of vertical stratification of water *pH*. There is a massive "bloom" of water in the lake in summer resulting in the *pH* of the surface layer of up to 9.2–9.7, and at the bottom, where the decomposition of organic matter and remains of organisms occurs, the values do not exceed 7.1–7.5 (Fig. 4.2) [73].

The concentration of dissolved oxygen in eutrophic and hypertrophic lakes, unlike oligotrophic reservoirs, can significantly vary due to the flurry of biological activity during the photosynthesis and respiration [109].

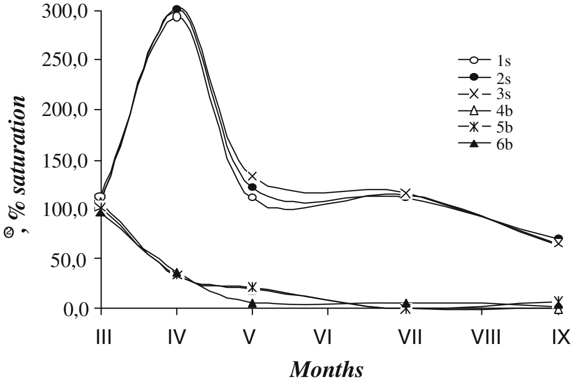
Phytoplankton and bacteria were found to be the main biological agents that evolve oxygen and consume it in a dissolved state. In the process of photosynthesis the surface layer of water is enriched with oxygen up to oversaturation (up to 180 %).

In some lake systems, for example in Lake Telbin, saturation of the surface layer of water, according to the results of our research, is even 300 % (Fig. 4.3).

Fig. 4.2 Water pH in Lake Telbin in the surface (*1s–3s*) and bottom (*4b–6b*) layers of the water



1–6 – water quality sampling stations



1–6 – water quality sampling stations

Fig. 4.3 The levels of water saturation by oxygen in Lake Telbin in the surface (*1s–3s*) and bottom (*4b–6b*) layers of the water

Large amounts of oxygen are evolved due to phytoplankton photosynthetic aeration. Thus, for some lakes in Belarus it is 1.9–19.2 times higher than it is contained in the water of these lakes [103]. The role of photosynthetic aeration increases with an increase of trophic status of a water body. While oxygen influx to the water of unproductive ponds with average depth ≈1.0 during the growing season is 10 times higher than the amount available in the water, the O_2 influx to the water of productive ponds is 40 and more times higher [103].

The amount of oxygen produced by phytoplankton varies and is subject on the biological productivity of reservoirs. Thus, the amount of oxygen produced by phytoplankton in the Ivankov reservoir (Russia) for the period from 1958 to 1973 was 2.4–3.4 g/m^2 day, in the Dnipro reservoirs—from 0.2 to 13.6 g/m^2 day, in the Bratsk reservoir (Russia)—from 0.6–2.16 to 3.0 g/m^2 day [103]. Submerged macrophytes are able to evolve from 10 to 40 g O_2/m^2 day. It is due to macrophytes that the aeration of bottom sediments occurs. Green filamentous algae that grows on various substrates release from 5.0 to 45.0 g O_2/m^2 day.

However, phytobenthos is characterized by much lower intensity of oxygen production. Although the bottom layer in the shallow water occasionally have high concentrations of dissolved oxygen due to Elodea, Chara and Nitella flexilis.

The basic processes that cause the oxygen consumption in natural surface water bodies include:

- microbiological oxidation of organic substances;
- bacterial respiration;
- respiration of higher level organisms, including phytoplankton and zooplankton;
- microbial oxidation of gaseous hydrogen or methane gas in anaerobic sediments;
- microbial oxidation of hydrogen sulphide, iron, ammonia, nitrites compounds etc;
- abiotic oxidation of inorganic compounds;
- abiotic oxidation of organic compounds.

Significant quantities of O_2 are consumed during biological oxidation of substances by microorganisms. During the microbial decomposition of organic matter not only large amounts of oxygen are consumed, but nitric acid is formed as well, which significantly lowers the pH of the water [33].

Oxygen consumption by bacteria in the water is much higher than by the algae (according to various sources, 4–12.5 times as high).

In the case of certain lakes it was found that dissolved oxygen consumption for the degradation process during the growing season is 1.0–3.5 g/m^2 day. This index essentially depends on the level of eutrophication of water bodies. Oxygen consumption for decomposition processes in Lake Sevan (Armenia) in the course of its eutrophication increased from 1.7 to 12.0 g O_2/m^2 day [103].

Dissolved oxygen consumption for respiration of aquatic organisms in the Dnipro cascade reservoirs is estimated to be within the range from 3.0 to 13.0 g O_2/m^2 day. With that, oxygen consumption for algae respiration during the growing season is in the range 1.0–3.35 g O_2/m^2 day, for bacterioplankton—2.0–4.5 g O_2/m^2 day, for zooplankton—about 0.6 g O_2/m^2 day. The proportion of oxygen consumed by bacteria, phytoplankton and zooplankton, is respectively 50, 30 and 20 % [103].

Decomposition of organic matter is much faster under aerobic conditions than anaerobic ones. The reason is that the presence of oxygen in water increases the activity of microorganisms involved in the processes of degradation and oxidation of organic compounds. Under oxygen deficiency, decomposition, sometimes commensurate with aerobic conditions, usually occurs due to an increased number of microorganisms. Decomposition rate of sugars in aerobic conditions increases significantly.

Abiotic oxidation rate depends largely on the concentration of dissolved oxygen in the medium: it increases with the disruption of bottom surface sediments and oxygen affecting the anoxic layer. At the same time it has been found that the intensity of respiration of mixed populations of aerobic benthos gradually decreases with reducing the concentration of available dissolved oxygen up to a certain critical level (about 1.4 mg/L).

Sulfate ions present in the surface water are a considerable reserve of biochemically bound oxygen. Sulfate-reducing bacteria use sulphate oxygen for oxidation of organic compounds to form hydrogen sulphide. Anaerobic bacteria are most abundant in anaerobic water and sediment. As these bacteria produce hydrogen sulphide, oxygen concentrations in the stagnant areas of surface water are significantly depleted. In parallel, the activity of hydrogen sulphide oxidating bacteria leads to production of sulfates. Another important reserve of biochemically bound oxygen in water are nitrates. However, they are easily deoxidated by many aquatic organisms, resulting in low concentrations of nitrates and ammonia accumulation often observed in natural water. Some bacteria use Fe^{3+} ions as electron acceptors reducing them to Fe^{2+}.

Oxygen regimen is markedly affected by bottom sediments as they accumulate much of inorganic and organic substances. But the bulk of oxygen is consumed in respiration of heterotrophic aerobic bacteria [19]. In particular, to take an example of Kola Peninsula water objects, it was found that in the process of decomposition of organic matter in the sediments there was a direct relationship between oxygen consumption and the number of bacteria [22]. Another study [11] describes a linear relationship between the number of heterotrophic bacteria present in sediments in the initial period, and the rate of oxygen consumption. The most noticeable oxygen loss is observed in summer, when the number of bacteria increases significantly.

In the oxygen balance of surface water the input is the oxygen coming from the atmosphere and, as already noted, from the production by phytoplankton and higher aquatic vegetation. It is photosynthetic activity of plant organisms which contributes most to the enrichment of the Dnipro reservoirs with oxygen during warm seasons. Oxygen concentrations in the surface layers of water can reach 23.5 mg/L (290 % saturation) [20]. Oversaturation of the surface layers in the Kyiv and Kaniv reservoirs in summer is slightly lower (180 %) than, for example, in the Kremenchuk (290 %) and Kakhovka (260 %) reservoirs. Although, there are no significant concentrations of oxygen in the surface layers in recent years due to the decrease in water "bloom" in the summer.

Meanwhile, oxygen consumption during oxidative processes is accompanied by a significant decline in its content in the bottom layers of water. In particular, water saturation with O_2 in the bottom layers of the Dnipro reservoirs does not exceed 30–40 %, and sometimes even 1–3 % [20]. Maximum oxygen concentrations in places with significant accumulations of naturally dying phytoplankton (formation on the surface of a blue film), are shifted to a depth of 1–3 m with further decrease closer to the bottom layer.

Most adverse conditions associated with deficiency of O_2 in the Dnipro reservoirs occur in dry years. Summer fish kill occurs in stagnant lake areas in the second half of July, due to the combination of prolonged calm weather, high water temperatures and mass accumulation of blue–green algae. Unfavorable oxygen regimen can also be recorded in the reservoir bays in summer. This is due to their small depths, which contribute to rapid warming of the entire water column. They feature earlier development of biological life.

During the growing season oxygen content in the surface layer of the Dnipro-Bug estuary reaches a maximum value—20–23 mg/L, and in coastal areas even 30 mg/L. Dissolved oxygen concentrations in bottom layers are much lower often displaying its deficit, which leads to the formation of anaerobic zones, where oxygen is absent, but hydrogen sulphide is there. A vertical gradient of dissolved oxygen concentration in these areas can reach 10 mg/L and more. Given a settled hydrometeorological situation in the region the thickness of an oxygen-free layer sometimes increases to 3 m. The highest degree of surface layer saturation with oxygen occurs in spring (166–320 %), it is somewhat reduced in summer, but remains quite high (208–248 %) and the smallest values are characteristic for autumn period (119–129 % saturation) [138].

Redox potential (Eh) in most natural aquatic ecosystems that contact with the atmosphere, varies in the range from −50 to +750 mV. In stagnant deep-water areas isolated from the atmosphere and in the bottom sediments Eh decreases to −400 mV. Eh highest values are characteristic to the medium with a high content of dissolved oxygen [109]. Living organisms reduce the Eh value not only by consuming dissolved oxygen, but also due to discharge of metabolism products. Hydrogen sulphide is an important element among the conventional products of anaerobic metabolism. Its accumulation in the bottom layer of water reduces the Eh value to—300 mV. The natural water environments with low Eh values include silty mud and relevant bottom sediments in lakes, reservoirs and rivers, as well as swamps dominated by aerophilous and anaerobic micro-microorganisms.

Low redox potential of an aquatic environment, which is determined by the level of oxygen saturation, becomes an obstacle to the growth of bacteria. A sharp drop in the redox potential of the water environment in anaerobic conditions leads to the reduction of sulfate ions concentration and accumulation of hydrogen sulphide, more intensive formation of ammonium salts that build-up in rather high concentrations instead of nitrites and nitrates. Given the shortage of oxygen and low Eh, the content in the water of reduced organic compounds, carbon dioxide, silicon phosphate ions, mangan and others increases.

4.2 Effects of Hydrobionts on the Dynamics of Concentrations of Biogenic Elements in Water Bodies with Slow Water Exchange

The concentrations of biogenic elements in water reservoirs and lakes change over a wide range of values depending on the season, surface are of a reservoir and its depth. Meanwhile, biotic factors associated with the development and functioning of hydrobionts become important along with the abiotic factors affecting the concentrations of biogenic elements. These changes become especially noticeable during the growing season. Depending on the distribution of phytoplankton the concentrations of biogenic elements undergo significant changes both throughout the surface area and the water column of the reservoirs [20].

The inorganic nitrogen compounds (NH_4^+, NO_2^-, NO_3^-) are easily absorbed by the phytoplankton and bacterial population, transforming into protein nitrogen. Therefore, during the growing season these forms of nitrogen are usually present in small amounts due to the intensive development of phytoplankton. However, the concentration of biogenic elements comes up again in the summer, particularly in its second half, as well as in autumn under the conditions of mass dying and bacterial decomposition of algae and the reduced biological processes in general, reaching maximum values by the end of winter period. Their highest concentrations are characteristic of the bottom layer of water, where the build-up of the organic matter mineralization products and bottom sediments occurs. This is typical first of all for ammonia nitrogen, whose concentrations in the bottom layer of water may rise to 1.5–2.5 mg/L, especially under anaerobic conditions. However, in the summer an increase of NH_4^+ is also possible in the upper layers, where there is amassment of decaying phytoplankton.

There is always an increase in the concentrations of all forms of nitrogen in the areas of dead plankton amassment, particularly in the “bloom” spots and run-up zones, in shallow water, bays with slow water exchange and bottom sediments rich in organic matter [135].

The concentrations of biogenic inorganic materials in the areas with accumulated and decaying blue–green algae are increased 5–10 times, with that of organic matter —20–50 times compared with water spaces containing algae with no signs of decomposition. The ratio C:N drops to 4–5. In “bloom spots” the concentration of NH_4^+ can usually grow to 2.0–3.5 mg/L [21].

Below (Table 4.3), as an example, are data on the concentrations of biogenic and organic materials in the water of the Kremenchuk reservoir during algal nuisance (water “bloom”) and decay of blue–green algae [135].

Table 4.3 Change of concentrations of nutrients and organic substances during mass growth (“bloom”) and decomposition of blue–green algae in the waters of the Kremenchuk reservoir [135]

Indicator	Concentration (mg/L)			Ratio of concentrations in “bloom” spot and beyond it
	In the “bloom” zone (beyond the spot)	In the “bloom” spot	Maximum values (blue and white films)	
NH_4^+, N mg/L	0.03–0.95	2.0–3.0	3.5	4–115
Norg, common	0.8–4.2	10.0–55.0	125.0	30–150
Norg, soluble	0.6–2.5	3.0–21.0	30.0	12–50
PO_4^{3-}	0.05–0.10	0.24–0.40	0.55	5–10
Porg, common	0.25–0.42	0.5–4.8	8.9	20–35
Porg, soluble	0.14–0.26	0.4–4.3	5.0	20–35
Permanganate COD, O mg/L				
Unfiltered water	10.0–22.0	25.0–80.0	245.0	10–25
Filtered water	9.0–18.0	20.0–30.0	35.0	2–4
Dichromate COD, O mg/L				
Unfiltered water	30.0–50.0	100.0–540.0	1135	20–40
Filtered water	25.0–35.0	45.0–140.0	175.0	5–7
Corg, common	10.0–20.0	40.0–200.0	425.0	20–40
Corg, soluble	9.0–13.0	17.0–50.0	65.0	5–7
C:N	6–8.5	4–5	3.5	0.4–0.6

With an intensive production of phytoplankton in the upper layers the concentrations of nitrate ions are minimal or they are absent at all. There is an inverse relation: with increasing of phytoplankton biomass the concentrations of NO_3^- decrease [20]. In the growing season the concentrations of nitrates in the reservoirs decrease downstream from the upper to near-dam areas, which is consistent with the phytoplankton dynamics, whose biomass is always much higher in the middle and lower areas, including the near-dam one, than in the upper areas. This demonstrates a significant role of phytoplankton in the process of self-purification of water from biogenic elements, especially given the removal of algal mass from the areas of its maximum accumulation during the “bloom” of blue–green algae [119].

We can provide data on changes in the concentrations of inorganic and organic phosphorus in “bloom spots.” Whereas in the areas of water “bloom” the concentrations of soluble inorganic phosphorus do not exceed 0.05–0.10 mg P/L, its concentrations in the “bloom spots” increases five to tenfold, reaching 0.25–0.55 mg P/L [21]. This also applies to the organic form of phosphorus, the concentrations of which in the areas of water “bloom” is 0.25–0.42 mg/L, while in “bloom spots” they increase to 0.5–8.9 mg P/L.

Diatoms actively absorb soluble silicon from the water [31]. Therefore, during the growth of this type of algae silicon concentrations in the water decrease. When the diatoms die off and decay, silicon content increases. For instance, according to estimations almost 25 % of soluble SiO_2 exported by runoff of the Amazon River is removed due to the production of the diatoms. It is characteristic that phytoplankton is not only able to consume soluble forms of silicon in water, but also to extract silicic acid from the crystal lattice of clay minerals.

4.3 The Role of Hydrations’ in Producing of Organic Substances in Surface Water Bodies

The composition and concentrations of organic materials in surface water are determined by a combination of many processes, different in nature and intensity. The most important of them are hydrobionts’ lifetime excreta and postmortem decomposition products, as well as inputs from atmospheric precipitation, from surface runoff with washouts from soil and vegetation cover of the catchment area, from other bodies of water, from wetlands, peatlands, from industrial and household wastewater.

Natural sources of organic substances in surface water include primarily plant and animal decay material as well as extracellular waste products excreted by plants and animals [10, 122]. From 15 to 50 % of the biomass may be lost in the process of decomposition of plant and animal material due to postmortem changes in the permeability of cell membranes and autolytic enzymes activity. The products of decomposition are composed of amino acids, keto-acids and fatty acids. Organism refractory components, including cellulose and chitin, can be decomposed only by bacteria [109]. From 5 to 30 % of extracellular metabolic products may be released in the form of soluble organic carbon due to carbon dioxide fixation during photosynthesis. Phytoplankton populations in general as well as their certain species excrete from 15 to 35 % of waste products during their lifetime. Extracellular metabolic products include polysaccharides, polypeptides, amino acids, glycolic acid and some biologically active compounds such as enzymes [109]. Much of carbon, out of its total amount present in the aquatic environment, is produced by plankton both, in the process of decay, and as a result their activity.

The composition of organic material in surface water is highly diverse. These include both, very complex macromolecular substances such as proteins, polysaccharides, and simpler compounds, in particular such as methane, formaldehyde, lower fatty acids, amines and others. Organic substances with a known structure and properties are encountered in surface water, but there are those, chemical nature of which is still not fully elucidated (humic and fulvic acids, a number of substances of so-called colorless humus). Surface water may contain any compounds—metabolism products, as well as substances produced in the course of their chemical and biochemical transformation.

Thus, hydrobionts, including phytoplankton, higher aquatic vegetation, zoobenthos and zooplankton, bacterioplankton rank high among the various sources of input and production of organic material in surface water. The main sources of enrichment of surface water with dissolved organic material (DOM) are summarized in a diagram contained in the monograph [107]. The mentioned diagram is shown in Fig. 4.4.

The enrichment of surface water with DOM is due to both allochthonous and autochthonous sources. The dominance of one or another largely depends on a number of factors, including the season, the hydrological regime of reservoirs and man-made load on them, weather conditions and so on.

Algae produce primary metabolites of four categories: proteins, nucleic acids, carbohydrates and lipids. In addition, algae provide biosynthesis of a large number of different organic compounds belonging to the secondary metabolites. These include saturated and unsaturated compounds, with backbone and branched carbon chains, aromatic and heterocyclic. The vast majority of them belong to low-molecular-weight organic compounds. Secondary metabolites are characterized by a great variety of properties—volatility, polarity, resistance to atmospheric oxygen, temperature, light, acids and bases [128].

Unlike primary metabolites, the content of which can be tens of percent of the algae weight, the content of secondary metabolites rarely exceeds a few percent (typically 1–2 %) and often is only a few thousandths of a percent.

As in the case of land plants, carbohydrates are often a prevalent component of algae biomass. However, the dominance of carbohydrates in general does not exclude that some species of algae may accumulate mainly lipids or be overrich in proteins etc.

Polysaccharides are built of hydrophilic monomers, so it is logical to expect that they will be easy to dissolve in water. But there are insoluble polysaccharides—cellulose, chitin.

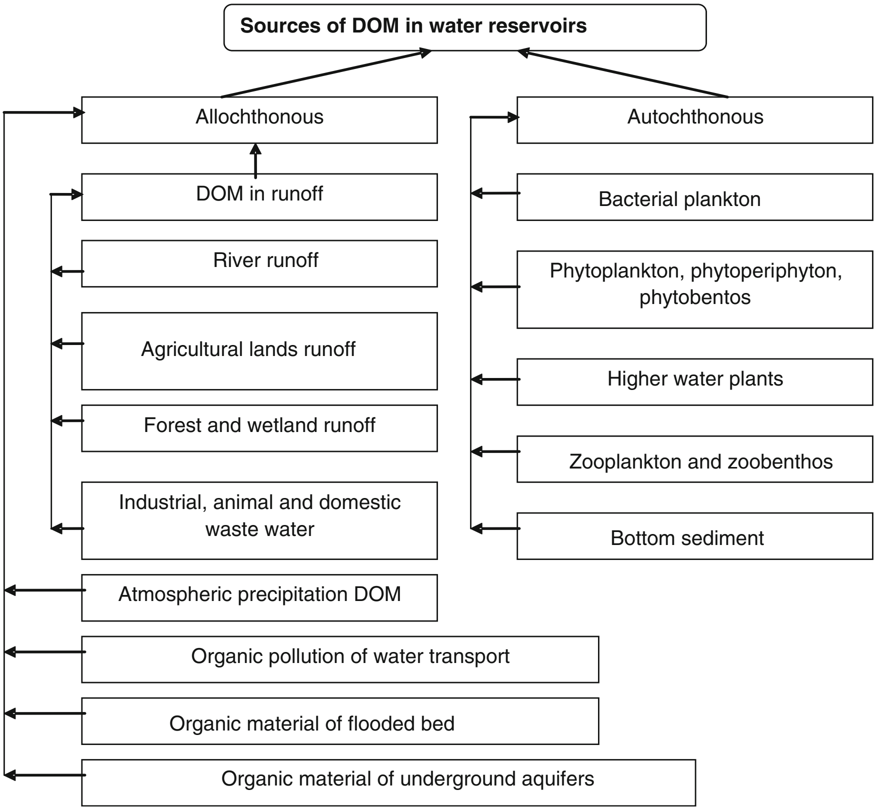


Fig. 4.4 The main sources of enrichment of surface water objects with dissolved organic material [107]

The release of organic substances by algae occurs not only after a cell death, but in the course of their normal physiological activities as well. By their chemical nature, algal extracellular products belong to different categories. In particular, these are organic acids, amino acids, amines, indoles, alkaloids, algotoxins, lipids, hydrophobic terpenes, alcohols, ethers, aldehydes and ketones, carbohydrates, phenols and others [10, 107, 122].

Higher aquatic plants also significantly affect the aquatic medium quality and biological productivity of the littoral zone of surface water bodies, including reservoirs. The role of higher aquatic vegetation in the biotic balance, the processes affecting water quality and biological conditions of water reservoirs is versatile and ambiguous. It is primarily determined by the fact that higher water plants, along with phytoplankton, periphyton and microphytobenthos produce new organic material in the process of photosynthesis. The role of the vegetation in the biological balance increases with the extension of overgrown littoral zone.

Higher aquatic vegetation serves as a biofilter at the land–water interface, as it intercepts and absorbs suspended and soluble organic material coming from the catchment area. Adsorption of suspended solids on the surface of plants is due to mucus that covers their submerged parts. During interception the suspended solids settle on the bottom of the reservoir and undergo decomposition by microorganisms [82]. The products of decomposition are absorbed and assimilated by plants. Therefore, in the thickets of higher water vegetation the water is usually illuminated and becomes much more transparent than in those areas where vegetation is absent. At that, water transparency increases from 0.08–0.1 to 1.5–2.0 m [66].

Due to the sedimentation of suspended solids in the dense thickets of reeds and cattail, silt deposition rate is 2–5 times higher than in bare areas.

In the process of their growth the aquatic plants absorb from the soil and water biogenic and trace elements, thereby clearing the aquatic environment. For example, 36.3 thousand tons of organic materials are produced in the Kyiv reservoir by higher aquatic vegetation, mainly submerged plants. At the same time, to produce this amount of biomass plants absorb 4.4 thousand tons of minerals [66].

The total mass of aquatic vegetation in the six Dnipro reservoirs is estimated to be within 300 thousand tons of dry matter, which means that it has bound about 10.5 ths. t of nitrogen, 1.1 ths. t of phosphorus, about 8 ths. t of calcium, magnesium and iron [66].

Chemical elements are fairly well retained by cell biopolymers, which results in their long-term exclusion from the cycle. Their return in the water only occurs at the end of the growing season and the plants dying off [66].

Semi-submerged plants bind biogenic elements for a long time as they have a very well developed root system, which sometimes accounts for 70–80 % of the total biomass, and their life time is 1.5–2 years. A considerable amount of substances absorbed by the plants is stored in the rootstock biomass, and with the adventitious roots and old rootstock they penetrate deep layers of sediments, in other words they are buried there. It is extremely important from the environmental point of view, as purification of the water medium from many toxins of both inorganic and organic origin occurs [66].

It is also important to pay attention to photosynthetic activity of higher aquatic plants, which is most intensive at a depth from 2 to 1 m. In the process of photosynthesis the higher aquatic vegetation saturates the water with oxygen, affecting the carbonate balance, which leads to a significant water alkalization around the assimilating organs [66].

The intensity of oxygen evolution depends on the biological characteristics of the species, lighting, availability of carbon and biogenic elements. Thus, the intensity of oxygen evolution by submerged macrophytes in the Kremenchuk reservoir varies from 2 to 28 mg O_2/g of dry matter per hour. More than 15 tons of free oxygen are evolved per 1 ha of a thicket in the growing season, given that the intensity of photosynthesis in clasping-leaved pondweed in summer is 5.7–7.0 mg O_2/g of dry matter per hour and of dry phytomass about 6 t/ha [66].

Aerobic environment around the aquatic plants and accumulation in the water of exogenous organic compounds contribute to the creation of favorable conditions for microflora, which intensifies the oxidative mineralization as an important link in purification of natural water [82]. The rate of decomposition of plant remains is the highest in the first 2–3 weeks after the plants dying-off. During this very period there is a maximum population of microorganisms, the number of which is subsequently reduced. The exception is a group of cellulose-decomposing bacteria, whose number remains high enough for a long time. As a result of the activity of microorganisms, inorganic nitrogen, which is released in the process of decomposition, is quickly transformed into organic forms and is not present in the water in a free state. For this reason it is not consumed by phytoplankton [66].

Macrophytes, using sunlight and inorganic biogenic elements (CO_2, NO_3^-, PO_4^{3-}), produce carbohydrates, amino acids and fats. Depending on the environmental conditions and plant species the latter are able to release in the water from 3 to 40 % of primary products as DOM, about 10 % are going to the food chain, the rest are decomposed after the plant dying-off and become suspended organic material (SOM) [31]. Higher aquatic plants release into the water biologically active compounds with phytoncide and bactericidal properties, thereby determining the specificity of plankton and periphyton cenosis in overgrown areas of the littoral zones of the reservoirs.

The negative impact of aquatic plants on water quality and biological productivity is enhanced with an increased density of their thicket. Dense thickets significantly reduce the intensity of photosynthesis, which is caused by shading and the lack of biogenic elements [66].

Reduced rate of photosynthesis of algae and submersed plants, increased oxygen uptake by plants during the hours of darkness cause deterioration of the gas regime of shoal waters, which displays itself most notably in oxygen deficiency and the accumulation of carbon dioxide. Under these conditions the mineralization processes of organic matter are slackened, resulting in its accumulation in the littoral zone of the reservoirs. Decomposition and decay of the organic matter leads to a decrease in pH of the water, thereby increasing the solubility and mobility of metals in the "bottom sediment-water" system and their income from bottom sediments. Anaerobic conditions also contribute to active introduction in the water of phosphorus and ammonia nitrogen. With the shortage of O_2 and enrichment of water with various chemicals the activity of aerobic microflora of the decomposers is reduced. These create suitable environment for intensive swamping of the littoral zone and peat formation [66].

A certain amount of organic matter in surface water bodies is decomposed in the aquatic medium under aerobic conditions (sometimes it is nearly 80 %) [135]. Meanwhile, organic substances deposited at the sludge-water interface, are often devoid of easy-to-assimilate fractions. They undergo degradation due to the activity either of aerobic heterotrophic bacteria (given the availability of oxygen in the bottom layer) or anaerobic microorganisms (in the absence of oxygen), or both. Initially, low molecular weight organic compounds are formed—fatty acids, which are decomposed to form methane from methyl groups, hydrogen and carbon dioxide. The end products of decomposition CH_4, H_2, H_2S then undergo oxidation with the involvement of methane-oxidyzing, hydrogen-reducing and thione groups of bacteria.

The results of perennial research of autochthonous flora in the reservoirs give reason to believe that bacteria play a crucial role in the circulation of substances, including organic, in the surface water bodies. They contribute to decomposing of organic matter of both, allochthonous and autochthonous origin (dead plant and animal residues, dissolved organic matter), thereby making them available to other aquatic animals. By participating in the reduction–oxidation processes microorganisms contribute to the purification of water bodies and increase their productivity, playing an important role in the stabilization of a hydro-biological regime.

A significant role is played by benthic organisms in the processes of biological purification of water bodies [135]. Its substance is in the mineralization of organic matter carried out by oligochaetes, as well as in removing from the water column of suspended solids with involvement of filter-feeding bivalves and chironomid larvae. Zebra mussel is most efficient filter-feeder in many reservoirs. Thus, it is found that about 2 ths. t of suspended organic matter are assimilated annually owing to zebra mussels in the Uchynsk reservoir (Russia), and more than 5 ths. t of seston are deposited as agglutinates and faeces [134].

When considering the effect of aquatic organisms on the chemical composition of surface water bodies, it is important to note that this effect depends largely on the intensity of metabolism [1]. The metabolic rate in aquatic organisms depends not only on seasonal fluctuations of ambient temperature, but also on the characteristics of their life cycles, including the degree of physiological or reproductive activity. For instance, the highest filtration activity and feeding rate in molluscs is recorded in summer, while in autumn, winter and early spring they are sharply reduced down up to a rest pause [1]. The filtration rate of bivalve molluscs also increases with an increase in their weight and size.

Numerous studies have revealed a close relationship between the metabolic rate, its intensity and the size of freshwater organisms. In most cases, the metabolic rate in animals increases, while its intensity decreases proportionally with an increase in their weight.

The research of the organic matter balance in lakes during the growing season showed that almost 80 % of autochthonous organic matter, which is formed in the water bodies, is undergoing degradation in the water column [103, 109].

Organic substances easily decomposable by microorganisms include most of compounds, including proteins, amino acids, sugars, liquid and gaseous hydrocarbons, the most resistant are humic substances. Phenols also have high microbial resistance.

Regarding the processes of disintegration of fatty acids, aldehydes and amines, only valuation assumptions are available in the printed works. For instance, most of the organisms that are able to break down salts of fatty acids, are commonly encountered in the surface layers of sediments. A decomposition of fatty acids results in the release of gases: carbon dioxide, hydrogen, methane and nitrogen.

4.3.1 Organic Acids

Organic acids are most common organic substances present in surface water. Their composition and concentration depend largely on the intensity of processes inside a water body related, on the one hand, to the life of algae, bacteria and animal organisms, on the other—to the input of these substances into the water from allochthonous sources.

The process of generation of organic acids inside a water body includes several stages [42]:

- postmortem income due to natural dying-off and lysis of cells of certain single-species populations;
- release of organic acids by groupings, associated with biochemical interaction of different organisms, such as algae and bacteria;
- enzymatic decomposition of macromolecular organic substances such as carbohydrates, proteins and lipids.

The content of organic acids in the biomass of algae cells is lower than in higher plants. They are accumulated mainly in the water medium. Thus, in the case of green algae the content of organic acids in the culture medium can reach 20–25 % of the total concentration of extracellular DOM [78]. The rate of organic acid release in the medium is the higher, the more intensive is the growth of algae. This leads to the conclusion that organic acids are released by algae during intense physiological processes [107].

The research on marine and freshwater algae has shown that the maximum amount of glycolic acid in the culture medium is reached during a lag phase, and the minimum is observed during the logarithmic phase and at the beginning of the phase of relative decrease in algae growth.

Formic, acetic, propionic, butyric, citric, tartaric, glycolic, malic, succinic, fumaric, oxalic, lactic acid are identified among the organic acids in the algae culture medium. Summary data on the qualitative composition of the extracellular non-volatile organic acids of some species of algae are presented in the monograph [107].

The concentration of organic acids in surface water bodies of different types varies widely (from $n \times 10^{-2}$ to $n \times 10^{-1}$ mmol-eq/L) because of different physical and geographic regions [113]. The distribution of concentrations of organic acids in reservoirs is characterized as uneven over time, and throughout the area and depth. The concentrations of organic acids in different portions of a reservoir can vary significantly (variations in values are 200–300 % and more). The most common are propionic and acetic acids, the concentrations of which range from $n \times 10$ to $n \times 10^2$ µg/L. Valeric, caproic and enanthic acids are encountered in much smaller concentrations. A number of higher fatty acids is available in natural water in very small quantities, which requires large amounts of water for analysis (20–50 L).

Water-soluble organic acids are found in surface water as non-dissociated molecules and partially in ionic form, depending on the pH of water (see Sect. 3.2.4). Higher fatty acids are concentrated at the separation interface. Most often this occurs on suspended particles and in the foam due to the formation of colloidal forms and suspensions. It should be also noted that organic acids are characterized by certain complexing properties, and therefore can be in the form of compounds with some metals, including iron, aluminum and some others (see Sect. 3.3.2).

High concentrations of organic acids in water, particularly butyric, propionic, acetic, formic, lactic, benzoic, lead to a significant deterioration in the organoleptic properties of the water. Since these acids undergo oxidation, it negatively affects the gas regime and general sanitary condition of water bodies.

Data on the concentration and constitution of this category of organic compounds in surface water bodies are important and necessary in the study of chemical weathering processes, migration of cells and formation of sedimentary rocks, as well as for clarification of the relationship between the medium and hydrobionts, as organic acids are an important source of carbon and energy for most aquatic organisms.

4.3.2 Protein Compounds

Nitrogen-containing organic compounds (proteins, amino acids) are of considerable interest because they are the main sources of biogenic elements and organic compounds.

Protein compounds, which are part of organic compounds in surface fresh water, greatly affect the viability of the living population and the physical and chemical processes that occur in the water and sediment. It is also important to note that proteins and their decay products are a source of various forms of organic carbon, nitrogen and phosphorus contained in the water and sediment of surface water bodies, on which depends the productivity of reservoirs. Proteins are involved in the interactions between hydrobionts, in metabolizing of pollutants, they are a source of energy and building material for living organisms, they affect water quality and contribute to the formation of phyto- and zoo-cenoses [125].

Protein compounds are introduced into surface water due to both, the processes inside a water body and their allochthonous income. The processes inside the water body are of primary importance in late summer, as they determine the income into water of polypeptide components of lifetime excretae and products of decomposition of hydrobionts, especially planktonic and benthic organisms, whose population increases in this time of year. Certain contribution to this process is made by remains of plankton and higher aquatic plants that die-off naturally [42, 43]. However, a significant amount of proteins and their decay products go into water due to interactions between hydrobionts. They account for various trophic relationships occurring in aquatic biocenoses when some organisms release in the water their excretae, including proteins, and other species or groups of organisms use them as a source of energy for growth and activity [57].

The content of proteins in blue–green algae such as *Anabaena cylindrica* and *Microcystis aeruginosa* is 30–35 % of dry weight [122]. Natural populations of *Aphanizomenon flos-aquae* contain more than 40 % of protein components. Protein quantitative content in blue–green algae is not usually steady and varies depending on the algae living conditions and physiological state. The highest protein content falls within the period of algae intensive reproduction. With lack of nitrogen in the medium and algae biological age the relative protein content is significantly reduced.

Albumins, globulins and alkali-soluble proteins are revealed among protein substances released by algae. According to [118], the protein components of *M. Aeruginosa* and *Aphanizomenon flos-aquae* contain 30 % of water-soluble proteins, about 12 % are proteins that are soluble in alkalis, and almost 60 % proteins remain in the sediment, i.e. they are hard to isolate.

The excretion rate of proteins by aquatic organisms is uneven and depends on several factors, among which important are water temperature, light, medium chemistry, physiological state of cells, water flow rate, time of year, mineralization intensity, oxygen regimen and composition of bottom sediments.

Protein compounds belong to the group of volatile organic substances that undergo degradation under the influence of various factors. Extracellular hydrolytic enzymes of animal, algal and bacterial origin cause distruction of proteins to peptides and amino acids which subsequently become part of metabolism of aquatic organisms in the same water body [20, 103].

The rate of degradation and mineralization of nitrogen-containing organic compounds determines, after all, the rate of biogenic elements turnover.

Often the disintegration of proteins occurs primarily as extracellular process through the activity of microorganisms that contain proteolytic enzymes. These enzymes hydrolyze protein molecules via peptide bonds to form simple molecules (peptides, amino acids). The smaller molecules, formed as a result of the breakdown, are able to diffuse into the cells, where their further decomposition occurs.

Bacterial decomposition of protein is more effective under aerobic condition and occurs mainly owing to intensive photosynthetic activity of the algae. It should also be born in mind that most algae are able to absorb minerals and certain organic compounds—decomposition products of proteins, which facilitates the process of self-purification of water. The deterioration of oxygen regimen in surface water results in slower biochemical oxidation of proteins. This applies in particular to nitrate bacteria which are quite sensitive to deteriorating oxygen conditions [103].

Protein decay rate in surface water depends on several factors, including temperature, the degree of oxygen saturation of the water and its chemical composition, lighting, and transparency. For example, a half-decay period of protein in the Dnipro reservoirs under aerobic conditions at a temperature of 10, 20 and 30 °C is respectively 9.5, 5.5 and 1.5 days. With a decrease of oxygen content in the water, protein decay rate declines. In anaerobic conditions the process takes longer and for all of the temperatures mentioned is almost 33 days [103].

Average annual and seasonal concentration indexes of soluble proteins in the water of the Dnipro reservoirs vary within 0.18–1.30 mg/L [20]. Their minimum concentrations are recorded in spring, and maximum—in autumn and winter. Seasonal dynamics of the concentrations of protein compounds is defined by two opposed processes: income of proteins in the process of hydrobiont cytolysis, the amount of which is usually proportional to the biological productivity of the reservoirs, and protein degradation with involvement of microorganisms producing proteolytic enzymes. The dominance of one or another process depends on the hydrochemical regime, the season, trophic status of a water body and so on. With the massive "bloom" of algae and their die-off the concentration of dissolved proteins in the Dnipro reservoirs may rise to 2.0 mg/L and more. However, in early spring, when the photosynthetic processes have not yet become intense enough, protein concentration is reduced to 0.2 mg/L [20].

4.3.3 Amino Acids

Rising concentrations of amino acids are observed in surface water during periods of most intensive growth of phytoplankton and its next mass dying off [107]. Maximum concentrations of amino acids are recorded in the aquifers with the greatest amounts of algal biomass [107]. It is also characteristic that the concentrations of proteinaceous substances out there are significantly higher than the content of free amino acids. The maximum amount of amino acids is released by algae during the lag-phase and stationary growth phase. However, the growth of biomass and production of bacteria leads to a significant decrease in the concentration of proteinaceous substances and free amino acids due to intensive decomposition of nitrogen-containing organic compounds.

Depending on the conditions in the surface water, amino acids experience decay through deamination or decarboxylation.

The analysis of amino acid concentrations in the Dneprodzerzhinsk and Dnipro (Zaporizhzhya) reservoirs in relation to the phytoplankton growth showed, that the most abundant were: cystine, cysteine, lysine, histidine, asparagine, arginine, aspartic and glutamic acid, serine, glycine, threonine, α-alanine, proline, tyrosine, tryptophan, methionine, valine, phenylalanine and leucine (all in all 19) [58, 59].

The concentrations of free amino acids in the Dnipro reservoirs, particularly in the Kyiv and Kremenchuk ones, vary depending on the season. The maximum values normally fall on spring and summer, and reduction of the amino acids takes place from summer to fall [20]. The surface layers of water feature much higher concentrations of amino acids than the lower layers. For example, the concentrations of free amino acids in the warm surface layers of the Zhovninsk islands water bodies reached 2,681 mg/L in May 1978, and at a depth of 2 m did not exceed 1,582 mg/L. The quite significant difference in the concentration of amino acids is caused by vertical migration of blue–green algae colonies. The viable colonies that are actively engaged in photosynthesis feature highest capacity for vertical migration [121]. High intensity of biosynthetic processes in the surface layers of the water was the cause of much higher concentrations of amino acids compared to the bottom layer [107].

Bottom sediments should also be regarded as an important source of amino acids in fresh water, as the formation of free amino acids in them is due to the hydrolysis of residues of dead organisms. There has been identified a correlation between the concentration of amino acids and the population and biomass of phytoplankton [121].

Heterotrophs' trophic chains are an integral part of the free algae extracellular amino acids turnover in the surface water, as these organisms (bacteria, algae, microzooplankton) are able to absorb and utilize amino acids directly from the water [107]. It is believed that the rate of assimilation of amino acids by heterotrophs varies depending on the rate of their release by phytoplankton [52].

Anaerobic decomposition of algae, which usually occurs in the areas of their wind-induced pileup, is accompanied by bacterial digestion of amino acids to form substances that significantly affect the water quality. Thus, indole and skatole are formed in the process of bacterial digestion of tryptophan [54].

It is possible that plant and microorganism growth stimulators can be formed in the process of amino acid transformations [66]. Decarboxylation of amino acids is accompanied by the formation of corresponding amines, especially histamine, tyramine, putrescine, cadaverine and some others that are characterized by high biological activity [107]. Combination of glycocol, glutamic acid and cysteine accounts for the production of glutathione which plays an important role in the regulation of oxidation–reduction processes and enzymosis environment in the organism.

4.3.4 Amines

Decarboxylation processes occurring during protein degradation due to bacteria and fungi decarboxylase and amination are an important source of amines formation in surface water. Low boiling aliphatic amines including methylamine, dimethylamine, ethylamine, diethylamine, triethylamine and some others are detected in uncontaminated or slightly contaminated surface water [111]. High boiling aliphatic or aromatic amines are not found.

Amines are the least studied group of nitrogen-containing organic compounds in surface water bodies. This applies both to their content in the water and involvement in the processes inside the water bodies [113]. These organic substances are actively involved in the regulation of nucleic-protein metabolism and are characterized by high biological activity. Many of them are described as toxic substances with unpleasant smell which have a direct bearing on the organoleptic properties of the water substantially affecting its taste and odor [55, 120]. The presence or introduction of amines in the water with a significant deficit of dissolved oxygen exacerbates fish kill in the reservoirs. Therefore, the concentrations of amines in surface water must be limited in compliance with sanitary-toxicological requirements. For some of them the maximum permissible concentrations are as follows: for diethylamine—2.0, for dipropylamine—0.5, for isopropylamine 2.0, for diisopropylamine 0.5 mg/L [2]. In commercial fishery reservoirs amine concentrations should be even smaller. For example, the value of maximum permissible concentration for dipropylamine is set at 0.01 mg/L.

Phytoplankton and precipitation are considered to be the sources of appreciable amounts of amines in surface water bodies. Biogenic amines are identified in algal cultures as endogenous and exogenous metabolites [55]. The spectrum of identified amines is very broad and includes almost 60 substances, among which there are identified primary, secondary, tertiary, di- and polyamines, as well as heterocyclic compounds [55].

In the algae culture medium amines accumulate in two ways. The first one implies an exocytic release, the second one is through the transformation of amino acids as they are released in large quantities by algae and are decarboxylated further with the involvement of bacteria. Trimethylamine, dimethylamine, methylamine, diethylamine and propylamine are revealed in cellular debris of blue–green algae, including *Microcystis aeruginosa*. Ethylamine, ethanolamine and phenylethylamine [94, 106] have been identified in addition to the mentioned amines in the products of anaerobic decomposition of *M. aeruginosa* and *Aphanizomenon flos-aquea*. Volatile amines are formed most intensively during the first month of degradation of the algal mass with further subsiding of the process. However, volatile amines are also formed during the algae growing season. The profile of amines has been best investigated for green algae, and di- and polyamines of these algae were studied on a number of objects. For example, the following amines were concurrently identified in the cells of *Scenedesmus acutus*: methylamine, dimethylamine, ethylamine, ethanolamine, 1.3 diaminopropan, putrescine, cadaverine, spermidine, spermine, norspermidyn, homospermidyn, 2-phenylethylamine, tyramine and piperazine [55, 100]. 18 amines were identified in the medium in the process of anaerobic decomposition of algae, specifically during the degradation of *S. acutus*. The profile of diatom amines has been studied to a lesser extent, although they are quite abundant in freshwater bodies.

The following amines have been identified in the natural phytoplankton: methylamine, dimethylamine, ethylamine, ethanolamine, diethylamine, putrescine, propylamine, cadaverine, spermidine, homospermidyn, norspermidyn, tyramine, 1.3 diaminopropan, tryptamine, β-phenylethylamine, histamine, piperazine, trimethylamine [106].

Total concentration of amines in river water varies from 10 to 200 mg/L [113]. No clear zoning in the distribution of this group of organic substances has been determined. Seasonal changes in the concentration of amines are more regular: in summer and autumn their content in water increases, and in spring, especially during floods, it is reduced. Amine concentrations in reservoirs and lakes range from 10 to 100 mg/L. Amine concentration range in productive (eutrophic) water bodies is wider. However, unproductive lakes and reservoirs are characterized by low values of their concentration.

In surface water amines are present mostly in dissolved and partly in adsorbed state. They form relatively stable complex compounds with some metals.

Amine concentrations (methylamine, ethylamine and diethylamine) in the Dnipro reservoirs do not exceed 1.5 mg/L. Their notably higher concentrations are recorded in summer, during the "bloom" of blue–green algae. Thus, the concentrations of amines (methylamine and dimethylamine) in the Kremenchuk reservoir during this period reach 8–16 mg/L [20]. Somewhat higher concentrations of amines are reported in fresh surface water. It is alleged in particular that the concentration of volatile amines nitrogen can reach 40–180 mg N/L [88].

An increase in overall biological productivity of a reservoir is accompanied by increasing concentration of amines in the water. This is a convincing evidence of phytoplankton being an important source of amines in surface water.

4.3.5 Indoles, Alkaloids, Algotoxins

Indoles, alkaloids and algotoxins were identified among a variety of organic compounds which appeared due to the growth and functioning of phytoplankton. According to [6], the concentrations of dissolved indoles in the water of the Dnipro reservoirs vary within a wide range—from 0 to 395 mg/L. The distribution of indole compounds is quite uneven. They usually feature highest concentrations in the areas with muddy bottoms, and the lowest—in the areas with sandy bottoms. Algae physiological state determines the level of accumulation of indole compounds in the water. Their content is significantly reduced from spring to summer (0–97 mg/L), and only in the areas of wind-induced seston pileup, where an intense decay of organic material occurs, indole concentrations increase significantly. This suggests that accumulation of indoles in water and increase in their concentration occur predominantly after the dying-off and decomposition of algae. In summer, the content of indoles in the surface layers of water is higher than in the bottom layers, which is accounted for the growth of algae biomass. The larger is the population of algae, the higher is the content of indole compounds in the water. Growing concentrations of this organic material is observed from summer to fall (from 0 to 254 mg/L). Indoles may be present in the aquatic medium born in free form and in bound state.

Alkaloidal substances are produced not only by aquatic plants but also by many species of blue–green algae. High interest in these compounds is provoked by their toxic properties. Toxins released by natural populations of blue–green algae, are well soluble compounds that have no color or smell and can withstand sterilization by boiling and autoclaving [107].

Algotoxins by their toxic potential surpass even the strongest poisons such as curare and botulin toxin [64]. The chemical structure of one of these compounds, called anatoxin-*a*, was first discerned in 1971. This alkaloid with high neurologic toxicity was isolated from the algae *Anabaena flos-aquae*, which together with *Microcystis aeruginosa* belongs to the most toxic blue–green algae [16, 50, 120].

Table 4.4 The chemical nature of the toxins released by blue–green algae (according to data [15] cited in the monograph [107])

Producer algae	Toxin	Compound nature
Lyngbya majuscula	Lyngbya-toxin-A	Alkaloid
	Debromaplysiatoxin	Phenol
Schizothrix calcicola	Debromaplysiatoxin	Phenol
Oscillatoria nigrovudis	Oscillatoxin A	Phenol
Nodularia spumigena	Nodularia-toxin	Unknown
Microcystis aeruginosa	Microcystin	Peptide
	Microcystin-C-type	Peptide
Anabaena flos-aquae	Anatoxin-a	Alkaloid
Aphanizomenon flos-aquae	Aphanotoxin	Alkaloid
Oscillatoria agardhii	Oscillatoria-toxin	Unknown

The abilities to produce toxins were also revealed in other species of blue–green algae, except that these compounds are of different nature (alkaloids, peptides, phenols), which is sometimes unknown [15]. Thus, Lyngbya-toxin-A and Aphanotoxin were found, apart from Anatoxin-*a*, among the alkaloids. Microcystin and Microcystin-C-type are released by *Microcystis aeruginosa* and belong to the peptides. Debromaplysiatoxin and Oscillatoxin A belong to phenolic compounds. A list of toxins released by certain types of blue–green algae in natural water is given in Table 4.4.

4.3.6 Lipids

In natural water lipids occur mainly in the liquid phase, but as they are poorly soluble, their droplets form suspended loads in the water column or of film on its surface [109]. Lipids produced by plankton, nekton and benthos are eventually destroyed by lipolytic microorganisms which accumulate only at the lipids–water interface, but not inside the droplets themselves. Lipase is released from microorganisms as exoenzyme and by hydrolyzing glycerides forms glycerol and free fatty acids.

The lipids group includes fats, waxes, phospholipids, glycolipids, steroids, hydrocarbons and several other organic substances [107]. Fats (triglycerides) of natural origin are formed during photosynthesis and biosynthesis and are part of the reserve and intracellular lipids [113]. Fats of biogenic origin are always present in the surface water where algae grow. Fats are not only present in algae cells, but in organic suspensions in the surface water. And, as has been demonstrated [105], all lipid fractions are available in the suspended matter throughout the year. Hence, regular metabolism of plant and animal organisms and their decay after dying-off are the main natural source of fat in natural surface water.

Fats migrate in the surface water in dissolved and emulsified state, as well as being adsorbed on suspended particles and bottom sediments. Fats are also part of soluble complex compounds with proteins and carbohydrates, that are present in the water in dissolved and a colloidal state [113].

Fat concentrations in surface water vary in quite a wide range—from a few hundredths of a milligram to a few milligrams in 1 L [113]. The main factors that reduce the fat content in the water, are the processes of their enzymatic hydrolysis and biochemical oxidation.

Triglycerides represent 10–20 % in the lipids group. Fats in large amounts significantly degrade water quality and its organoleptic properties, stimulate the development of microorganisms, including pathogenic. The biochemical processes of fats transformation cause substantial deterioration of oxygen regimen in the reservoir and the formation of compounds with more severe negative effect than the fats themselves. The latter can be degraded in both aerobic and anaerobic conditions, but such decay is much slower than that of carbohydrates and proteins.

Lipids, including unsaturated fatty acids, are often attributed to the most labile fraction of DOM. They are susceptible to peroxidation forming biologically active intermediates—peroxides, hydro-peroxides, epoxy-compounds and other substances and, ultimately, aldehydes and ketones, which are characterized as toxic. Since the lipid fraction reaches 20–30 % of DOM, the products of its peroxidation, due to their transformation in algotoxins, can cause hydrobionts' toxicosis and self-poisoning [124].

The concentration of lipids in surface water is subject to seasonal fluctuations, which is due to the development and subsequent demise and decomposition of phytoplankton. It should be noted that the suspended lipids (seston) include virtually all fractions, including polar lipids, fatty acids and hydrocarbons, whose share amounts to nearly 76 % of the total lipid content [107].

Fatty acids are found in the habitats of algologically and bacterially pure cultures of blue–green, green and diatoms algae [53, 136]. Fatty acids often happen to be the intermediate products of oxidation of hydrocarbons as components of the lipid complex of algae cells. Hydrocarbons are the compounds highly resistant to chemical transformations. However, despite this, no their mass accumulation in natural water is observed. These organic compounds are present in a broad variety in the cell mass of algae and bacteria [107]. Hydrocarbons are present in higher plants usually in the form of waxes, which include also fatty acids and high-molecular monohydric fatty alcohols. The high content of waxes is characteristic of microorganisms. With some bacteria it reaches 11.5 % of dry weight. Substances like waxes are also found in microalgae [34, 94].

There were identified nearly 60 compounds as part of the hydrocarbon complex in natural populations of blue–green algae dominated by *Microcystis aeruginosa* colonies. The predominant among them were n-nonadekan, 7.7-dimethyl-3,4-oktadiyen, 2-methyl-5-etylheptan, n-undecane, n-dodecane, 3.4 three-dekadiyen, n-tridecane, n-peptadekan, n-hexadecane, n-heptadecane, n-octadecane, n-nonadekan, 3,4-eicosadien, n-hexakosan and others [107].

4.3.7 Terpenes, Alcohols, Ethers, Aldehydes and Ketones

Apart from the above mentioned organic compounds, hydrophobic terpenes, alcohols, ethers, aldehydes and ketones are found among algae metabolites. The research of terpenes concentrations in the Dnipro reservoirs has shown that the accumulation of terpene alcohols in the water is accounted for the growth of phytoplankton, whereby the greater is algae biomass, the higher is the concentration of these alcohols [107]. Thus, with phytoplankton biomass 14 mg/L terpene alcohol concentration in the surface layers of water in some segments of the Kremenchuk and Kakhovka reservoirs reached 350–360 mg/L. It is the viable algae cells that are the source of these unsaturated alcohols in the water, and not the ones dying off. This conclusion is based on relevant data regarding the number and functionality of the algae. It was also found out that preponderance of degradation over production did not contribute to increased concentrations of terpene alcohols in the water [107].

Important results have been obtained regarding the dynamics of esters in fresh water bodies, depending on the development of phytoplankton [114]. Periodic increase in the concentration of esters in the water is observed during mass development of phytoplankton (July, August). Introduction of esters in the water within this period is accounted for the intensive autolysis and lysis of macrophyte cells that are concomitant with the massive development of phytoplankton. Green algae are major producers of esters, as they are characterized by much higher ability to accumulate lipids, including esters, compared to diatomic, flagellate and blue–green algae.

Carbonyl compounds, which include aldehydes, ketones, ketoacids and more complex multifunctional carbonyl-containing substances, occur in surface water due to algae metabolic byproducts, biochemical and photochemical oxidation of alcohols and organic acids, decomposition of organic substances such as lignin, metabolic byproducts of benthic bacteria and others [113]. Algae accumulate in their cells ketoacids and aldehydes which enter water after their natural dying-off. Acetone is formed during acetone fermentation of blue–green algae, and furfurol, vanillin and methylfurfurol—as intermediate products of melanoid production [122].

Carbonyl compounds are present in surface water mainly in dissolved state. An average concentration of these organic substances in rivers and reservoirs is within $(1–6) \times 10^{-3}$ mmol-eq/L. The concentration of carbonyl compounds in lakes, depending on their trophicity, reaches $(6–40) \times 10^{-3}$ mmol-eq/L. Their concentration in water increases usually in the spring and summer season.

Only concentrations of certain compounds with carbonyl function are typically standardized with regard to reservoirs of sanitary and domestic use. In particular, concentrations of methyl-ethyl ketone and cyclohexanone (MPC respectively 1.0 and 0.2 mg/L) are regulated according to organoleptic characteristics, formaldehyde (MPC 0.05 mg/L)—according to sanitary and toxicological requirements, acetone (MPC 2.2 mg/L) according to general sanitary requirement [2].

Oxidability, volatility and relatively high trophic value of individual groups of carbonyl-containing substances are the factors contributing to lower concentrations of the group in surface water.

4.3.8 Carbohydrates

The sources of carbohydrates in surface water include, first of all, lifetime excreta and post-mortem autolysis of aquatic organisms. Algae are seen as a powerful indigenous source of carbohydrates in fresh surface water, especially those having "blooms" of certain types of blue–green, green or diatom algae [107].

Carbohydrates occur in surface water in dissolved and suspended state in the form of reduced free sugars which are a mixture of mono-, di- and trisaccharides, as well as complex carbohydrates, oligo- and polysaccharides and carbohydrate-like compounds, where they are part of a complex set of other categories of substances [113].

The concentrations of reduced free sugars and polysaccharides in river water expressed in terms of glucose is respectively 100–600 and 250–1000 mg/L, where the concentration of these two groups of substances is normally expressed by values of the same magnitude, although in some cases the concentration of reduced sugars is higher than that of complex carbohydrates [112]. Carbohydrate concentrations of these fractions in water reservoirs are respectively within 100–400 and 200–300 mg/L. Much wider fluctuations in reduced sugars and polysaccharides concentrations are characteristic of lakes—80–6500 and 140–6900 mg/L respectively [113]. Seasonal fluctuations in carbohydrate concentration in surface water are caused by several concurrent processes. They are quite complex in nature. Development and decomposition of algae, bacterial activity, input of terrigenous matter and other deserve special attention. There is a fairly clear correlation between carbohydrate concentration and phytoplankton growth rate. An increase in water "bloom" is accompanied by higher concentrations of extracellular carbohydrates [107]. They are accounted for the increased inflow of extracellular metabolites caused by growing algal biomass, i.e. lifetime excreta. However, there is a massive autolysis of cells in the colonies of major "bloom" agents in the areas of their wind-induced pileup, leading to a sharp increase in the concentration of carbohydrates. For example, carbohydrate concentration in Tyasmynska Bay of the Kremenchuk reservoir reached 11–190 mg/L in the summer of 1975 [115]. Large amounts of seston, 60 % of which are carbohydrates, amass in the Dnipro reservoirs in the areas of phytoplankton wind-induced pileup.

Carbohydrates are one of the groups of organic substances characterizing the chemical-biological condition of a reservoir. Carbohydrates undergo enzymatic hydrolysis in surface water, resulting in the formation of mono- and disaccharides which are important nutrients for bacterioplankton. The intensity of hydrolysis is determined largely by algae population density and the number of bacteria [41, 107]. Galactose, glucose, mannose, arabinose, xylose, rhamnose, fucose are detected as part of the extracellular polysaccharide hydrolysis products. Processes that lead to the formation of substances like melanoids occur in the water with the involvement of carbohydrate-feeding microorganisms [113]. The process of oxidation of carbohydrates, depending on conditions, may result in the products of their complete degradation (H_2O, CO_2), or in the formation of a number of organic compounds (alcohols, organic acids, aldehydes, esters, etc.) [110].

The results of experimental studies of the intra- and extracellular carbohydrate groups released by algae showed that they contain mainly polysaccharides, while monosaccharides were not found, or were found in small amounts [115, 116]. However, polysaccharides, released by algae into the aquatic medium, undergo transformation with the involvement of extracellular enzymes of algae and bacteria, as already mentioned above, with the formation of simple carbohydrates. Subsequently, some of the simple carbohydrates are assimilated by aquatic organisms, including bacteria and algae, and the rest undergoe biological and chemical oxidation [107].

Decomposition of sugars in surface water is quite rapid, usually within 4–6 days, being accompanied by an increase in the biochemical oxygen demand (BOD) and in saprophytic microflora population.

4.3.9 Humic Substances (Plankton Humus)

Humic substances (HS) in natural surface water are represented by polymeric acids which are relatively resistant to biodegradation [79]. Humus is formed partly in the autochtonous medium as a byproduct of the microbiological transformations of various biochemical compounds formed from dead cells and extracellular metabolic products of various aquatic organisms. Some aquatic HS are produced in the autochtonous medium from algae proteins, carbohydrates and lipids [109]. Humus also contains phenols, which are formed as phytoplankton extracellular metabolic products. The formation of humus in a reservoir can occur under aerobic and anaerobic conditions, being more intensive in the first case. The degree of humification in the process of humus formation in the water depends on the sedimentation regime: humus generally has a higher density in deep sediments than in the shallow ones.

Fulvic and humic acids make up to 60–80 % of DOM in many types of surface water [26, 75, 97]. Actually, HS are the most common group of organic compounds in natural surface water bodies, regardless of their physical and geographical location. The concentration of fulvic acids (FA) is typically by an order of magnitude higher than the concentration of humic acids (HA), and by 3–4 orders of magnitude higher than the concentration of dissolved metals [132]. Undoubtedly, to discern allochthonous HS from those generated in the reservoir is an extremely difficult task.

It should be noted that the concentration of HS in the water undergoes certain changes because of their flocculation and adsorption on particles of clay and silt. At the same time, owing to this condition, the adsorption capacity of such particles significantly increases.

An important feature of HS is their ability to form complexes with different non-humus organic compounds like amino acids, carbohydrates, fatty acids, phenols and porphyrins. Due to such binding with humus, the substances become biochemically resistant and, to some extent, protected from bacterial decomposition.

HS in the water cannot be completely resistant to biodegradation, as they are synthesized by biochemical reactions. Due to the process of humification the elements of biochemical compounds are partly transformed from easily metabolizable forms into relatively resistant substances. Therefore the humification process in water tends to lower the average rate of recycling of biologically important elements, which increases stability of organic substances in aquatic ecosystems.

The effect of humus on aquatic ecosystems is considered from different perspectives, often diametrically opposed. Immobilization of trace elements, light absorption, acidity and possible presence of antibiotics, such as phenols—this is an incomplete list of reasons for the low productivity of aquatic ecosystems, enriched with HS [109]. However, the positive effects of humus on the water are much more sizeable. Through binding heavy metals and other soluble toxic substances, humus contributes to their detoxification. HS make available to the algae nutrient cations such as Fe^{3+}, they increase respiration rate of microbial cells, perform certain functions during physiological processes in microorganisms and stimulate their growth. Metal humates play an important role in the binding and release of phosphates. The most favorable effect of HS is their ability to maintain the stability of aquatic ecosystems, as humus plays an important role in the functioning of the biota.

4.3.10 Phenolic Compounds

Among the wide variety of surface water pollutants great attention is paid to the research of phenolic compounds as they are synthesized by plants and algae and can be released in the aquatic medium.

The release of phenolic compounds by the higher water vegetation is only possible after their complete decomposition. And this decomposition process is usually slower than the degradation of algal biomass not containing in their cells lignin and other macromolecular compounds. Highly active algicides such as hydroquinone, catechol, resorcinol and others are incoming into the aquatic environment in the process of disintegration of higher aquatic plants. These compounds adversely affect the condition of blue–green algae, inhibiting their growth [107].

Phenols are divided into two groups: volatile phenols, which include phenol, cresols, xylenols, guaiacol, thymol, and non-volatile phenols, which include resorcinol, catechol, hydroquinone, pyrogallol and several other polyhydric phenols.

The concentration of phenols in unpolluted or slightly polluted surface water is typically less than 20 mg/L. However, in contaminated water phenol concentration reaches tens and even hundreds of micrograms in 1 L [113].

The concentrations of phenols in surface water used for fish farming and water supply must be limited. This is because the chlorination of water containing phenols, in the course of its treatment for drinking purposes leads to the formation of chlorophenols. And these organic compounds off-flavor water even at concentrations of 1.0 mg/L. Volatile phenols are characterized by much higher toxicity and odor intensity during the chlorination than the non-volatile ones.

The requirement for phenol concentration in surface water in terms of organoleptic and toxicological indicators is limited at 1.0 mg/L [2]. The growth of phenol content in water bodies is accompanied by a deterioration of their general sanitary condition, affecting the living organisms not only for its toxicity, but also for a significant change in oxygen regimen. For fish, hydroquinone is the most toxic agent. Toxicity of other phenols is reduced in the following order: naphthenes > xylenols > catechol > cresols > phenol > resorcinol > pyrogallol > phloroglucinol [25]. The presence of phenolic compounds in the water slows down growth and reproduction of blue–green algae, and causes changes of the physiological state of their cells [62, 63].

Phenols are unstable compounds and undergo biochemical and chemical oxidation, the intensity of which depends on several factors. These include water temperature, *pH*, content of dissolved oxygen, phenol composition and concentration, concentration and composition of organic substances, etc. [51]. Monohydric phenols undergo predominantly biochemical oxidation. Phenol (carbolic acid) is fastest to decompose, cresols are decomposed more slowly followed by xylenols. Polyhydric phenols are more resistant to biochemical oxidation and are broken down mainly by chemical oxidation.

The concentrations of phenols in surface water undergo significant seasonal fluctuations. With higher temperature the decay rate of all phenols increases. This is one of the reasons why phenol concentration in the water decreases in the summer and increases with lower temperatures.

In surface water phenols occur in dissolved state as phenolates, phenolate ions and free phenols [113]. Entering into the condensation and polymerization reactions phenols form complex humus-like and other fairly stable compounds. Adsorption of phenols on suspended solids and bottom sediments is usually negligible.

A decisive influence on the concentrations of phenolic compounds in the Dnipro cascade reservoirs is exerted by natural factors, and not by anthropogenic ones [107]. The bulk of dissolved phenolic compounds in the Dnipro reservoirs is formed by higher aquatic plants such as water lilies, cattail, reeds, glyceria, naiad, hornwort and others.

The highest concentrations of phenolic compounds (906–1055 mg/L) in the Kyiv reservoir are found in the water of the Dnipro and Pripyat arms, which is accounted for their generation by higher aquatic plants, as well as the inflow with the Pripyat runoff, which is formed in swamp and forest areas. Massive remains of dead plants release in the water large amounts of phenolic compounds, which eventually enter the reservoir. This is consistent with relevant data on the concentrations of phenolic compounds in the water of the Pripyat arm in August 1988 and in 1995, which amounted to 1680–1850 and 320–410 mg/L respectively. Such a great difference in the concentrations is primarily accounted for the volume of the Pripyat runoff [107].

The concentrations of phenolic compounds in the Kaniv reservoir gradually decrease from the top to the bottom section (from 706 to 583 mg/L) and depend on the inflow of the Kyiv reservoir, discharges of the Bortnychi channel and intensity of blue–green algae "bloom". Shallow areas with thickets of higher aquatic vegetation in the Kaniv reservoir have much lower concentrations of phenols in comparison with the Kyiv reservoir [107].

No distinct patterns of distribution of phenolic compounds in the Kremenchuk reservoir were identified. Their concentrations in shallow areas varied within 420–753 mg/L (an average of 538 mg/L), and along the stretch from Cherkassy city to the city of Svitlovodsk—in the range from 363 to 480 mg/L, i.e. ware lower. The Sula River bay has the maximum values of phenolic compound concentrations, reaching 863–645 mg/L. However, in the areas of algae wind-induced pileup the concentrations of these substances increased to 1428 mg/L. The left-bank part and near-dam portion of the reservoir are characterized by the lowest concentrations of phenolic compounds (328–363 mg/L) [107].

The Kakhovka reservoir is characterized by significantly lower content of phenolic compounds compared with other reservoirs of the Dnipro cascade. Only in the shallow areas phenol concentrations reached 440 mg/L. They were almost twice higher in the areas with intense water "boom" (near the cities of Energodar, Nikopol and Novovorontsovka). The concentration of phenolic compounds in the near-dam portion of the reservoir was within 212–290 mg/L [107].

The highest concentrations of phenolic compounds in the reservoirs are observed in "bloom spots" during the decomposition of blue–green algae. Meanwhile, the concentration of phenol in the water, filtered in the "bloom spots", may differ depending on the intensity of the process of decomposition of algae. The more intense is the process, the higher is the concentration of phenol in the water. Depending on the area in which the "blooming spot" is located—in "plankton" or "decay" one, an overall concentration of phenolic compounds and volatile phenols in the water will be different. The overall concentration of phenolic compounds in the "plankton" zone is much lower than in the "decay" zone. However, the content of volatile compounds is usually minimal in the "decay" zone and significantly increases in the "plankton" zone. Further below are given concentration values of phenolic compounds in different zones of "blooming spots" based on the case-study of the Kremenchuk reservoir (Table 4.5) [61].

Thus, the maximum concentrations of phenolic compounds are found in the decay zone of a "blooming spot". Therefore, the pollution of surface, including coastal, waters by phenolic compounds occurs in the "blooming spots" during the

Table 4.5 The concentrations of phenolic compounds in the water of “blooming spots” located in different zones (a case study of the Kremenchuk reservoir), according to [61]

“Blooming spot” zone	The concentration of phenolic compounds in the water (mg/L)	“Blooming spot” zone	The concentration of phenolic compounds in the water (mg/L)
“Blooming spot” in Adamivka Bay		“Blooming spot” in Tyasmynska Gulf	
Plankton	3.12 ± 0.05	Plankton	1.46 ± 0.06
Hyponeuston	32.20 ± 8.68	Hyponeuston	15.40 ± 1.15
Degradation	53.50 ± 1.31	Degradation	28.50 ± 0.0

mass dying of blue–green algae. Thus, it can be argued that it is “blooming spots” in a state of decomposition that are a powerful source of accumulation of phenolic compounds in natural water.

The highest concentrations of phenols are characteristic of shallow, low flow water areas overgrown with higher aquatic plants. This is confirmed by the relevant aggregated data on phenol concentrations in different portions of the Dnipro reservoirs (Table 4.6).

In areas with limited water exchange and overgrown with higher aquatic plants, the concentrations of volatile phenols in the surface layers of water during the decomposition of blue–green algae organic substances may be as high as hundreds of micrograms in 1 L. But such phenomena may be observed, provided an intensive development of phytoplankton. For instance, the concentrations of the said phenols in the Kremenchuk reservoir in 1968–1971 reached 185–190 mg/L [60].

Thus, phenolic compounds in certain concentrations inhibit development of blue–green algae, at the same time stimulating the growth of green algae. Therefore, the growth of blue–green algae in the areas of shallow water and overgrown with higher aquatic plants is usually inhibited.

It should be noted that in the 90s of last century, the concentration of phenols in the Dnipro cascade of reservoirs declined, which is accounted for a decrease in their water “bloom” [108].

Table 4.6 Distribution of dissolved phenols (mg/L) in different portions of Dnipro reservoirs (average values received in 1987–1990) [107]

Reservoirs	Reservoir segments		
	Near-dam	Middle	Shallow (thickets of HWP)
Kyiv	422 ± 37	465 ± 50	963 ± 89
Kremenchug	390 ± 30	427 ± 31	737 ± 68
Dniprodzerzhynsk	310 ± 29	380 ± 35	697 ± 70
Kakhovka	205 ± 21	240 ± 23	480 ± 53

4.4 Effects of Hydrobionts on Organic Matter Cycle

There is a variety of organic compounds in natural surface water that are metabolized by heterotrophic bacteria. Depending on the type of biodegradation these compounds are divided into three groups [109]:

- substances that are readily metabolized by most microorganisms: amino acids, monosaccharides, organic acids and others;
- substances that are moderately resistant to biodegradation, in particular cellulose and chitin;
- substances resistant to biodegradation, including water humus.

For most of the year, the total production of organic matter in a thin photosynthetic layer of the water column in great many of natural surface water actually exceeds its mineralization. An analysis of organic matter regime in an ecosystem would reveal, that more than 99 % of organic matter produced in a closed system is decomposed rather quickly. The fraction that remains (humus) proves to be quite resistant to biodegradation. But actually, the stability of humus is not absolute, since it consists mainly of plant and animal residues produced in a given aquatic environment. In addition, some humus is of terrain origin. Thus, involvement of humus and other resistant organic material implies the slowest turnover of organic matter. The turnover degree of humus in hypertrophic water is several hundred times lower than that of easily metabolized substances, like amino acids, in water bodies with the same level of trophicity [109].

Turnover time of organic substances that are easily metabolized in eutrophic surface water is a few days, that of substances that are moderately resistant to biodegradation—from several dozen days to several months, and that of highly resistant substances—several years. Turnover time of the said organic substances in hypereutrophic water bodies is respectively less than several days, from several days to several dozen days, and from 6 months to 1 year [109].

Fluctuations of DOM concentrations and bacterioplankton biomass occur according to sine function, maintaining equilibrium between input of organic substances that are produced mainly by phytoplankton, and their loss due to consumption mostly by bacterioplankton. Even if the amount of organic matter is growing in the early stages of phytoplankton bloom, subsequently, as it is consumed, there is an increase in bacterioplankton population. An increase in bacteria population density is accompanied by active consumption of organic matter and release of inorganic nutrients which account for the next stage of phytoplankton bloom. These processes vary according to sine function the amplitude of which depends mainly on the intensity of phytoplankton bloom [109].

4.5 Effect of Hydrobionts on Migration of Metals in Surface Water

The concentration of chemical elements in surface water bodies is directly related to the total biomass of aquatic organisms and its seasonal dynamics in the ecosystems [89, 93].

Assessing the effect of hydrobionts on the chemical composition of water one should take into account the fact that this effect is to a large extent related to their metabolic rate. Meanwhile, the metabolic rate of hydrobionts is determined not only by seasonal changes in the ambient temperature, but also by specifics of their life cycles, including the level of physiological or reproductive activity [1].

Knowledge of patterns of metals distribution among the components of aquatic ecosystems is of particular importance from the environmental point of view, including the issues of environmental regulation and projecting of water body condition with regard to the possibility of their severe contamination by metal compounds that can come as a result of unforeseen emergency discharges of wastewater.

In reservoirs metal ions undergo transformation, as due to chemical and physical interaction they enter into complexing reactions and are adsorbed on suspended particles. This is an abiotic component of metals migration and transformation processes in surface water. However, along with these interactions metal ions are engaged by hydrobionts inhabiting water column. The results of field studies indicate that plankton, even at relatively low levels of biomass, are able to accumulate a significant proportion of heavy metals that are part of aquatic ecosystem cycle [7, 84].

The effect of hydrobionts on the migration of metals in surface water can be direct and indirect.

Hydrobionts have bearing on the form in which heavy metals are present in surface water [92]. Most studies have been devoted to phytoplankton behavior in the water with the presence of heavy metals and their involvement in the transformation of metal ions [93]. The indices of metal ions distribution in abiotic and biotic components of aquatic ecosystems and especially of their transformation into other forms are varied, depending on the speed of the processes that determine such distribution. The transformation of heavy metals caused by phytoplankton occurs in several stages: initially it occurs on the surface of algal organisms through adsorption and surface biochemical conversion, and subsequently—inside the cells.

Crucial role in the transformation of metals in a natural aquatic medium with growing phytoplankton is played by complexing processes with the involvement of dissolved organic matter and consumption by living algae. However, as was found in the case of Cu(II), copper is absorbed by phytoplankton in much larger quantities than it is bound in complexes with organic substances [133]. It should be noted, that the initial level of Cu^{2+} concentration has much lesser bearing on the complexing ability of dissolved organic matter than on the phytoplankton absorption ability. Thus, the complexing ability of natural organic ligands in respect of Cu(II) is little

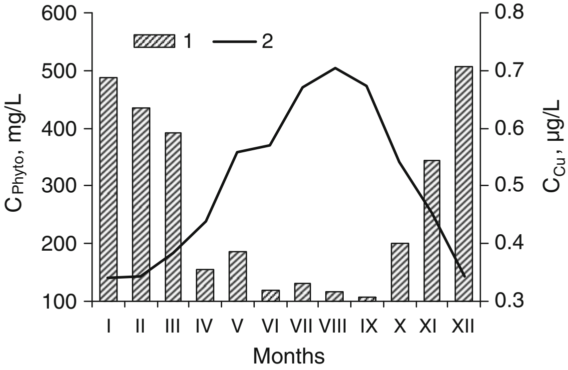


Fig. 4.5 The dynamics of concentration of soluble copper (*1*) and phytoplankton biomass (*2*) in the Usman River based on long-term averages (1977–1981, 1983–1984.) [89, 90]

changed with its initial concentrations ranging from 1.0 to 3.0 mg/L, while the amount of copper absorbed by phytoplankton is more than tripled given such a change in the concentration. As a result of the complexing and absorption of Cu^{2+} ions by phytoplankton the bulk of copper is transformed into a non-toxic form, with about 25–30 % of free Cu^{2+} ions remaining in the aqueous solution.

The results of a special study of the relationship between seasonal changes of phytoplankton biomass and concentration of dissolved copper in water of the Usman River (Voronezh Biosphere Reserve) showed, that these parameters have an inverse relation (Fig. 4.5), i.e. at the maximum values of phytoplankton biomass the concentration of copper in the water was minimal [89, 90]. At the same time, transformation of copper (II) forms was observed.

The concentration of Cu_{sol} in the water significantly decreased (Fig. 4.6), and Cu_{sus} (copper as part of suspended solids), by contrast, increased proportionally with the increase in algae biomass. Most likely, it is accounted not only for the consumption of copper (II) as a trace element in the process of algae development, but also for its adsorption on the surface of algal mass.

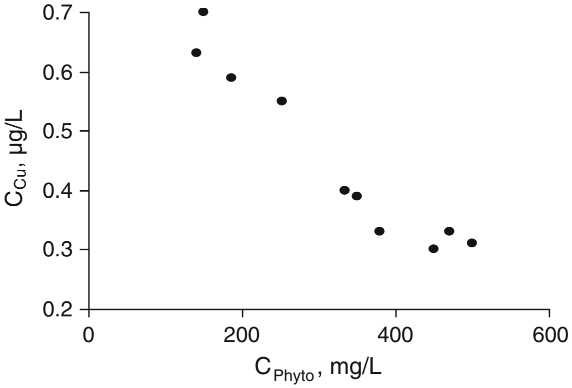


Fig. 4.6 Dependence of soluble copper concentration (C_{cu}, µg/L) on phytoplankton biomass (C_{phyto}, mg/L) in model biotopes of the Usman River (Voronezh Biosphere Reserve) in 1977–1981, 1983–1984 [89, 90]

Two stages of metals absorption kinetics by phytoplankton are distinguished. The first (photonic) stage implies binding of metal ions on the surface of cells at elevated *pH* during photosynthesis. The second stage (dark) is characterized by transport of metal ions inside the cells at lower *pH* values, as local concentration of carbon dioxide increases due to respiration [85].

The rate of metals absorption by phytoplankton, the intensity of metals concentration decline in water, the growth of their content in the bottom sediments and algae biomass growth rate are all interrelated [47, 49, 85].

The concentration of chemical elements in freshwater ecosystems depends largely on total biomass of aquatic organisms and its seasonal dynamics, which can be demonstrated by the example of phytoplankton (see Fig. 4.5). Seasonal changes of biomass refer not only to phytoplankton, but to zooplankton and periphyton as well. These aquatic organisms also directly affect metal concentrations in the water.

The results of experimental studies have shown that biota metal assimilation constant and complexing ability constant relating to organic matter dissolved in surface water are comparable [89]. Thus, when metals enter aquatic ecosystems, dissolved organic substances, even at their high levels of concentration in the water, will not be able to bind all free metal ions, being the most toxic form of metals, into complexes, until they start to be absorbed by biota [89].

Most active absorption of metals by phytoplankton occurs during spring and autumn growing seasons [31]. Estimations of the Don River regime have shown that annual consumption of elements by algae several times exceeds their inflow in dissolved state with the water of the river. Most of the elements are repeatedly consumed by phytoplankton throughout the year.

Highly relevant is the fact that the dead algae also adsorb heavy metals [39, 49]. With that, the adsorption of trace metals on seston surface goes proportionally to their concentration in the solution up to 10^{-4}–10^{-3} mol/L, given a constant diffusion coefficient. Considerable proportion of seston in surface water bodies with slow water exchange (lakes, reservoirs) is composed of suspended organic material —detritus. This is especially true of eutrophic water bodies. According to different authors [95, 96, 98], the proportion of detritus incorporated in seston can reach 60–90 %. Owing to suspended organic matter within detritus a certain part of metals is accumulated in seston and during the precipitation of suspended particles goes to the bottom sediments.

Organic detritus enters the bottom sediments not only in the result of precipitation, but also as part of feces produced during the assimilation of phytoplankton, organic and inorganic detritus, including authigenic particles, by zooplankton organisms with filterability [31]. There is evidence that the entire water mass of the upper layer in many estuaries can be filtered within few days, which will result in intense settling of aggregated particles on the bottom. It is possible that much of the detritus rich in organic matter may undergo repeated biofiltration before available organic matter is assimilated by the organisms. Biofiltration process facilitating the aggregation of small particles causes the detention of suspended fines in the estuary. The chemical composition of aggregates may differ significantly from the initial composition of the suspended solids due to declined ratio of carbon to nitrogen and higher concentrations of numerous metals.

Consequently, the effect of hydrobionts on the transformation of one form of metals into another implies intensification of sorption-accumulation processes, as well as enhanced complexing ability, which account for the redistribution of metals between suspended particles and sediments, on the one hand, and aqueous solution on the other.

Macrophytes also play an important role in the migration of metals.

Indirect effect of hydrobionts on the migration of metals is associated with changes in oxygen regimen of water bodies. Oxygen consumption during the decomposition of organic substances is accompanied by a decrease in its concentration with the depth of a reservoir. Given low flow rate, suitable conditions are created for reduction of near bottom sediments and sometimes in the water column, when polyvalent metals change their form. In particular, mangan passes from the solid phase to solution form being reduced to Mn^{2+}. These processes are most active at the bottom sediment–water interface. Occurring concentration gradients cause the emergence of directed flows of numerous chemical components between the near-bottom and pore water. Bacterial activity in reservoir bottom sediments rich in organic matter leads to the generation of H_2S, NO_2, NH_3, CO_2, CH_4 and other gases. Introduction of hydrogen sulphide to the bottom layer of water can significantly affect the migration ability of metals in a bottom sediments–water system. The formation of slightly soluble sulphides may dramatically slow down the outflux of metals from the sediments.

The surface layer of bottom sediments often experiences intensive bioturbation resulting in a markedly increased flow of soluble, solid and gaseous components through the bottom sediments–water interface. This also applies to a great extent to metals.

Bottom sediments of highly productive reservoirs contain significant amounts of organic substances having different properties and capable of retaining metal compounds. Of particular interest are low-solubility organic substances that precipitate together with binded metals. These include, for example, lipids. These complexes are well preserved after cell death and, entering silty muds with detritus, enrich them with metals. Thus, this is another example of hydrobionts' indirect effect on the redistribution of metals among abiotic components of aquatic ecosystems.

4.6 The Role of Hydrobionts' Exometabolites in Heavy Metal Detoxification Processes

Toxicity of heavy metals depends largely on the form they are present in the water. Free (hydrated) metal ions are one of their most toxic forms. Binding of metal ions in complexes with natural organic ligands helps significantly reduce their toxicity or fully eliminate it [26, 70, 72, 74, 76, 77, 83, 86, 139].

Potential ability of DOM to bind much higher concentrations of metals than are those typical for surface water bodies makes up the basis of complexing ability of natural water, which is an essential component of the buffer capacity of aquatic ecosystems in relation to metals, characterizing the ability of an aquatic environment to cope with their detoxification [67, 70, 71].

DOM, which determine the complexing ability of surface water, are divided by their composition and origin into three groups: exometabolites of aquatic biota, transformed organic matter, which includes primarily humic acids (HA and FA), and organic substances of human nature [67]. The first group includes polyphenols, proteins, carbohydrates and some other specific organic substances.

Most studied is the detoxifying ability of humic substances as an important component of DOM in surface water bodies [26, 70, 72, 77, 86]. It is common knowledge that hydrobionts play an important role in the formation of DOM in surface water. The so-called plankton humus is produced from organic substances —products of lifetime excreta and postmortem decomposition products of aquatic organisms. Organic substances that are part of "plankton humus" may be involved in complexing processes owing to which chemical and biological activity of metals will be substantially reduced.

The composition of aquatic organisms' extracellular products is a subject of continuous studies. Exometabolites of various algae species are presently the most extensively studied area [107]. At the same time, exploring of complexing ability of organic substances—exometabolites of aquatic organisms was conducted during the investigation of complexing ability of heavy metal ions with the whole range of organic excreta of separate algae species which are discribed as a "Collective ligand."

The scientific literature contains scarce data on the mechanism how organic substances—metabolites of aquatic organisms affect the process of detoxification. However, some works have studied these issues in great detail. Two types of ligands have been identified among the organic substances in surface water, including among exometabolites of aquatic organisms. The first type of ligands creates with metal ions relatively labile complexes, whereas the second type, by contrast, binds metal ions in rather stable complex compounds (respectively for these types of complexes Cu(II) $0.5 < lg\ \mathrm{K}^* < 7.0$ and $7.0 < lg\ \mathrm{K}^* < 10.2$, where K* is the conditional stability constant) [38]. Exometabolites of *Daphnia magna* also form two types of complex compounds having different values of conditional stability constants (logarithms of conditional stability constants are respectively 8.6 and 6.4 at *pH* 6.3) [24].

The concentration of ligands of the second type is always much lower than that of the first type. Ligands of the first type usually include organic acids, carbohydrates and polyphenols, while the second type—proteins, polypeptides and hydroxamic acids released by algae, including blue−green ones, during "algal blooms" [81].

Paper [130] studies the complexing properties of substances released by some types of blue–green algae (*Anabaena cylindrica*, *Navicula pelliculosa* and *Scenedesmus quadricauda*), as well as the ability of these substances to detoxify

Cu^{2+} ions. It has been found that organic substances released by the algae form with Cu(II) rather stable complex compounds, logarithms of conditional constants of which are respectively 7.7, 8.1 and 8.6. *Chlorella vulgaris* was used in the experiments to investigate the ability of these organic compounds to reduce the toxicity of Cu^{2+} ions by monitoring the changes in primary production. It was found that chlorella primary production in the filtrate of *A. cylindrica* at a concentration of Cu^{2+} ions 10–200 mg/L decreased by only 8 %. During a control test corresponding reduction was 60 and 83 % at concentrations of Cu^{2+} ions 50 and 200 mg/L. At the same time, the reduction of primary production of *Chl. vulgaris* in the filtrates of *N. pelliculosa* and *Sc. quadricauda* was more pronounced and was 45 and 36 % of the initial value. Obviously, in such a case detoxification of Cu^{2+} ions depended not only on the strength of their binding in complexes, but also on the degree of binding, which was determined by the amount (weight) of released organic substances. Under the same conditions the algae *A. sylindrica* release in culture medium 6.73×10^6 mol/L organic substances that bind Cu^{2+} ions, while *Sc. quadricauda*—less by almost an order of magnitude (0.66×10^{-6} mol/L).

Stable complexes are formed through binding of Cu^{2+} ions by organic substances released by blue–green algae. The logarithms of conditional stability constants of these complexes were in the range 7.0–10.2 [81]. About the same strength is intrinsic to complex compounds of Cu(II) with bacterial extracellular polymers (logarithm of relative stability constant 7.7) [102].

The topic of high stability of metal compounds with phytoplankton exometabolites is also highlighted in several other works [80, 123]. And not always a clear correlation can be traced between the decrease in toxicity of a metal and its binding force with organic substances-exometabolites. This situation is explained by the fact that the substances released by algae may exhibit themselves toxic effects on other species of phytoplankton. Moreover, not all organic substances released by phytoplankton are capable of detoxifying heavy metals, as they are not part of complexing processes [30]. Thus, organic compounds with a molecular weight <0.5 kDa did not bind Cu(II) in complexes, and substances molecular weight of which was in the range between ≥ 0.5 and 10.0 kDa were actively involved in the complexing, whereby toxicity threshold of Cu(II) increased from 25 mg/L in the former case to 100–500 mg/L in the latter case.

There are compounds with a wide range of molecular weight values occurring among the organic substances-metabolism products. Thus, iron complexes with such substances in a closed water ecosystem were characterized by the following values of molecular weight: ≤ 1 kDa—48.4 %, 10.1 kDa—25.0 %, 10–30 kDa—5.4 %, 30–300 kDa—4.1 % > 300 kDa—17.6 % [87].

Complexing activity with the involvement of organic substances-exometabolites plays an important role in detoxification of heavy metals not only in water medium, but also inside aquatic organisms. In this case, of great importance are metallothioneins—low molecular weight proteins produced in the body of shellfish, fish, crabs [12, 56, 137]. Molecular weight of metallothioneins, according to different authors [56, 137, 139], is estimated within the range from 1 to 10–12 kDa.

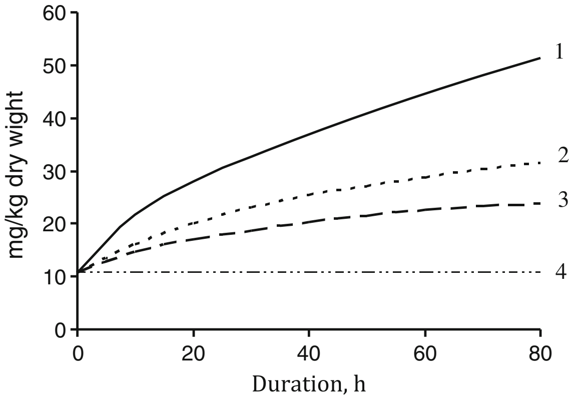
Owing to the high content of cysteine in metallothioneins (almost 30 % of all amino acid residues), these proteins are characterized by high affinity for heavy metal ions. However, toxic effects of metals, for example, Cd^{2+}, Hg^{2+}, are only offset provided that the complexing ability of metallothioneins produced in the body is not excessive. In case of such excess Cd^{2+} or Hg^{2+} ions become part of metalloenzymes and exhibit toxic properties inside the cells. Therefore, it is believed that a critical survival factor of an organism is not the total concentration of heavy metals in the tissues, organs or body, but the part of which compounds they are—metallothioneins or metalloenzymes [139].

4.7 Buffer Capacity of Freshwater Ecosystems in Relation to Metals

Buffer capacity of freshwater ecosystems regarding metals is a characteristic that allows estimating of such a maximum dose of a metal, which being present in a reservoir does not lead to a serious disturbance of natural functioning of the entire ecosystem [89, 90]. The above definition of an important characteristic contains elements of uncertainty, as far as the terms "serious" and "functioning" are difficult to quantify. Nevertheless, it's worth mentioning that the buffer capacity of freshwater ecosystems regarding heavy metals is based on the correlation of several key factors that determine the distribution and migration of metals in abiotic and biotic components of aquatic ecosystems. Among them are accumulative capacity of aquatic organisms, complexing ability of dissolved organic matter in surface water and depositing ability of bottom sediments. Thus, behavior of metals in surface water is significantly affected by at least three major processes: absorption of metals by aquatic biota, their complexing with DOM and adsorption by suspended particles and bottom sediments. Therefore, the distribution of metals in surface water is largely dependent on the rate of their binding by various components of aquatic ecosystems [91].

It has long been known that aquatic organisms are able to accumulate significant amounts of pollutants, including heavy metal compounds. However, in natural conditions it is not always possible to quantify important parameters such as kinetics of accumulation of substances by hydrobionts and their potential accumulative ability. Most often they are determined by experimental studies. For instance, it was found during culturing of the cyanobacteria *Chroococcus paris* in water with a concentration of heavy metals (Cd, Cu, Zn) 2.0 mg/L, that 90 % of all the metals were absorbed by its cells within 1 min, and within 10 min the process of binding was virtually complete [68]. Sorption capacity of the cells appeared to be high enough and at pH 7.0 was respectively for cadmium, copper and zinc 53.0, 120.0 and 65.0 mg/g dry weight.

It is clear enough, that the parameters of metal absorption by other aquatic organisms may vary. It depends on the organisms themselves and on the form of the metals in the aquatic environment. For comparison, Fig. 4.7 shows the results of



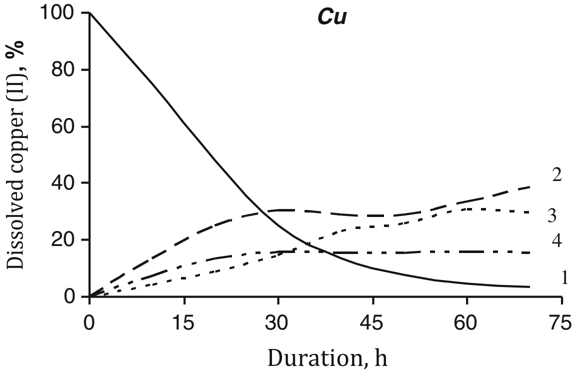
1 – free copper ions, 2 – inorganic forms, 3 – organic (humic and amino acids) forms of copper, 4 – control

Fig. 4.7 The kinetics of accumulation of ionic, inorganic and organic forms of copper by shellfish *Lymnaea stagnalis* [89]

experimental studies on the kinetics of assimilation of different forms of *Cu*(II) by the shellfish *Lymnaea stagnalis*. Copper is most actively absorbed by shellfish when it is available in the form of free ions, and least actively when it is mainly in organic forms, that is, when it is bound with humic and amino acids.

Adding to aquarium water of humic and amino acids in concentrations of 10.0 mg/L resulted in a significant reduction of *Cu*(II) accumulation in the body of shellfish (almost three fold).

A detailed study of *Cu*(II) assimilation by biotic and abiotic components of freshwater ecosystems was carried out with the use of special mesocosms with capacity 150 L, which were located in the background section of the Usman River (Voronezh Biosphere Reserve). Water sampling was carried out in the course of three days. The free and bound *Cu*(II) ions were separated by chromatography using columns with cellulose ionites. The results showed (Fig. 4.8) that most intensive reduction in concentration of Cu^{2+} ions in mesocosm water was observed



1 – water, 2 – bottom sediments, 3 – biota, 4 – dissolved organic matter in natural water

Fig. 4.8 Distribution of *Cu* (II) among the main components in controlled freshwater ecosystem [89] during the first 24 h of the experiment (Curve 1). Subsequently, depositing ability of the bottom sediments and complexing ability of DOM regarding *Cu*(II) significantly decreased (respectively Curves 2 and 4). Meanwhile, the absorption of *Cu* (II) by the biota continued to increase (Curve 3). Based on the data obtained, constants of *Cu*(II) intake by biota and DOM (due to complexing) were calculated, being approximately of one order of magnitude—5–10^{-3} and 2–10^{-3} L/(mg h).

Analysis of the results of numerous studies indicate that the complexing activity in natural surface water has significant affects on the behavior, migration and distribution of metals between abiotic and biotic components of aquatic ecosystems, their bioavailability and reducing toxicity in respect of aquatic organisms.

Therefore, the issue of research of potential complexing ability (CA) of surface water in respect of heavy metals remains relevant in today's environment, where water bodies are subject to significant anthropogenic impact. Under such conditions, it is extremely important to assess to what extent the water environment is able to "neutralize" the toxic effects of pollution by heavy metal ions. CA depends largely on the chemical composition of water and is determined by the total concentrations of organic and inorganic ligands in the water being able to form stable complexes with metal ions [67]. Since CA is one of the most important characteristics in the system of evaluation of "buffer capacity" of aquatic ecosystems in relation to heavy metals, its determination is of particular importance in predicting their resistibility to increasing anthropogenic load of this group of toxins [48, 71].

Studies indicate that CA is most often determined by the presence in the water of organic substances, because they bind metal ions in complexes much stronger than inorganic ligands like sulfates, carbonates, fluorides etc. [37, 129]. Humus substances, as a dominant component of DOM, are characterized by pronounced complexing properties and often determine potential CA of surface water [67, 97]. This is evidenced by numerous scientific data and the results of in-house studies of the chemical nature of metal complexing with DOM in various types of surface water, including the reservoirs of Dnipro cascade [67, 74, 75, 77, 83, 86].

Organic ligands with molecular weight 1.0–10.0 kDa and higher [18, 67, 70, 71] are most actively involved in complexing activity. Most likely, this is because the most stable metal complexes are formed with the involvement of humic substances (HA and FA), proteins, polypeptides and hydroxamic acids [18, 67].

Most data on DOM complexing capacity in surface fresh water were obtained using *Cu*(II) (Table 4.7). This is because Cu^{2+} ions actively bind into complexes to form rather stable compounds with many natural organic ligands. In addition, to determine the concentration of so-called free Cu^{2+} ions, high-sensitivity analysis, like chemiluminescent and electrochemical, methods are available, including inversion voltammetry and its varieties.

As seen from the above data, the range of DOM CA values of different types of surface water is extremely wide, which is accounted for the concentration of organic substances in them and their chemical nature. River water generally have the lowest CA values, because quite often their values of C_{org} content are much lower than in reservoirs or lakes. But not always there is a positive correlation between the concentration of C_{org} and DOM CA. There are cases when water with

Table 4.7 DOM complexing ability in some types of surface water

Water objects	Metals used to establish CA	Complexing ability (μmol/L)	Research method	Literature
Lakes and ponds in USA	Cu(II)	0.0–8.60	Potentiometric titration	[29]
	Cd(II)	0.0–0.30		
	Pb(II)	3.8–16.5		
Surface waters in New Hampshire	Cu(II)	1.1–15.1	Dialysis equilibrium method	[127]
	Cd(II)	0.0–0.97		
US Channels	Cu(II)	15.0–23.0	Solubility method	[65]
US rivers and estuaries	Cu(II)	0.4—2.9	Fluorescence quenching method	[104]
Surface waters in USA	Co(II)	0.8–14.0	Stripping voltammetric titrations	[36]
The rivers and lakes of Canada	Cu(II)	23.0−49.0	Potentiometric titration	[35, 99]
	Cd(II)	5.0		
	Pb(II)	19.0		
	Hg(II)	55.0		
Lakes of Canada	Cu(II)	0.05–0.15	Stripping voltammetric titrations Ion-exchange method with the use of Mп0_2	[129]
	Cu(II)	0.20–0.68		
Waccamaw Lake Black Lake	Cu(II)	91.0	Stripping voltammetric titrations	[117]
	Cu(II)	126.0		
Albert Perry Lake	Cu(II)	0.36	Solubility method	[9]
Lakes Ontario, Erie; Niagara River	Cu(II)	0.15–0.73	Differential pulse stripping voltammetry	[17]
Rivers Yamaska, St. Francois	Cu(II)	0.74–1.5	Solubility method	[14]
Mississippi River	Cu(II)	0.88–1.08	Solubility method	[44]
Rivers of Australia	Cu(II)	0.46–0.70	Solubility method	[38]
Estuaries of France	Cu(II)	0.1	Fluorescence quenching method	[8]
Humber Estuary (UK)	Cu(II)	0.03–0.40	Cathodic stripping voltammetry method	[131]
	Zn(II)	0.03–0.15		
Rivers of Europe (in total 14)	Cu(II)	0.1–0.5	Differential pulse anodic stripping voltammetry method	[13]
Rivers of Great Britain (in total 36)	Cu(II)	0.04–0.5	Cathodic stripping voltammetry method	[28]
Rivers of Russia	Cu(II)	0.26–10.49	Size-exclusion chromatography method	[23, 89]
Rivers Shuya, Usman, Lopan (Russia)	Cu(II)	0.19–1.63	Size-exclusion chromatography method	[67, 89]

(continued)

Table 4.7 (continued)

Water objects	Metals used to establish CA	Complexing ability (μmol/L)	Research method	Literature
			using Molselekt G-10 gel (Hungary)	
Lake Plyescheyevo, Cryve, Ladoga (Russia)	Cu(II)	0.39–1.78	Size-exclusion chromatography method	[23, 89]
Rivers of USA	Cu(II)	0.04–0.07	Differential pulse anodic stripping voltammetry method	[101]
Reservoirs Rybinsk, Tsimlyanskoe (Russia)	Cu(II)	1.76–2.14	Size-exclusion chromatography method	[67]
Surface waters in Fly River basin (Australia)	Cu(II)	0.17–0.41	Anodic stripping voltammetry method	[5]
Anllóns River (Galicia, Northwest Spain)	Cu(II)	1.10–1.70	Differential pulse anodic stripping voltammetry method	[4]
Guanting Reservoir, China	Cu(II)	0.40–2.00	Differential pulse anodic stripping voltammetry method	[45]
Kiryu River, Japan	Cu(II)	0.56–0.75	Extraction method using dithizone	[46]
Rivers of New Zealand	Al(III)	6.5–9.8	FIA method	[40]

high DOM concentrations have low CA and vice versa [13, 27]. The reason is that organic ligands in natural surface water originate from different sources. These may be biological exudates, organic substances leached from soils and those contained in wastewater of different industries [27]. It is also possible that complexing centers of organic ligands are already saturated with metal ions and further binding is either not possible, or occurs in small proportion and only due to the competition on the part of metals which are able to form more stable complexes.

The collating of total concentrations of copper (II) in different types of surface water bodies with the defined values of DOM CA in the surface water testifies, that the buffer capacity of aquatic ecosystems, which is accounted for the said factor (CA being one of its components), should be viewed as a sufficient prerequisite for copper (and many other metals) to be found with low-toxicity properties. This is confirmed by the results of numerous studies which show that most of the copper in surface water is in bound state [13, 28, 45, 70, 71, 76, 126]. For instance, the fraction of fixed copper in the Usman River amounts to 94 % C_{sol}. This situation is typical for many other water bodies. Thus, the fraction of Cu(II) bound with DOM in complexes in the Dnipro cascade reservoirs varies within 71–86 % C_{sol} [75, 76].

Low CA of DOM in river water (see Table 4.7) is indicative of their significantly lower resistance to heavy metal "load". However, more intensive adsorption processes on the surface of suspended particles should be expected in these water compared with the complexing activity. They also contribute to reducing both chemical and biological activity of metal ions and their toxicity. In slow flow river stretches suspended solids tend to settle out, which results in the removal of metals from the aquatic environment and there self-cleaning.

The binding of metal ions in complexes with DOM in surface water or products of humic substances (HS) occurs rather slowly—from several days to dozens of days [71, 72].

It depends on several factors, including DOM composition, conformational changes in HS macromolecules, concentration of metals in natural water and their ability to compete for binding centers, *pH*, solution ionic strength and others. Therefore, reliable CA values can only be determined when a balance in the investigated system is achieved [71].

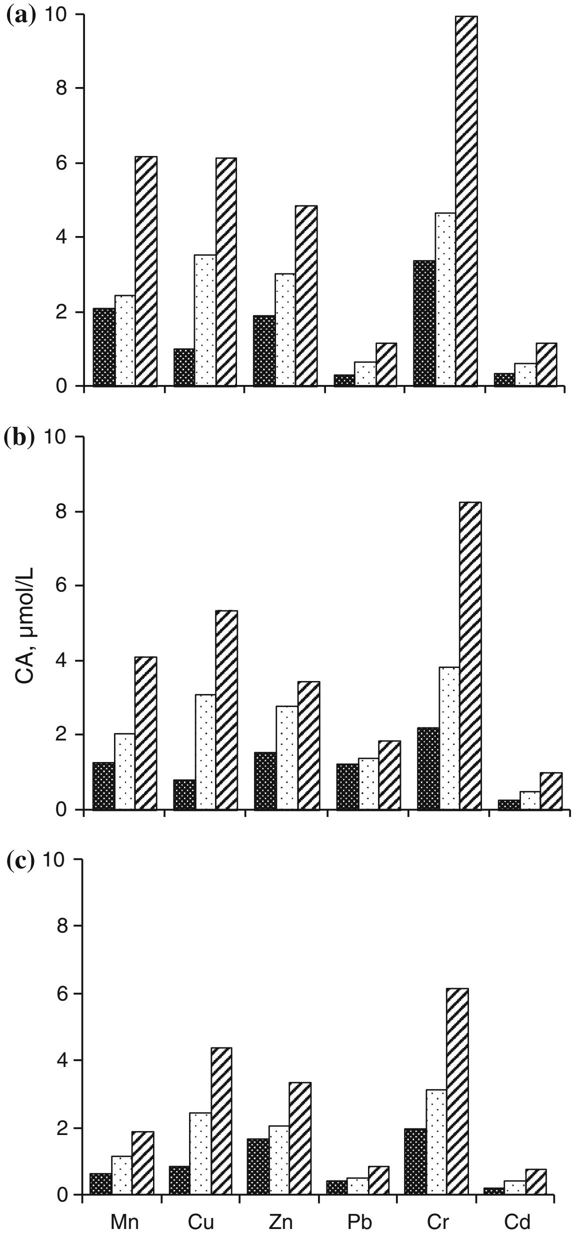
Using a case study of the Dnipro cascade reservoirs it was found that their water environment is characterized by a certain margin of DOM potential to bind metal ions in complex compounds. At the same time, the CA values vary within a wide range and markedly differ for certain metals [69], which is due to the chemical properties of the metals as well as seasonal variability in DOM composition. Among the metals we have studied (*Cd*, *Cu*, *Cr*, *Mn*, *Zn*, *Pb*), Cr^{3+} ions bind in complexes with DOM most actively, and the least active are Cd^{2+} ions (Fig. 4.9). The significant difference in CA values, determined by the concentrations of various fixed metals, is evidenced by data presented in Table 4.7.

Complexing ability of surface water is subject to seasonal fluctuations which is due to changes in DOM composition [3, 4, 71, 76, 101]. Seasonal variability of DOM CA most often found its expression in the water we have studied through a decrease in its values in late spring and early summer. In late summer and fall CA substantially increases, usually reaching its maximum values (Fig. 4.10). It is most likely, that not only humic substances as the largest DOM fraction are involved in the complexing process during this period, but organic compounds-products of metabolism and decomposition of dead aquatic organisms as well. This is confirmed by a specific distribution of metals among the compounds with DOM of different chemical nature in certain seasons (Fig. 4.11).

The proportion of complexes with HS (anionic complexes) is decreasing from spring till autumn and winter. However, the autumn–winter period is characterized by a growing proportion of cationic and neutral complexes (accordingly with proteinaceous compounds and carbohydrates).

Similar seasonal dynamics of DOM CA are described in a number of works by other authors [3, 4, 101].

Fig. 4.9 DOM complexing ability in Dnipro cascade reservoirs: Kyiv (**a**) Kremenchug (**b**) Kakhovka (**c**) regarding individual metals



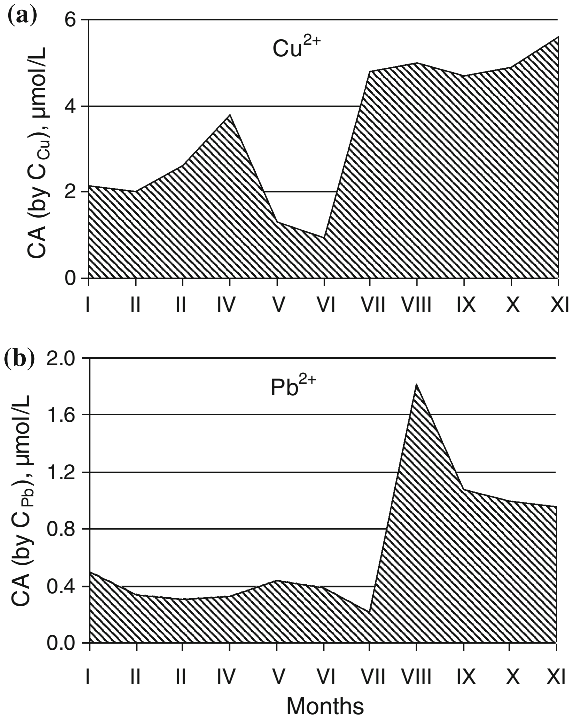


Fig. 4.10 Complexing ability of dissolved organic matter from Kyiv reservoir based on concentrations of bound in complexes Cu^{2+} (**a**) and Pb^{2+} (**b**) ions in different seasons

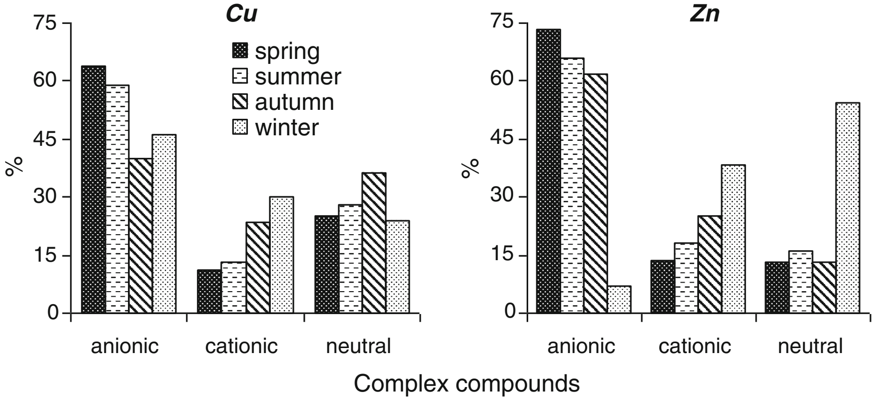


Fig. 4.11 Seasonal dynamics of chemically different metal complex compound ratios in the *upper* segment of Kaniv Reservoir: anionic, cationic and neutral—metal complexes with accordingly humic substances, proteinaceous compounds and carbohydrates

References

1. Alimov AF (1981) Funktsionalnaya ekologiya presnovodnykh dvustvorchatykh mollyuskov (Functional ecology of fresh water clams). Nauka, Leningrad
2. Altunin VS, Belavtseva TM (1993) Kontrol kachestva vody (Handbook). Kolos, Moscow
3. Antello JM, Arce F, Penedo FJ (1998) Effect of seasonal changes on the complexing of *Cu* (II) by dissolved organic matter in river water. Water Res 32(9):2714–2720
4. Antello JM, Arce F, Penedo FJ (2000) Effect of pH on the complexation parameters for organic matter dissolved in river water. Chem Speciat Bioavailab 12(1):9–15
5. Apte S, Rowland R, Patney H (2000) Size distribution of copper complexing ligands in tropical freshwaters. Chem Speciat Bioavailab 12(3):79–88
6. Arendarchuk VV (1978) Indolsoderzhaschie veschestva i rost sinezelyonykh vodorosley, vyzyvayuschikh “tsvetenie” vody (Indole-containing substances and the growth of blue-green algae generating water “bloom”. Dissertation, Taras Shevchenko National University of Kiev
7. Batoyan VV (1991) Mikroelementy v fitoplanktone Kuybyshevskogo vodokhranilischa (Microelements in phytoplankton of the Kuybyishev reservoir). Ecology 1:80–83
8. Berger P, Evald M, Liu D, Weber JH (1984) Application of the fluorescence quenching titration method to the complexation of copper (II) in Gironde estuary (France). Mar Chem 14(3):289–295
9. Blutstein H, Shaw RF (1981) Characterization of copper binding capacity in lake water. Environ Sci Technol 15(9):1100–1102
10. Braginsky LP (1968) Pyatna tsveteniya, nagonnye massy, vybrosy sinezelyonykh vodorosley i proiskhodyaschie v nikh biologicheskie protsessy (Bloom fields, piled-up water, blue-green algae emissions and the biological processes occurring there). Water bloom. Nauk dumka, Kyiv, pp 122–130
11. Brewer WC, Abernathy AR, Paunter MJ (1977) Oxygen consumption by freshwater sediments. Water Res 11(5):471–473
12. Brown DA, Parsons TR (1978) Relationship between cytoplasmic distribution of mercury and toxic effects to zooplankton and chum salmon (Oncorhynchus keta) exposed to mercury in a controlled ecosystem. J Fish Res Board Can 35(6):880–884
13. Buykx SEJ, Cleven RFMJ, Hoegee-Wehmann AA, van den Hoop MAGT (1999) Trace metal speciation in European River waters. Fres J Anal Chem 363:599–602
14. Campbell PGC, Bisson M, Gagne R, Tessier A (1977) Critical evaluation of the copper (II) solubilization method for the determination of the complexation capacity of natural waters. Anal Chem 49(14):2358–2362
15. Carmichael WW (1994) The toxins of cyanobacteria. Sci Amer 270(1):78–86
16. Carmichael WW, Azevedo MFO et al (2001) Human fatalities from cyanobacteria: chemical and biological evidence for cyanotoxins. Environ Health Perspect 109(7):663–668
17. Chau YK (1973) Complexing capacity of natural water—its significance and measurement. J Chromat Sci 11(11):579
18. Chau YK, Gachter R, Lum Shue-Chan K (1974) Determination of apparent complexing capacity of lake waters. J Fish Res 31:1515–1519
19. Denisova AI, Nahshina EP, Novikov BI, Ryabov AK (1987) Donnye otlozheniya vodokhranilisch i ikh vliyanie na kachestvo vody (Reservoir bottom sediments and their influence on water quality). Nauk dumka, Kyiv
20. Denisova AI, Timchenko VM, Nahshina EP et al (1989) Gidrologiya i gidrokhimiya Dnepra i ego vodokhranilisch (Hydrology and hydrochemistry of the Dnieper and its reservoirs). Nauk dumka, Kyiv
21. Denisova OI, Maistrenko YuG (1962) Gidrokhimiya Kakhovskogo vodoymyscha (Hydrochemistry of Kakhovka reservoir). Pub of AN URSR, Kyiv
22. Drabkova VG (1973) Destruktsiya organicheskogo veschestva i chislennost baktery v donnykh otlozheniyakh ozyor Kolskogo poluostrova (Organic substance destruction and

bacterial count in the bottom sediments of Kola Peninsula lakes. Hydrochemical activity of microorganisms in ponds and mineral deposits). Nauka, Moscow, pssp 205–215

23. Edigarova IA, Krasyukov VN, Lapin IA, Nikanorov AM (1989) Kompleksoobrazuyuschaya sposobnost rastvorennogo organicheskogo veschestva prirodnykh vod (Complexing ability of dissolved organic substance in natural water). Water Resour 4:122–129
24. Fish W, Morel FMM (1983) Characterization of organic copper-complexing agents released by Daphnia magna. Can J Fish Aquat Sci 40(8):1270–1277
25. Flerov BA (1973) Eksperimentalnoe issledovanie fenolnogo otravleniya u ryb (Experimental investigation of phenolic poisoning of fish. Effect of phenol on hydrobyontov. Nauka, Moscow, pp 5–58
26. Förstner U, Wittmann GTV (1983) Metal pollution in the aquatic environment, 2nd edn. Springer, Berlin, Heidelberg, New York
27. Gardner M, Comber S (2003) Copper complexation capacity in waters and effluents—limitations of using DOC or colour as general predictors. Chem Speciat Bioavailab 15(1):1–5
28. Gardner M, Dixon E, Comber S (2000) Copper complexation in English Rivers. Chem Spec Bioavail 12(1):1–8
29. Giesy JP, Briese LA, Leversee GL (1978) Metal binding capacity of selected marine surface waters. Environ Geol 2:257–268
30. Gnassia-Barrelli M, Romeo M, Laumond F, Pesando D (1978) Experimental studies of the relationship between natural copper complexes and their toxicity to phytoplankton. Mar Biol 47(1):15–19
31. Gordeev VV (1983) Rechnoy stok v okean i cherty ego geokhimii (The river runoff into the ocean and the properties of its geochemistry). Nauka, Moscow
32. Goryunova SV, Demina NS (1974) Vodorosli - produtsenty toksicheskikh veschestv (Algae–producers of toxic substances). Nauka, Moscow
33. Gundersen K, Mountain CW (1973) Oxygen utilization and pH change in the ocean resulting from biological nitrate formation. Deep-Sea Res 20(12):1083–1091
34. Guseynova VP, Sakevich AI (2007) Uglevodorody kletochnykh obolochek presnovodnykh vodorosley i nekotorye aspekty ikh ekologicheskogo metabolizma (Hydrocarbons of cell membrane of fresh-water algae and some aspects of their ecological metabolism). Hydrobiol J 43(4):62–75
35. Guy RD, Chakrabarti CL (1976) Studies of metal-organic interactions in model systems pertaining to natural waters. Can J Chem 54(16):2600–2611
36. Hanck KW, Dillard JW (1977) Evaluation of micromolecular complexometric titrations for the determination of the complexing capacity of natural waters. Anal Chim Acta 89:329–338
37. Hart BT (1981) Trace metal complexing capacity of natural water: A review. Environ Technol Lett 2:95–110
38. Hart BT, Davies SHR (1981) Copper complexing capacity of waters in the Magela Creek system, Northern Australia. Environ Technol Lett 2:205–214
39. Hassett JM, Jennett JC, Smith JE (1980) Heavy metal accumulation by algae. In: Baker RA (ed) Contaminants and sediments, vol 2. Ann Arbor Science Publisher, pp 409–424
40. Hawke DJ, Powell KJ, Gregor JE (1996) Determination of the aluminium complexing capacity of fulvic acids and natural waters, with examples from five New Zealand rivers. Mar Freshw Res 47(1):11–17
41. Haylov KM (1968) Mikrobiologicheskie protsessy vnekletochnogo gidroliza polisakharidov, rastvoryonnykh v morskoy vode (Microbiological processes of extracellular hydrolysis of polyose dissolved in marine water). Microbiology 37(3):518–522
42. Haylov KM (1971) Ekologichesky metabolism v more (Ecological metabolism in the sea). Nauk dumka, Kyiv
43. Haylov KM (1974) Biokhemicheskaya trofodinamika v morskikh pribrezhnykh ekosistemakh (Biochemical trophic dynamics in marine coastal ecosystems). Nauk dumka, Kyiv

44. Hoffman MR, Yost EC, Eisenreich SJ, Maier WJ (1981) Characterization of soluble and colloidal-phase metal complexes in river water by ultrafiltration. A massbalance approach. Environ Sci Technol 15(16):655–661
45. Huang S, Wang Z, Ma M (2002) Measuring the bioavailable/toxic concentration of copper in natural water by using anodic stripping voltammetry and Vibrio-qinghaiensis sp. Nov.-Q67 bioassay. Chem Speciat Bioavailab 15(2):37–45
46. Itabashi H, Kawamoto H, Niibe N, Tsunoda K, Akaiwa H (1995) Simultaneous determination of complexing capacity and lability of soluble copper(II) complex in natural water by dithizone extraction. Anal Sci 11:263–265
47. Izrael YuA, Nikanorov AM, Lapin IA et al (1985) Otsenka bufernoy yomkosti malykh vodotokov k tyazhyolym metallam (Assessment of beck surge capacity to heavy metals). AN USSR's reports, vol 283, no 3, pp 703–706
48. Izrael YuA, Nikanorov AM, Lapin IA, Zhulidov AV, Dubova NA (1985) Otsenka bufernoy yomkosti malykh vodotokov k tyazhyolym metallam (The assessment of surge capacity of minor streams to heavy metals). USSR's Acad Sci Rep 283(3):703–706
49. Jackson TA (1978) A biogeochemical study of heavy metals in lakes and streams, and a proposed method for limiting heavy metal pollution of natural waters. Verh Int Ver Theor und Angew Limnol 20(3):1945–1946
50. Jacoby JM, Collier DC, Welch EB, Harody FJ, Crayton M (2000) Environmental factors associated with a toxic bloom of Microcystis aeruginosa. Can J Fish Aquat Sci 51(1):P.231–240
51. Kaplin VT (1967) Prevraschenie organicheskikh soedineny v vodoyome (Conversion of organic compounds in pond). Hydrochem Mater 45:207–226
52. Keller MD, Mague TN, Badenhausen M, Glover H (1982) Seasonal variation in the production and consumption of aminoacids by coastal microplankton. Estuar Coast Shelf Sci 15(3):301–315
53. Kirilova VS (1969) Izuchenie lipidnogo kompleksa nekotorykh predstaviteley azotfiksiruyuschikh sinezelyonykh vodorosley i khlorelly (Study of lipid complex of some forms of nitrogen-fixing blue-green algae and chlorella). Dissertation, Zabolotny Institute of microbiology and virology
54. Klein G (1975) Bildung von Tryptophanmetaboliten beim anaeroben obau von Algen und deren Bedeutung fur Gewasser und Wasserwirtschaft. Vortrag auf Fachtagung der Deutschen Section fur Limnologie in der internationalen fur Limnologie, Siegburg, 6–10 Oct 1975
55. Klochenko PD (1994) Aminy – ekzo-i- endometabolity vodorosley (Amines – exo-endometabolites of algae). Hydrobiol J 30(5):42–62
56. Konovalov YuD (1993) Svyazyvanie kadmiya i rtuti belkami i nizkomolekulyarnymi tiolovymi soedineniyami ryb (obzor) (Cadmium and mercury binding by proteins and fish low molecular weight thiol compouds). Hydrobiol J 29(1):42–51
57. Konovalov YuD (1995) Anionnaya i kationnaya formy belkov v vodakh Desny i Dnepra na uchastke nizhnego byefa Kievskogo vodokhranilischa (Anionic and cationic protein forms in the Desna and Dnieper water on the site of the downstream pool of Kiev reservoir). Hydrobiol J 31(2):82–95
58. Korableva AI (1977) Sostav i kachestvo aminokislot v organicheskom veschestve, rastvoryonnom v vode Dneprodzerzhinskogo i Zaporozhskogo vodokhranilisch (Composition and quality of amino acids in organic substance dissolved in the water of Dnepropetrovsk and Zaporozhye reservoirs. Biological aspects of safety and environmental management). Pub NII of Biology, Dnepropetrovsk, pp 102–107
59. Korableva AI (1978) Raspredelenie i ekologo-funktsionalnaya kharakteristika azotistykh komponentov rastvorennogo organicheskogo veschestva v vode Dneprodzerzhinskogo i Zaporozhskogo vodokhranilisch (Distribution and ecologo-functional characteristic of nitrogenous components of dissolved organic substance in Dneprodzerzhinsk and Zaporozhye reservoirs). Dnepropetrovsk

60. Kozitskaya VN (1971) K voprosu ob istochnikakh nakopleniya fenolov v vodokhranilischakh dneprovskogo kascada (On sources of phenol accumulation in the Dnieper cascade reservoirs). Hydrobiol J 7(4):57–62
61. Kozitskaya VN (1975) Fenolnye soedineniya v “pyatnakh tsveteniya” vodorosley (Phenol compounds in “bloom fields” of algae). Biological self-purification and water quality formation. Nauka, Moscow, pp 81–84
62. Kozitskaya VN (1979) Vozdeistvie ekzogennykh fenolnykh soedineny na rost Microcytis aeruginosa (Influence of exogenic phenol compounds on the growth of Microcystis aeruginosa). Hydrobiol J 15(3):50–54
63. Kozitskaya VN (1984) Ingibiruyuschie veschestva, produtsiruemye nekotorymy Cyanophyta (Inhibitory substances produced by some Cyanophyta). Hydrobiol J 20(2):51–55
64. Kulsky LA, Sirenko LA, Shkvaro ZN (1986) Fitoplankton i voda (Phytoplankton and water). Nauk dumka, Kyiv
65. Kunkel R, Manahan SE (1973) Atomic absorption analysis of strong heavy metal chelating agents in water and waste water. Anal Chem 45:1465–1468
66. Landau Yu, Sirenko L (eds) (2004) Gidroenergetika i okruzhayuschaya sreda (Hydroenergetics and environment). Libra, Kiev
67. Lapin IA (1988) Kompleksoobrazuyuschaya sposobnost prirodnykh vod v sisteme opredeleniya bufernoy yomkosty vodnykh ekosistem k tyazhyolym metallam (Complexing capacity of natural water in the system of surge capacity determination of aquatic ecosystems to heavy metals. Ecological regulation and modeling anthropogenic impact on aquatic ecosystems, vol 1. Hydrometeoizdat, Leningrad, pp 83–95
68. Les A, Walker RW (1984) Toxicity and binding of copper, zinc, and cadmium by the blue-green algae, Chroococcus paris. Water Air Soil Pollut 23(2):129–139
69. Linnik PN (2004) Formirovanie gidrokhemicheskogo rezhima vodokhranilisch. (Formation of a reservoir hydrochemical regime). In: Landau Yu, Sirenko L (eds) Hydroenergetics and environment Libra, Kiev, pp 219–236
70. Linnik PN, Nabivanets BI (1986) Formy migratsii metallov v presnykh poverkhnostnykh vodakh (Metal migration forms in fresh surface water). Hydrometeoizdat, Leningrad
71. Linnik PN, Nabivanets Yu, Iskra IV et al (1994) Kopleksoobrazuyuschaya sposobnost rastvoryonnykh veschestv prirodnykh vod kak sostavnaya chast “bufernoy yomkosty” vodnykh ekosistem (Complexing capacity of natural water dissolved organic substances as a percent of “surge capacity” of water ecosystems). Hydrobiol J 30(5):87–99
72. Linnik PN, Scherban EP (1999) Otsenka toksichnosti form medi v prirodnykh vodakh metodom biotestirovaniya v sochetanii s khemilyuminestsentnym opredeleniem kontsentratsii svbodnykh ionov Cu^{+2} (Assessment of copper form toxicity in natural water with the help of a biotesting method combined with chemiluminescence detection of free ion concentration Cu^{2+}. Ecolog Chem 8(3):168–176
73. Linnik PN, Timchenko OV, Zubko AV et al (2008) Kislorodny rezhim vodoyomov kak vazhneyshy factor migratsii razlichnykh form metallov v sisteme “donnye otlozheniya-voda (Reservoir oxigen regime as the most important factor for migration of different metal forms in the “bottom sediments-water” system)”. Hydrobiol J 44(6):94–116
74. Linnik PN, Vasilchuk TA (2001) Rol gumusovykh veschestv v protsessakh kompleksoobrazovaniya i detoksikatsii (na primere vodokhranilisch Dnepra) (The role of humic substances in the processes of binding and detoxification (for the Dniper reservoirs)). Hydrobiol J 37(5):98–112
75. Linnik PN, Vasilchuk TA (2005) Role of humic substances in the complexation and detoxification of heavy metals: case study of the Dnieper reservoirs. Use of humic substances to remediate polluted environments: from theory to practice. In: Perminova IV, Hatfield K, Hertkorn N, (eds). NATO Science Series. IV: earth and environmental series, pp 135–154. Printed in the Netherlands, Springer, vol 52
76. Linnik PN, Vasilchuk TA, Linnik RP Ignatenko II (2007) Sosuschestvuyuschie formy tyazhyolykh metallov v poverkhnostnykh vodakh Ukrainy i rol organicheskikh veschestv v ikh migratsii (Coexistent heavy metal forms in surface water of Ukraine and the role of

organic substances in their migration. Methods and objects of chemical analysis, vol 2, no 2, pp 130–145

77. Linnik PN, Vasilchuk TA, Linnik RP (2004) Gumusovye veschestva prirodnykh vod i ikh znachenie dlya vodnykh ekosistem (obzor) (Humic substances of natural water and their importance for water ecosystems (an overwiew)). Hydrobiol J 40(1):81–107
78. Maksimova IV, Pimenova MV (1971) Vnekletochnye produkty zelyonykh vodorosley (Extracellular products of blue-green algae. Bioactive biogeneous compounds. MGU Press, Moscow, pp 51–58
79. Manskaya SM, Drozdova TV (1964) Geokhimiya organicheskogo veschestva (Geochemistry of organic substance). Nauka, Moscow
80. McKnight DM, Morel FMM (1979) Release of weak and strong copper-complexing agents by algae. Limnol Oceanogr 24(5):823–827
81. McKnight DM, Morel FMM (1980) Copper complexation by siderophores from filamentous blue-green algae. Limnol Oceanogr 25(1):62–71
82. Mihaylenko LE (1999) Bakterioplankton dneprovskikh vodokhranilisch (Bacterial plankton of the Dnieper reservoirs). Kiev
83. Moiseenko TI, Kudryavtseva LP, Gashkina NA (2006) Rasseyannye elementy v poverkhnostnykh vodakh sushi: Tekhnofilnost, bioakkumulyatsiya i ekotoksilologiya (Trace elements in surface water: Technophility, bioaccumulation and environmental toxicology). Nauka, Moscow
84. Molodkin PF (ed) (1991) Biogeokhimichesky tskil tyazhyolykh metallov v ekosisteme Nizhnego Dona (Biogeochemical cycle of heavy metals in the Lower Don ecosystem). Rostov unity Press, Rostov-on-Don
85. Morel F (1985) Iron uptake and phytoplankton growth. Rev Port Quim 27:1–2. In: 2nd international conference on bioinorganic chemistry abstract, Algarve, pp 140–141
86. Mur JV, Ramamurti S (1987) Tyazhyolye metally v prirodnykh vodakh: Kontrol i otsenka vliyaniya (Heavy metals in natural water: Control and assessment of influence). Mir, Moscow
87. Murphy TP, Lean DRS (1975) The distribution of iron in a closed ecosystem. Verh Int Verein Limnol 19(1):258–266
88. Nemtseva LI, Semenov AD, DatskoVG (1964) Metod kolichestvennogo opredeleniya letichikh aminov v prirodnykh i zagryaznyonnykh vodakh (Quantification method of volatile amine detection in natural and foul water). Hydrochem Mater 38:150–155
89. Nikanorov AM, Zhulidov AV (1991) Biomonitoring metallov v presnovodnykh ekosistemakh (Biomonitoring metals in fresh water ecosystems). Hydrometeoizdat, Leningrad
90. Nikanorov AM, Zhulidov AV, Dubova NA et al (1988) Bufernaya yomkost presnovodnykh ekosistem k tyazhyolym metallam i gidrobiologicheskie faktory eyo opredelyayuschie (Fresh water surge capacity to heavy metals and hydrobiological factors determining it. Ecological regulation and modeling anthropogenic influence on water ecosystems, Issue 1. Hydrometeoizdat, Leningrad, pp 58–69
91. Nikanorov AM, Zhulidov AV, Lapin IA et al (1989) Kineticheskie kharakteristiki protsessov akkumulyatsii metallov bioticheskimi i abioticheskimi komponentami presnovodnykh ekosistem (Kinetic processes of metal accumulation by biotic and abiotic components of fresh-water ecosystems). USSR’s Acad Sci Rep 305(5):1274–1276
92. Nikanorov AM, Zhulidov AV, Pokarzhevsky AD (1985) Biomonitoring tyazhyolykh metallov v presnovodnykh ekosistemakh (Biomonitoring heavy metals in fresh water ecosystems). Hydrometeoizdat, Leningrad
93. Nikolishin IY (1978) Vozmozhnosti ispolzovaniya rasteny v kachestve indikatorov nakopleniya i deystviya tyazhyolykh metallov v ekologicheskom monitoringe (Plant application abilities as an indicator of heavy metal accumulation and activity in ecological monitoring. Problems of ecological monitoring and ecosystem modeling, vol 1. Leningrad, pp 42–56

94. Osipov LF (1980) Metabolity sinezelyonykh vodorosley i ikh rol v formirovanii rastvorimogo organicheskogo veschestva vody (Blue-green algae metabolites and their role in formation of dissolved organic water substance). Dissertation, Institute of Hydrobiology of Ukranian Academy of Sciences
95. Ostapenya AP (1979) Detrit iego rol v vodnykh ecosystemakh (Detritus and its role in water ecosystems). Research framework of water ecosystems. Leningrad, pp 257–271
96. Pavelyeva EB (1974) Vertikalnoe raspredelenie, sezonnaya dinamika sestona i rol detrita v ekosisteme oz. Dalnego (Altitude distribution, seasonal dynamics of seston and the role of detritus in ecosystem of lake Dalnoe). Hydrobiol J 10(3):20–24
97. Perminova IV, Hatfield K (2005) Remediation chemistry of humic substances: theory and implications for technology. Use of humic substances to remediate polluted environments: from theory to practice. In: Perminova IV, Hatfield K, Hertkorn N (eds) NATO Science Series. IV: Earth and environmental series, vol 52. Printed in the Netherlands, Springer, pp 3–36
98. Priymachenko AD (1981) Fitoplankton i pervichnaya produktsiya Dnepra i dneprovskikh vodokhranilisch (Phytoplankton and primary product of the Dnieper and its reservoirs). Nauk. dumka, Kyiv
99. Ramamoorthy S, Kushner DJ (1975) Heavy metal binding components of river water. J Fish Res Board Can 32(10):1755–1766
100. Rolle I, Hobucher HE, Kneifel H et al (1977) Amines in unicellular green algae. 2. Amines in Scenedesmus acutus. Anal Biochem 77:103–109
101. Rozan TF, Benoit G (1999) Geochemical factors controlling free Cu ion concentrations in river waner. Geochim Cosmochim Acta 63 (19/20): P.3311–3319
102. Rudd T, Sterritt RM, Lester JN (1984) Formation and conditional stability constants of complexes formed between heavy metals and bacterial extracellular polymers. Water Res 18 (3):379–384
103. Ryabov AK, Sirenko LA (1982) Isskusstvennaya aeratsiya prirodnykh vod (Artificial aeration of natural water). Nauk dumka, Kyiv
104. Ryan DK, Weber JH (1982) Copper (II) Complexing capacities of natural waters by fluorescence quenching. Environ Sci Technol 16(12):866–872
105. Sabyilina AV (1978) O sezonnoy dinamike i nekotorykh zakonomernostyakh vertikalnogo raspredeleniya otdelnykh fraktsy lipidov vo vzvesi, vydelennoy iz prirodnykh vod (On seasonal dynamics and some regularities of altitude distribution of lipid fractions in the suspension extruded from natural water. Organic substance and biogenic elements in inland water. Theses, Tallinn, 3–4 Oct 1978. Pub. AN ESSR, Tallinn, pp 94–95
106. Saekevich AI (1985) Ekzometabolity presnovodnykh vodorosley (Fresh water algae exometabolites). Nauk, Dumka, Kyiv
107. Saekevich OY, Usenko OM (2008) Alelopatiya v gidroekosistemakh (Alelopatiya in aquatic ecosystems). NAN of Ukraine, Inst of Hydrobiology, Kiev
108. Scherbak VI (1998) Mnogoletnyaya dinamika “tsveteniya” vody dneprovskykh vodokhranilisch (Over-year dynamics of the Dnieper reservoir water “bloom”). NAN of Ukraine’s reports, vol 7, pp 187–189
109. Seki H (1986) Organicheskie veschestva v vodnykh ekosistemakh (Organic substances in aquatic ecosystems). Hydrometeoizdat, Leningrad
110. Semenov AD (1966) O soderzhanii otdelnykh grup organicheskikh veschestv v vodakh nekotorykh rek Sovetskogo Soyuza (On certain group content of organic substances in some rivers of the USSR). Hydrochem Mater 42P:171–177
111. Semenov AD (1967) Khimicheskaya priroda organicheskikh veschestv poverkhnostnykh vod (Chemical nature of organic substances of surface water). Hydrochem Mater 45:155–172
112. Semenov AD (1971) Organicheskie veschestva v poverkhnostnykh vodakh Sovetskogo Soyuza (Organic substances in surface water of the Soviet Union). Dissertation, Hydrochemical institute
113. Semenov AD (ed) (1977) Rukovodstvo po khimicheskomu analizu poverkhnostnykh vod sushi (Manual for surface water chemical analysis). Hydrometeoizdat, Leningrad

114. Semenov AD, Bryizgalo VA, Pozdnyakova AN (1974) O svyazi mezhdu dinamikoy biomassy, sostavom fitoplanktona i vnutrigodovymi izmeneniyami soderzhaniya rastvorennykh organicheskikh veschestv v vodoyome (On relationship among biomass dynamics, phytoplankton content and intrannual changes of dissolved organic substance content in the pond). Hydrochem Mater 60:155–160
115. Shnyukova EI (1977) Produkuvannya pozaklitynnykh vuglevodiv deyakymy sinezelenymy vodorastyami (Extracellular carbohydrate production by some blue-green algae). Ukr botan J 34(3):225–229
116. Shnyukova EI, Pirozhenko SU (1972) Kharakteristika polisakharidnogo kompleksa fitoplanktona v period “tsveteniya” vodoyoma (Polyose complex characteristics of phytoplankton during pond “bloom”. Hydrobiol J 8(5):36–41
117. Shuman MS, Woodward GPJr (1977) Stability constants of copper-organic chelates in aquatic samples. Environ Sci Technol 11(8):809–813
118. Sirenko LA (1972) Fiziologicheskie osnovy razmnozhenia sinezelyonykh vodorosley v vodokhranilischakh (Physiological fundamentals of blue-green algae reproduction in reservoirs). Nauk dumka, Kyiv
119. Sirenko LA, Gavrilenko MYa (1976) “Tsvetenie” vody i evtrofirovanie (metody ego ogranicheniya i ispolzovanie sestona) (Water “bloom” and eutrophication (the methods of its restriction and seston usage)). Nauk. dumka, Kyiv
120. Sirenko LA, Kozitskaya VN (1988) Biologicheski aktivnye veschestva vodorosley i kachestvo vody (Biologically active substances of algae and water quality). Nauk dumka, Kyiv
121. Sirenko LA, Sakevich AI, Arendarchuk VV et al (1971) Vydeleniya vodorosley i ikh rol v formirovanii vodnykh biotsenozov (Algae detection and their role in aquatic biocenosis formation. Transient biologically active compounds of biogenious nature). MGU Press, Moscow, pp 74–83
122. Sudina EG, Shnyukova EI, Kostlan NB, Mushak PA, Tupik ND (1978) Biokhimiya sinezelyonykh vodorosley (Biochemistry of blue-green algae). Nauk dumka, Kyiv
123. Sueur S, van den Berg CMG, Riley JP (1982) Measurement of the metal complexing ability of exudates of marine macroalgae. Limnol Oceanogr 27(3):536–546
124. Telitchenko MM (1974) Gipoteticheskie algotoksiny i perekisnoe okislenie rastvoryonnykh organicheskykh veschestv (Hypothetical algotoxins and dissolved organic substance perooxidating). Hydrobiolog J 10(6):97–107
125. Telitchenko MM, Ostroumov SA (1990) Vvedenie v problemy biokhemicheskoy ekologii (Problems of biochemical ecology in brief). Nauka, Moscow
126. Town RM, Filella M (2000) A comprehensive systematic compilation of complexation parameters reported for trace metals in natural waters. Aquatic Sci 62:252–295
127. Truitt RE, Weber JH (1981) Determination of complexing capacity of fulvic acid for copper (II) and cadmium (II) by dialysis titration. Anal Chem 53(2):337–342
128. Usov AI, Chizhov OS (1988) Khimicheskie issledovaniya vodorosley (Chemical study of algae). Znanie, Moscow
129. Van den Berg CMG, Kramer JR Determination of complexing capacities of ligands in natural waters and conditional stability constants of the copper complexes by means of manganese dioxide. Anal Chim Acta 106(1):113–120
130. Van den Berg CMG, Wong PTS, Chau YK (1979) Measurement of complexing materials excreted from algae and their ability to ameliorate copper toxicity. J Fish Res Board Can 36 (8):901–905
131. Van Veen E, Gardner M, Comber S (2001) Temporal variation of copper and zinc complexation capacity in the Humber estuary. J Environ Monit 3:322–323
132. Varshal GM, Velyuhanova TK, Koscheeva IYa, Kubrakova IV, Baranova NN (1988) Kompleksoobrazovanie blagorodnykh metallov s fulvokislotami prirodnykh vod i geokhemicheskaya rol etikh protsessov (Complexation of precious metals with natural water fulvic acids and the geochemical role of these processes). In Ermakov AN

(ed) Analytical chemistry of rare elements: Collection of studies. Nauka, Moscow, pp 112–146

133. Vasyukov AE, Blank AB (2007) Khimicheskie aspekty ekologicheskoy bezoopasnosti poverkhnostnykh vodnykh obyektov (Chemical aspects of surface-waterbody ecological safety). Institute of Monocrystals, Kharkov
134. Vinborg GG (ed) (1980) Bentos Uchinskogo vodokhranilischa (Benthos of the Uchinsk reservoir). Nauka, Moscow
135. Vodokhranilischa i ikh vozdeistvie na okruzhayuschuyu sredu (1986) (Reservoirs and their influence on environment). Nauka, Moscow
136. Volkova NS (1980) Komponentny sostav nekotorykh diatomovykh vodorosley i ikh rol v formirovanii zapakhov vody (The component composition of some diatomic algae and their role in water odour formation. Dissertation, Taras Shevchenko National University of Kiev
137. Wiedow MA, Kneip TJ, Garte SJ (1982) Cadmium-binding proteins from blue crabs (Callinectes sapidus) environmentally exposed to cadmium. Environ Res 28(1):164–170
138. Zhukinsky VN, Zhuravleva LA, Ivanov AI et al (1989) Dneprovsko-Bugskaya estuarnaya ekosistema (The Dnieper-Bug estuarial ecosystem). Nauk dumka, Kyiv
139. Zhulidov AV (1988) Fiziko-khimicheskoe i khimicheskoe sostoyanie metallov v prirodnykh vodakh: toksichnost dlya presnovodnykh organizmov (Physico-chemical and chemical condition of metals in natural water: toxicity for fresh-water organisms). Ecological regulation and modelling anthropogenic influence on water ecosystem, vol 1. Hydrometeoizdat, Leningrad, pp 78–82

Chapter 5
General Description of Effects of Anthropogenic Factors on Surface Water Quality

It is common practice to distinguish among the natural factors affecting chemical composition of surface water direct ones, i.e. those that directly cause changes in their composition, and indirect, whose effect is manifested through the forming of certain conditions in which substances interact. The first group includes rocks, soil, living organisms, the second one–the climate, terrain, hydrological regime, vegetation, hydro-geological conditions and so on. The said interactions occur through a number of processes, resulting in a change of the chemical composition of water.

At the same time, surface water are natural ecosystems, consisting of biotic and abiotic components functionally interconnected through material and energy exchange. The functioning of such systems is supported by a number of diverse processes.

Figure 5.1 shows the relationship between the chemical composition of surface water and physical, physic-chemical and biological processes that occur in it. Hydrological processes have more bearing on the development and functioning of hydrobionts and less on physico-chemical processes. There is a strong interrelation between the physico-chemical and biological processes, but it cannot be described by certain generalized mathematical relationships, because the biological processes are extremely complex and depend on the structural and functional characteristics of hydrobionts symphagiums.

Most river and lake systems are widely used in anthropogenic activity, being at the same time sources of water supply and receivers of industrial, municipal and agricultural wastewater. Almost half of all consumed water is used by industries. The production profile in Ukraine is dominated by water-intensive sectors—steel producing, chemical and coal industries. The most aggressive waste water are discharge by the chemical industry. In general, the industrial facilities discharge nearly 85 % of the total polluted wastewater.

The other half of the water consumed is spent roughly in equal proportion on public supply needs and agriculture, with their wastewater causing significant

V. Osadchyy et al., *Processes Determining Surface Water Chemistry*,
DOI 10.1007/978-3-319-42159-9_5

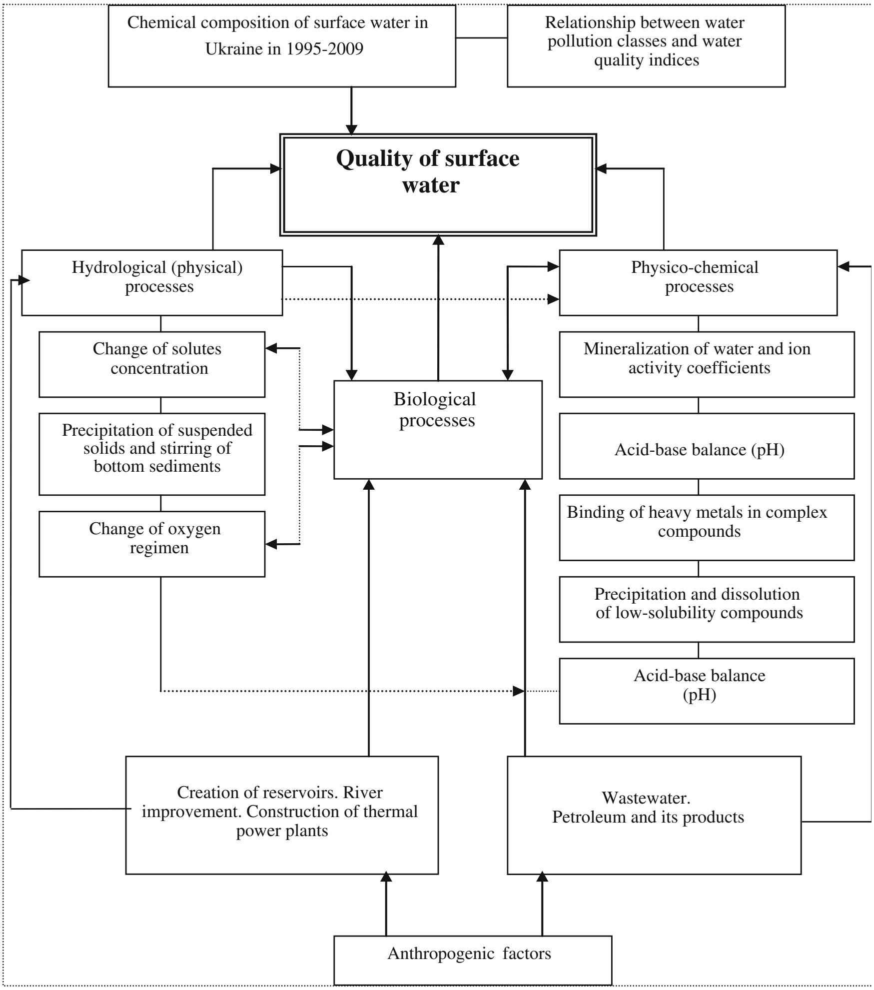


Fig. 5.1 The processes affecting the quality of surface water

pollution of water bodies. As a rule, wastewater of utility companies are previously purified at treatment plants, but the latter's performance is inefficient in many cities. Most villages virtually do not have treatment facilities. In addition, large volumes of polluting substances are washed off in the built-up areas of the cities.

Large amounts of nitrogen and phosphorus compounds enter surface water objects in the result of leaching out from farmlands containing fertilizers. Drainage effluents of irrigation systems cause contamination of natural water by pesticides and mineral salts. The main pollutants that come from livestock facilities include nitrogen, phosphorus, organic matter, potassium and heavy metals.

Thus, an intensive use of natural surface water significantly affects the quantity and quality characteristics of water bodies, changes their hydrological budget, hydrologic behavior, natural hydro-chemical processes, leads to an increase in many components, causes contamination of natural objects by extrinsic synthetic chemicals. Anthropogenic factors may also cause changes in the composition of bioplasm.

By the degree of influence on the chemical composition of surface water bodies anthropogenic factors are often comparable with natural ones, sometimes even exceeding them. Changes in economic production, undergone by Ukraine and other Eastern European countries in connection with the disintegration of the former Soviet Union, clearly show the degree of impact of human activities on the environment.

The degree of production decline in the process of restructuring of Ukraine's economy was estimated using such an aggregated index, reflecting the general level of anthropogenic footprint, as emissions of greenhouse gases (GHGs). While in 1990 GHG emissions in Ukraine amounted to 892 million tons of CO_2-eq., in 2004 they fell to 381 million tons of CO_2-eq. Structurally the share of energy in total emissions amounted to 74–3 %, industry—3–4 %, agriculture—13–18 %. Wastewater account for the lowest GHG emission rate, but, unlike other sources, their share increased from 7.9 million tons of CO_2-eq. in 1990 to 8.9 million tons of CO_2-eq. in 2004. Despite this, the actual volume of waste water was significantly reduced during the period 1990–2003. The volume of wastewater in Ukraine reached its maxima in 1992 amounting to over 4 billion m^3. This was followed by a gradual decrease in their volume, which in 2003 reached the mark 2.872 billion m^3, i.e. became 1.4 times less than the maximum value [10]. In parallel with the reduction of waste water volume, the proportion of human waste products in them also decreased, which can be traced by the curve of organic matter content (according to the determinations of biochemical oxygen demand) in the wastewater (Fig. 5.2). This is accounted for the following factors. According to statistics, there is a steady downward trend in consumption of protein-containing products in Ukraine. While in 1990 the figure averaged 105.3 g protein/person day, in 2004 it reached only 76 % of that value, that is, 79.7 g protein/person day [12].

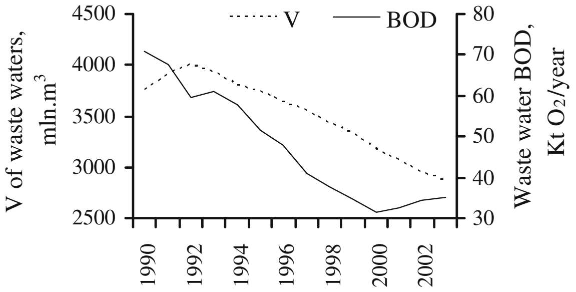


Fig. 5.2 Changes in the volume of waste water discharge in Ukraine and content of organic substances (according to biochemical oxygen demand–BOD) in the period 1990–2003

At the same time, the number of population in the country decreased significantly (9 %) during that period.

The restructuring of the economic system in Ukraine in the early 90th of the XX century led to the economic crisis that also affected the condition of water resources. While in 1990 an aggregated Environmental Sustainability Index (I_E), estimated on the basis of average indicators for certain river basins, was as follows: the Danube (3.27) < rivers of the Crimea (3.33) < Dnipro (3.46) < Dniester (3 51) < Southern Bug (3.64) < Siversky Donets (3.85) < Western Bug (4.13) < rivers of the Azov Sea area (4.19), in 2006 the absolute values of I_E dropped and were distributed among the basins as follows: rivers of the Crimea (2.57) < Dniester (2.92) < Dnipro (3.03) < Western Bug (3.1) < Siversky Donets (3.15) < Southern Bug (3.26) < Danube (3.31) < rivers of the Azov Sea area (4.15).

This is a clear example that the elimination of one of the major causes of natural surface water pollution, namely reducing waste water discharge, leads to their recovery as a result of natural processes of self-purification. On the other hand, the above situation suggests an effective way of improving quality of the country's water resources. This strategy is being successfully implemented by the European community in the upper and middle stretches of the Danube. For example, only in Hungary treatment plants were commissioned more than in 20 cities over the past decade, and in 2005 the last city in Hungary, which until then was devoid of a waste water treatment facility, was provided with the one.

By the nature of the affect on surface water the anthropogenic factors are divided into two groups.

The first one includes the regulation of rivers and construction of hydropower stations and reservoirs, construction of thermal and nuclear power plants. These factors affect primarily hydrological and biological processes, causing changes in the concentration of dissolved substances, including oxygen, settling of suspended organo-mineral substances with toxic compounds adsorbed on them, decrease in turbidity, temperature changes and biological productivity of water masses. Hydraulic engineering allows addressing numerous economic issues of large regions, primarily pertaining to water supply of the water-deficient areas, water transport, land reclamation, development of fisheries, improvement of utility services etc. However, along with the positive economic effects such construction entails unwanted negative implications resulting in disbalance of natural ecosystems that historically functioned in these regions. [8] This is largely true of aquatic ecosystems in connection with the creation of reservoirs on the rivers. It is common knowledge that oxygen regimen significantly deteriorates during the first years after the construction of reservoirs, since significant amounts of dissolved oxygen (30 %) are spent for the oxidation of organic matter in the flooded areas [18]. The incidence of oxygen deficit have become more frequent not only in winter, but in summer as well, there is a growing concentration of organic and biogenic substances coming from the flooded floor, and the intensity of self-purification processes is reduced due to slow water exchange. Subsequently, significant problems arise due to the intensive development of phytoplankton (water "bloom") and overgrowth of shallow water areas of the reservoirs with higher vegetation. Much of pollutants are accumulated in the bottom sediments of the reservoirs due to the precipitation of suspended solids prompted by slow currents. However, the accumulation and disposal of various chemical substances in the bottom sediments should not be regarded as irreversible, as under certain conditions they may be a powerful source of secondary water pollution [1, 2].

The second group of factors includes industrial, municipal and agricultural wastewater and petroleum products, affecting mainly the physico-chemical and biological processes. The operation of urban water resources utilization systems are an important factor influencing the quantitative and qualitative indicators of water resources, whose impact will steadily grow. Describing the transformation of the chemical composition of surface water as a result of the impact of urban agglomerations, there is a good reason to consider the cumulative effect of point and non-point sources of pollution. The former includes wastewaters discharged through the waste outlet, and the second–urban and industrial runoffs. Total sewage runoff in modern cities is usually a mixture of municipal and industrial wastewater. Domestic effluents not containing industrial wastewater at all or their small volume, are found only in sewer networks of small settlements or small towns. Today about 24 % of sewage networks are in disrepair due to financial difficulties. As a result, on average 2 accidents per 1 km of network occur per year, which is significantly higher than the corresponding figure in Europe. Due to an increase of housing construction and unbalanced development of urban water resources utilization systems, there is a disparity between the capacities of water supply and sewage treatment plants, with the amount of wastewater in mid-1990s reaching 1,000,000 m^3/day. Moreover, most of the cities face the problem of so-called snowmelt-storm sewage, which are directly discharged into water bodies and pollute them with petroleum products, pesticides and other chemicals that are washed off from the city area. By the degree of chemical contamination storm-snowmelt runoffs often approximate the municipal ones. Industrial wastewater undergo certain regulation through reducing of production water intensity and introducing of reverse water supply systems. According to [4], there has been a significant reduction in the industrial water consumption in the city of Lutsk since 1970 owing to the commissioning of closed water recycling systems.

Table 5.1 presents substances most often encountered in the wastewater.

Acids, alkalis and hydrolysable heavy metal salts have some effect on surface water *pH*, depending on the buffer capacity of water carbonate system. Sulfates, chlorides and other salts of alkali and alkaline-earth elements enhance the solubility of slightly soluble compounds, and in most cases inhibit heavy metals’ complexing ability by affecting the activity coefficients of ions, which are part of relevant equations.

Growing concentrations of soluble organic compounds due to their income to water bodies with municipal and agricultural wastewater inevitably leads to a decrease in dissolved oxygen concentration.

Dissolved oxygen deficit as well as the formation of anaerobic zones in the near-bottom layers of water, low *pH* values at the bottom sediments and water

Table 5.1 Typical composition of wastewater [3, 9, 13]

Wastewater	Chemical composition
Industrial	Acids, alkalis, mineral salts, heavy metal compounds, nitrogen, ammonia, sulfates, phenols, flotation agents, pesticides, organic dyes, synthetic surfactants and other organic compounds
Domestic	Detergents, feces, organic compounds, compounds of biogenic elements (N, P, K)
Agricultural	Organic matter, biogenic elements (NH_4^+, PO_4^{3-}, K^+)
Petroleum and its products	Alkane, naphthenic, polycyclic aromatic hydrocarbons, phenols, sulfur and nitrogen compounds (mercaptans, thiophenes, pyridine homologs etc.)

interface are the major factors which intensify the income of substances from the sediments to the water column. Under these conditions, there is a significant increase in the concentration of ammonia nitrogen, phosphorus, phosphate, iron, mangan, aluminum and organic compounds in the water [6, 7, 16, 19–21]. The hazard of secondary water pollution due to bottom sediments is not only associated with the increase in the concentration of various chemicals in the water, but also with the possibility of substances with severe toxic and carcinogenic properties to enter the aquatic medium. Given the shortage of dissolved oxygen, there is practically no oxidation of ammonia nitrogen, Mn(II) and Fe(II), therefore these forms of nitrogen and metals are accumulated in the aquatic medium.

Petroleum products and synthetic surfactants have similar affects, forming in addition surface films and thereby preventing diffusion of oxygen from the atmosphere into the water column. Toxic heavy metals compounds inhibit the photosynthesis by water plants, thus reducing the accumulation of dissolved oxygen in the water. These processes lead to a decrease in redox potential (Eh) and create conditions for growing proportion of reduced elements with variable degrees of oxidation ($NO_3^- \rightarrow NH_4^+$, $MnO_2 \rightarrow Mn$(II), Fe(III) $\rightarrow Fe$(II), $CrO_4^{2-} \rightarrow Cr$(III), $SO_4^{2-} \rightarrow H_2S$ etc.)

Wastewater with high content of biogenic elements (NH_4^+, PO_4^{3-}) contribute to excessive biological productivity of surface water and appearance of such a negative phenomenon as water “bloom”.

Thus, the inflow of inadequately treated wastewater to surface water bodies lead to the intensification of those physico-chemical and biological processes, which mainly degrade the quality of surface water.

There are no reliable techniques today to analyze quantitative and qualitative changes of water resources due to urban activity; the analysis is mainly made by comparing the chemical composition of water in the cities’ upstream and downstream measuring sections.

For instance, estimations of the impact of urban areas on surface water quality in the Dnipro basin showed that the relative increase in runoff of chemicals downstream of the cities averaged 132 % for P_{min}, almost 80 % for ammonium and nitrite forms and 40 % for nitrate form of nitrogen [11].

Urban areas are the source of new types of natural water contamination with manmade substances–synthetic surfactants (SS), petroleum products, heavy metals. Contamination with SS is one of the most severe types of surface water pollution. The concentration of most common anionic SS in water bodies downstream of the cities varies within 0.1–0.3 mg/L, but may be considerably higher. Calculations showed that an average increase in toxic components runoff in the Dnipro River basin such as phenols and heavy metals (zinc, chromium (6+), copper) fluctuated within 10–30 %, concentrations of substances like SS and petroleum products were higher downstream of the cities. The ionic composition of water is least affected by urban activity.

According to hydro-chemical monitoring of the SES of Ukraine, the rivers Udy and Poltva respectively receiving wastewater from the cities of Kharkiv and Lviv, are considered to be the most polluted water bodies in Ukraine.

Rivers Udy, Lopan, Kharkiv Kharkiv is one of the largest cities in Ukraine, and in terms of population, which is about 2 million people, ranks No. 2. It is a powerful industrial center with high proportion of heavy industry. In the year 2000 only Instrument Engineering Plant named after T.H. Shevchenko discharged 0.01 million m^3 of wastewater. The rivers Kharkiv, Udy and Lopan are running through the urban agglomeration, the latter two being the main receivers of domestic and industrial wastewater of the city. The natural runoff rate of these rivers is negligible. For the Lopan River it was 208 and 68 million m^3 in 1994 and 1995 respectively, and for the Udy River—636 and 362 million m^3. This gives one ground to suggest a significant impact of Kharkiv City sewage water on the ecosystems of these rivers and further of the Siversky Donets River, to which they fall in. The impact of the cities can be exerted at several levels: direct discharge of wastewaters by enterprises (so-called local point pollution), aerosol precipitation and municipal non-point runoff.

There was high incidence of break-downs during the operation of waste-water treatment plants in the city of Kharkiv, the largest accident occurring in July 1995 after a heavy downpour. A transfer station pumping municipal wastewater to the treatment plants was flooded due to the technical failure of most of the pumps (out of 9 only 3 were operational). Sewage and storm water directly entered the rivers Udy, Lopan and Kharkiv. According to official data, the accident recovery lasted two weeks, but the restoration of the river ecosystems is a long-term process. To elucidate the situation, there was conducted a quantitative assessment of Kharkiv City's impact on the Udy and Lopan rivers in 1994 and 1995 (the period of maximum contamination) [15]. The measuring at the monitoring sections of the Udy River within the city of Kharkiv and 9 km downstream of the city showed that the average concentration of dissolved oxygen within the city during the study period was 9.5 mg/L (88 % saturation), and 9 km downstream of the city its content was twice as low and averaged only 4.5 mg/L (67 % saturation) (Fig. 5.3). These data show that dissolved oxygen is actively consumed in the river for the oxidation of organic matter.

During the accident at the treatment facilities in 1995 the oxygen content decreased significantly and fluctuated within 4–0 mg/L.

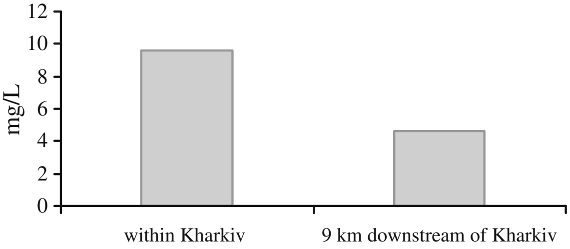


Fig. 5.3 Concentration of dissolved oxygen in the Udy River in the area of the city of Kharkiv, 1994–1995

The impact of the city on water mineralization was much less evident. Thus, the total salt content in the water in the survey area ranged from 570 mg/L within the city to 675 mg/L 9 km downstream of the city, which was 18 % higher in comparison with the upper section. Changes in water salinity level occurred mainly due to increased concentrations of soluble ions–sulfates and chlorides. The content of sulfate ions (SO_4^{2-}) increased from 95 mg/L within the city to 120 mg/L 9 km downstream of the city. The concentration of chloride ions (Cl^-) varied respectively from 45 to 75 mg/L.

The effect of municipal wastewater shows itself primarily in the growth in the receiving rivers of concentrations of biogenic components–nitrogen and phosphorus. High concentration of mineral forms of nitrogen were observed within the city (especially in the Lopan River) and in the monitoring section 9 km downstream of the city of Kharkiv (Fig. 5.4). This is primarily due to the disrepair of sewer systems of the city, which resulted in a constant inflow of untreated wastewater into the rivers. These water are characterized by a high content of organic compounds, biogenic elements and other pollutants.

Among the various inorganic forms of nitrogen it is ammonium nitrogen which prevails in the water of the rivers of interest. This indicates insufficient nitrification process, which means that the river has received the so-called fresh domestic sewage. An average annual concentration of NH_4^+ is elevated both within the city and downstream, and is respectively 1.4 and 6.5 mg N/L. As can be seen, the content of NH_4^+ in the secton 9 km downstream of the city is nearly 5 times higher than within the city.

Considering the dynamics of ammonia nitrogen concentrations in the rivers running within Kharkiv metropolitan area, one can see that the concentration of NH_4^+ within the city is often higher than in the section downstream of the city (Fig. 5.5). This is due to contingency situations arising in the sewer network and the

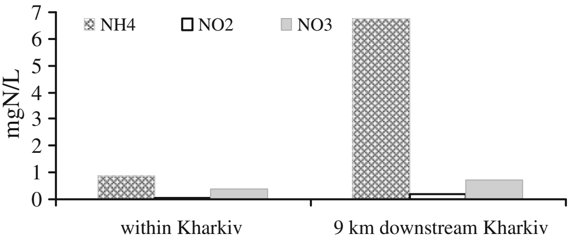


Fig. 5.4 Concentration of inorganic forms of nitrogen in the Udy River in the area of the city of Kharkiv, 1994–1995

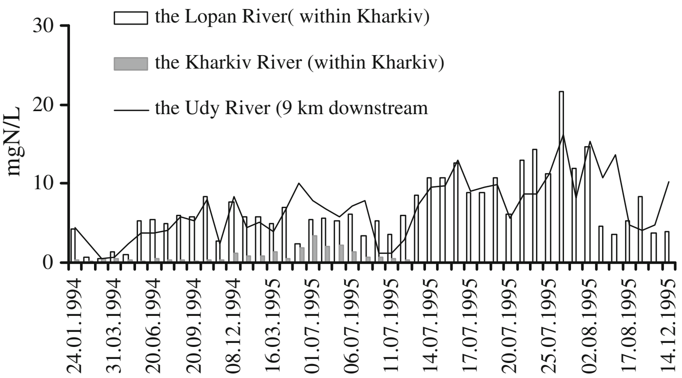


Fig. 5.5 Concentration of ammonia nitrogen in the rivers of Kharkiv metropolitan area, 1994–1995

sudden discharge of wastewater. Thus, the concentration of ammonia nitrogen in the surface water within the city at the time of the accident in 1995 reached nearly 20 mg N/L.

The dynamics of NH_4^+ in the Udy River in the section 9 km downstream of the city of Kharkiv indicate, that after the accident the self-cleaning ability of the river was only restored in 1998.

Similar distribution is characteristic of other forms of inorganic nitrogen–nitrite and nitrate ones. The average concentration of nitrite nitrogen (NO_2^-) varied from 0.04 mg N/L within the city to 0.2 mg N/L in the monitoring section 9 km downstream of the city. The highest annual average concentration of nitrate nitrogen (NO_3^-) in the water was observed in the section downstream of the city (0.7 mg N/L), and within the city its concentration was 0.38 mg N/L.

Elevated concentrations of biogenic elements in the Udy River in their turn adversely affect water quality in the Siversky Donets River. While upstream of the Udy River confluence average concentration of ammonia nitrogen in the Siversky Donets River in 1995 was 0.7 mg N/L, its value downstream of the Udy River confluence more than doubled. An increase in nitrite nitrogen concentration to 0.1 mg N/L and nitrate–up to 0.65 mg N/L was also observed in the Siversky Donets River downstream of the Udy River confluence.

A significant increase in the concentration of inorganic forms of phosphorus and silicon was also noted in the Udy River downstream of Kharkiv City, compared with their concentration in the river within the city. Annual average values of concentrations of these components in 1995 reached 0.9 mg P/L and 14.4 mg Si/L respectively.

The concentrations of dissolved organic substances in the rivers flowing within the city of Kharkiv are given in Table 5.2, showing that the degree of their contamination by organic substances is also high, which indicates a massive wastewater inflow.

Table 5.2 Content of dissolved organic matter in the rivers of Kharkiv metropolitan area in 1995[a]

River	COD, mg O/L	BOD$_5$, mg O_2/L
Lopan	13.2–09.0 42.3	1.17–3.4 7.46
Kharkiv	10.1–6.9 38.4	1.23–0.3 4.5
Udy	10.1–00.0 43.1	1.43–5.4 7.34

[a] Above the line—fluctuation limits, below the line—annual average values

No significant changes in the concentration of such man-made factors as heavy metals and phenols were registered in the sections upstream and downstream of the city of Kharkiv, indicating the predominance of household sewage in the contaminated water.

There is an abundance of vehicles in big cities, contributing to additional influx of petroleum products due to surface run-off. However, the analysis of average concentrations of petroleum products in the investigated cross-sections indicates a relatively minor impact of Kharkiv City. The average concentration of petroleum products ranged from 0.28 mg/L within the city to 0.32 mg/L downstream of the city.

Comparative analysis of water chemistry in the Udy River in the sections upstream and downstream of the city of Kharkiv for a long period (from 1990 to 2004) shows that the city exerts a significant impact on the Udy River's ecosystem, but it manifests itself differently depending on chemical components [14]. The slightest was the city's impact on the concentration of dissolved oxygen, water salinity, concentration of chromium, COD and surfactants. Mean changes of these components in relative units in the section downstream of the city did not exceed 50 %. More substantive (50–100 %) were changes in concentrations of sulphate ions and copper, amounting respectively to 79 and 58 %. Maximum water pollution of the Udy River is caused by biogenic elements and organic matter, which are major components of municipal wastewater. The relative average increase of this group of components in order of descending is as follows: NO_2^- (1030 %) > NO_3^- (492 %) > N_{miner} (438 %) > NH_4^+ (397 %) > phosphate ions (261 %) > total phosphorus (159 %) > Cl^-(144 %) > petroleum products (126 %) > BOD$_5$ (119 %).

Thus, the city of Kharkiv has a significant impact on the ecosystems of the rivers Udy, Kharkiv and Lopan, and subsequently on the Siversky Donets River, mainly due to income of untreated and inadequately treated municipal wastewater.

The results of long-term research also show a significant effect of the city of Lviv on the chemical composition and quality of water in the Western Bug River. Lviv sewage enters the Poltva River which joins the Western Bug in the city of Busk. Water influx from the Poltva River leads to deterioration of the chemical composition of water within a considerable stretch of the Western Bug River (Figs. 5.6, 5.7) [17].

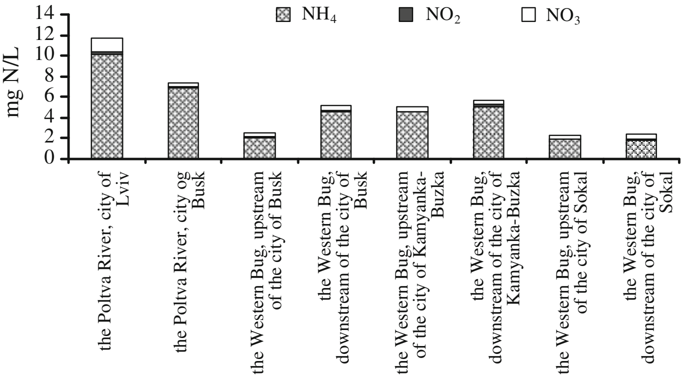


Fig. 5.6 Changes in average concentrations of inorganic forms of nitrogen in the Western Bug along its length for 1989–2002

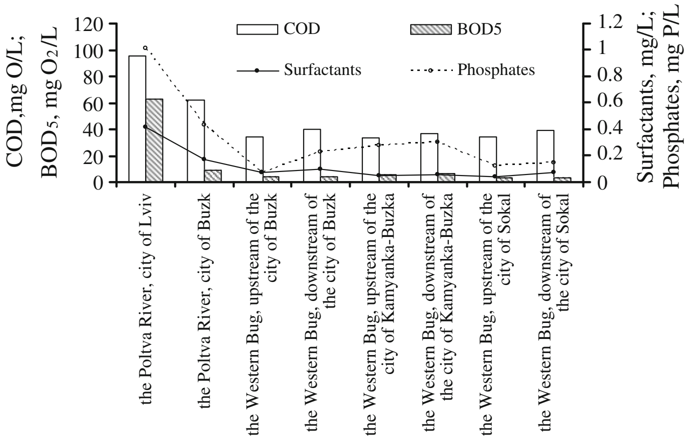


Fig. 5.7 Changes in average concentrations of organic substances and phosphates in the Western Bug along its length for 1989–2002

In fact, after the confluence of the Poltva River with the Western Bug water chemistry of the latter is restored only in the section downstream of the city of Kamyanka-Buzka, and as per certain indicators—further downstream in the section of the city of Sokal.

Assessment of the relative impact of the Poltva River, which is a receiver of sewage from the city of Lviv, on the chemical composition of the Western Bug River at their confluence (the city of Busk) shows that this tributary exerts a significant influence on the chemical composition of water in the Western Bug, especially in its upper portion. The relative share of water runoff of the Poltva River in the Western Bug runoff is 58 % in the Kamenka-Buzka section, and 23 % in the conventional hydrologic section, closing the Ukrainian part of the basin. [5] At the

Table 5.3 Share of biogenic elements runoff of the Poltva River (city of Busk) in the runoff of these substances in the Western Bug River (city of Kamyanka-Buzka) and in the conventional hydrologic section, % [5]

River, Station	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	N_{total}	PO_4^{3-}	Si
Western Bug River, city of Kamyanka-Buzka	70	66	51	68	80	67
Western Bug River, conventional hydrologic section	47	28	23	44	71	30

same time, the share of ionic runoff of the Poltva River reaches respectively 66 and 28 %. As per total nitrogen content, this parameter increases and is respectively 68 and 44 %, and for inorganic phosphorus it increases to 80 and 71 % (Table 5.3).

It also should be noted that the anthropogenic factors do not always lead to negative consequences. For example, construction of dams, through which water of small rivers is discharged, contributes to the saturation of water with dissolved oxygen improving its quality; slowing the flow rate of water in reservoirs leads to sedimentation of suspended solids along with toxic substances adsorbed on them, which also has a positive effect on water quality, and so on. Therefore, given the integrated effect of anthropogenic factors one should determine the top-priority ones and make appropriate conclusions about their impact on surface water quality.

The influence of each factor is determined on the basis of quantitative transfer of agents in the systems “solid phase—water”, “atmospheric air—water”, “water—water”, “hydrobionts—water.” These interactions are affected through certain deterministic processes, whose speed and finite concentration of substances in the water are affected by quite a number of factors.

Parameterization of these processes makes it possible to model water chemistry, to study patterns of its development and effects in different climatic conditions. Of course, taking into account the whole body of influences is an extremely difficult task, fulfilling of which at the present level of research is virtually impossible. Depending on the purpose of research, it is advisable to determine the main processes involved in the formation of chemical composition of natural surface water, and figure on them in modeling.

References

1. Denisova AI (1979) Formirovanie gidrokhemicheskogo rezhima vodokhranilisch Dnepra i metody ego prognozirovaniya (The Dnieper reservoir hydrochemical regime formation and its forecasting methods). Nauk dumka, Kyiv
2. Denisova AI, Nahshina EP, Novikov BI et al (1987) Donnye otlozheniya vodokhranilisch i ikh vliyanie na kachestvo vody (Reservoir bottom sediments and their influence on water quality). Nauk dumka, Kyiv

3. Denisova AI, Timchenko VM, Nahshina EP et al (1989) Gidrologiya i gidrokhimiya Dnepra i ego vodokhranilisch (Hydrology and hydrochemistry of the Dnieper and its reservoirs). Nauk dumka, Kyiv
4. Dzigirey VS, Storozhuk VM, Yatsuk RA (2000) Osnovy ekologii ta okhorona navkolyshnyogo prirodnogo seredovyscha (Ecology fundamentals and environment protection (Ecology and environment protection)). Afisha, Lviv
5. Fesyuk VO (2001) Vodo-gospodarsky kompleks Lutska—model suchasnogo stanu vodokorystuvannya mist i yogo vplyvu na otochuyuche seredovysche (Water resources utilization system of Lutsk—a modern state model of a city water use and its influence on environment. Hydrology, hydrochemistry and hydroecology, vol. 2. Nika-Centre, Kyiv pp. 535–543
6. Linnik PM, Morozova AO (2006) Desorbtsiya spoluk azotu, fosforu i zaliza z donnykh vidkladiv za dii riznykh chynnykiv (Nitrogen, phosphorus and iron compound desorbtion from bottom sediments due to various factors). Hydrology, hydrochemistry and hydroecology, vol. 10, pp. 73–81
7. Linnik PM, Zubenko IB (2000) Role of botton sediments in the secondary pollution of aquatic environments by heavy-metal compounds. Lakes Reserv Res Manag 5(1):11–21
8. Linnik PN, Vasilchuk TA, Zubenko IB (1999) Rol donnykh otlozheny vo vtorichnom zagryaznenii vodnoy sredy vodokhranilisch organicheskimi veschestvami i tyazhyolymi metallami (Role of bottom sediments in the secondary pollution of reservoir aquatic environment by organic substances and heavy metals. Chem Water Technol 21(1):30–46
9. Linnik PN, Zhuravleva LA, Samoylenko VN et al (1993) Vliyanie rezhima ekspluatatsii na kachestvo vody dneprovskykh vodokhranilisch i ustevoy oblasti Dnepra (Operation mode influence on the water quality of the Dnieper reservoirs and the Dnieper mouth area). Hydrobiol J 29(1):86–98
10. Linnik PN, Zubko AV, Zubenko IB et al (2009) Vliyanie pH na migratsiyu razlichnykh form metallov v sisteme “donnye otlozheniya—voda” v eksperimentalnykh usloviyakh (The influence of pH on the migration of different metal forms in the “bottom sediments—water” system in experimental conditions). Hydrobiol J 45(1):99–109
11. Lozanova IN, Orlov DS, Sadovskaya LK (1998) Ekologiya i okhrana biosfery pri khimicheskom zagryaznenii (Ecology and protection of biosphere under chemical pollution). MGU Press, Moscow
12. Natsionalna dopovid pro stan navkolishnyogo prirodnogo seredovyscha v Ukrayini u 2003 r (2006) (The national report on the state of environment in Ukraine in 2003). pub of Raevsky, Kyiv. ISBN: 966-7016-25-0
13. Osadchy VI, Osadcha NM, Mostova NM (2002) Vplyv urbanizovanykh territory na formuvannya khimichnogo skladu poverkhnevykh vod baseynu Dnipra (The influence of urbanized territories on the formation of the chemical composition of the Dnieper basin surface water), pp. 242–261. The collection of sci. works of UkrNDGMI, vol. 250
14. Statystychny zbirnyk za 2004r (2005) (Statistical collection of papers for 2004). [Electronic resource]: the State Committee of Statistics. Information publishing center of the State Committee of Statistics of Ukraine, Kyiv. Data access mode: http://ukrstat.org/uk/druk/katalog/katu/publlu.htm
15. Suharev SM, Chundak SYu, Suhareva OYu (2004) Tekhnologiya ta okhorona navkolyshnyogo seredovyscha (Technology and environment protection). Noviy Svit -2000, Lvov
16. Uhan OO, Osadchy VI (2010) Zakonomirnosti formuvannya khimichnogo skladu poverkhnevykh vod baseynu Siverskogo Dintsa (On regularity of the Severski Donets basin surface water chemical composition formation). Hydrology hydrochemistry hydroecology, vol. 18, pp. 166–179
17. Uhan OO, Osadchy VI (2011) Vplyv prirodnykh i antropogennykh faktoriv na formuvannya rezhimu biogennykh elementiv u poverkhnevykh vodakh baseynu Siverskogo Dintsa (The influence of natural and anthropogenic factors on nutrient regime formation in the Severski Donets basin surface water, pp. 163–178. The collection of sci. works of UkrNDGMI, vol. 261

18. Vasilchuk TO, Osipenko VP, Evtuh TV (2005) Donni vidklady yak dzherelo zabrudnennya vodnogo seredovischa organichnymy rechovynamy (Bottom sediments as a source of water environment organic substance pollution). Hydrology, hydrochemistry and hydroecology. Obriy, Kyiv 8:36–40
19. Zabokritska MP, Osadchy VI (2003) Kharakteristika antropogennogo navantazhennya v baseyni r. Zakhidny Bug (Characteristics of anthropogenic load in the Western Bug river basin). Hydrology, hydrochemistry and hydroecology, vol. 5, pp. 218–225
20. Zabokritska MR, Hilchevsky VK, Manchenko AP (2006) Gidroekologichny stan baseynu Zakhidnogo Bugu na territorii Ukrayiny (Hydroecological state of the Western Bug river basin on Ukranian territory). Nika Centre, Kyiv
21. Zhuravleva LA, Linnik PN (1989) Faktory formirovaniya ekstremalnykh situatsy v gidrokhimicheskom rezhime Dneprovsko-Bugskogo limana (Forming factors of extreme situations in the hydrochemical regime of the Dnieper-Bug liman). Hydrobiol J 25(3):69–73

Addendum

Table 1 Ionic activity coefficients of inorganic compounds most common in natural waters at different values of ionic strength

Ions	Activity coefficients at the ionic strength μ							
	0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
NH_4^+, Ag^+	0.975	0.964	0.945	0.924	0.898	0.850	0.800	0.750
K^+, Cl^-, NO_2^-, NO_3^-	0.975	0.964	0.945	0.925	0.899	0.850	0.805	0.755
OH^-, F^-, HS^-	0.975	0.964	0.946	0.926	0.900	0.855	0.810	0.760
Na^+, $H_2PO_4^-$	0.975	0.964	0.947	0.928	0.902	0.860	0.820	0.775
SO_4^{2-}, CrO_4^{2-} HPO_4^{2-}	0.903	0.867	0.803	0.740	0.660	0.545	0.445	0.355
Pb^{2+}, CO_3^{2-}, MoO_4^{2-}	0.903	0.868	0.805	0.742	0.665	0.550	0.455	0.370
Ba^{2+}, Cd^{2+}, Hg^{2+}	0.903	0.868	0.805	0.744	0.670	0.555	0.465	0.380
Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}	0.905	0.870	0.809	0.749	0.675	0.570	0.485	0.405
Mg^{2+}	0.906	0.872	0.813	0.755	0.690	0.595	0.520	0.405
PO_4^{3-}	0.796	0.725	0.612	0.505	0.395	0.250	0.160	0.095
Fe^{3+}, Al^{3+}, Cr^{3+}	0.802	0.738	0.632	0.540	0.445	0.325	0.245	0.180

Table 2 H^+ ions activity coefficients at different ionic strength values

Ionic strength, μ	0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
Activity coefficient, f_H+	0.975	0.967	0.950	0.933	0.914	0.880	0.860	0.830
$-\lg f_H+ = p\ f_H+$	0.011	0.015	0.022	0.030	0.039	0.056	0.066	0.081

V. Osadchyy et al., *Processes Determining Surface Water Chemistry*,
DOI 10.1007/978-3-319-42159-9

Table 3 HCO_3^- ions activity coefficients at different ionic strength values

Ionic strength, μ	f	Ionic strength, μ	f	Ionic strength, μ	f
0.001	0.97	0.008	0.91	0.035	0.83
0.002	0.96	0.009	0.91	0.040	0.83
0.003	0.95	0.010	0.90	0.045	0.82
0.004	0.93	0.015	0.88	0.050	0.81
0.005	0.93	0.020	0.87	0.060	0.80
0.006	0.92	0.025	0.85	0.080	0.79
0.007	0.92	0.030	0.84	0.100	0.78

Table 4 Ionic activity coefficients of some organic compounds most common in natural waters at different of ionic strength values

Ions	Activity coefficients at the ionic strength μ							
	0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
$HCOO^-$	0.975	0.964	0.946	0.926	0.900	0.855	0.810	0.760
CH_3COO^-, $NH_2CH_2COO^-$	0.975	0.964	0.947	0.928	0.902	0.860	0.820	0.775
$C_2O_4^{2-}$	0.903	0.867	0.804	0.741	0.662	0.550	0.450	0.360
$(CHOHCOO)_2^{2-}$, tartrate, $Tart^{2-}$	0.903	0.868	0.805	0.744	0.670	0.555	0.465	0.380
$C_6H_5O_7^{3-}$, citrate, Cit^{3-}	0.769	0.727	0.616	0.510	0.405	0.270	0.180	0.115
$C_6H_6O_7^{2-}$, hydrogen citrate, $HCit^{2-}$	0.903	0.867	0.804	0.741	0.662	0.550	0.450	0.360
$C_6H_7O_7^-$, dihydrogen citrate, H_2Cit^-	0.975	0.964	0.946	0.926	0.900	0.855	0.810	0.760
FA^{2-} fulvic acids and HA^{2-} humic acids (doubly charged anions' average activity coefficient)	0.903	0.867	0.804	0.742	0.665	0.552	0.455	0.370

Table 5 Ionic product of water at different temperatures $K_{H_2O} = a_{H^+}\ a_{OH^-} = [H^+]\ [OH^-] f_{H^+} f_{OH^-}$; $a_{H^+} = a_{OH^-} = \sqrt{K_{H_2O}}$

t °C	K_{H_2O}, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}	t °C	K_{H_2O}, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}
0	0.11	0.33	30	1.48	1.22
5	0.17	0.41	31	1.58	1.26
10	0.30	0.55	32	1.70	1.30
15	0.46	0.68	33	1.82	1.35
16	0.50	0.71	34	1.95	1.39
17	0.55	0.74	35	2.09	1.45
18	0.60	0.77	36	2.24	1.49
19	0.65	0.81	37	2.40	1.55
20	0.69	0.83	38	2.57	1.60
21	0.76	0.87	39	2.75	1.66
22	0.81	0.90	40	2.95	1.72

(continued)

Table 5 (continued)

t °C	K_{H_2O}, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}	t °C	K_{H_2O}, n10^{-14}	$\sqrt{K_{H_2O}}$, n10^{-7}
23	0.87	0.93	50	5.50	2.34
24	0.93	0.96	60	9.55	3.09
25	1.00	1.00	70	15.8	3.98
26	1.10	1.05	80	25.1	5.01
27	1.17	1.08	90	38.0	6.16
28	1.29	1.14	100	55.0	7.41
29	1.38	1.17			

Table 6 Solubility product of slightly soluble compounds (t = 25 °C)[a]

Compound formula	*SP*	Compound formula	*SP*
$Al(OH)_3$ $[Al^{3+}, 3OH^-]$	1×10^{-32}	$[Fe(OH)_2^+, OH^-]$	1×10^{-17}
$[AlOH^{2+}, 2OH^-]$	1×10^{-23}	$FePO^4$	1.3×10^{-22}
$[Al(OH)_2^+, 3OH^-]$	1.6×10^{-13}	FeS	5×10^{-18}
$AlPO_4$	5.8×10^{-19}	$Hg(OH)_2$ $[Hg^{2+}, 2OH^-]$	3.0×10^{-26}
$CaCO_3$[a]	3.8×10^{-9}	$[HgOH^+, OH^-]$	6×10^{-16}
CaF_2	4.0×10^{-11}	HgS, red	4×10^{-53}
$Ca(HPO^4)$	2.7×10^{-7}	$Mg(OH)_2$ $[Mg^{2+}, 2OH^-]$	7.1×10^{-12}
$CaSO_4$	2.5×10^{-5}	$[MgOH^+, OH^-]$	2.7×10^{-9}
$Cd(OH)_2$ $[Cd^{2+}, 2OH^-]$	2.2×10^{-14}	$MgCO_3$	2.1×10^{-5}
$[CdOH^+, OH^-]$	2.6×10^{-8}	$MnCO_3$	1.8×10^{-11}
$CdCO_3$	1.0×10^{-12}	$Mn(OH)_2$ $[Mn^{2+}, 2OH^-]$	1.9×10^{-13}
CdS	1.6×10^{-28}	$[MnOH^+, OH^-]$	1.5×10^{-9}
$CoCo_3$	1.05×10^{-10}	MnS	2.5×10^{-13}
$Co(OH)_2$ $[Co^{2+}, 2OH^-]$	1.6×10^{-15}	$NiCO_3$	1.3×10^{-7}
$[CoOH^+, OH^-]$	4×10^{-11}	$Ni(OH)_2$ $[Ni^{2+}, 2OH^-]$	2.0×10^{-15}
CoS, β	2×10^{-25}	$[NiOH^+, OH^-]$	1.7×10^{-10}
$Cr(OH)_3$ $[Cr^{3+}, 3OH^-]$	6.3×10^{-31}	NiS, γ	2.0×10^{-26}
$[Cr(OH)^{2+}, 2OH^-]$	7.9×10^{-21}	$PbCO_3$	7.5×10^{-14}
$[Cr(OH)_2^+, OH^-]$	4×10^{-13}	$Pb(OH)_2$ $[Pb^{2+}, 2OH^-]$	7.9×10^{-16}
$CrPO_4$	1.0×10^{-17}	$[PbOH^+, OH^-]$	6.3×10^{-9}
$CuCO_3$	2.5×10^{-10}	$Pb_3(PO_4)_2$	7.9×10^{-43}
$Cu(OH)_2$ $[Cu^{2+}, 2OH^-]$	2.2×10^{-20}	PbS	2.5×10^{-27}
$[CuOH^+, OH^-]$	2.2×10^{-13}	$PbSO_4$	1.6×10^{-8}
CuS	6.3×10^{-36}	$ZnCO_3$	1.5×10^{-11}
$FeCO_3$	3.5×10^{-11}	$Zn(OH)_2$ $[Zn^{2+}, 2OH^-]$	1.2×10^{-17}
$Fe(OH)_2$ $[Fe^{2+}, 2OH^-]$	8×10^{-16}	$[ZnOH^+, OH^-]$	3.0×10^{-13}
$[FeOH^+, OH^-]$	3×10^{-10}	ZnS	1.6×10^{-24}
$Fe(OH)_3$ $[Fe^{3+}, 3OH^-]$	6.3×10^{-38}		
$[FeOH^{2+}, 2OH^-]$	5×10^{-27}		

[a] Effect of water temperature on the solubility product of $CaCO_3$, see Table 12

Table 7 Standard redox potentials E_0 of some systems characteristic of natural waters (t = 25 °C)

Oxidant	+ne	Reductant	E_0, v
$CrO_4^{2-} + 4H_2O$	+3e	$\downarrow Cr(OH)_3 + 5OH^-$	–0.13
$CrO_4^{2-} + 8H^+$	+3e	$Cr^{3+} + 4H_2O$	+1.48
Cu^{2+}	+e	Cu^+	+0.159
$\downarrow MnO_2 + 4H^+$	+2e	$Mn^{2+} + 2H_2O$	+1.23
Fe^{3+}	+e	Fe^{2+}	+0.771
$\downarrow Fe(OH)_3$	+e	$\downarrow Fe(OH)_2 + OH^-$	–0.56
$NO_3^- + H_2O$	+2e	$NO_2^- + 2OH^-$	+0.01
$NO_2^- + 6H_2O$	+6e	$NH_4OH + 7OH^-$	–0.15
$NO_3^- + 10H^+$	+8e	$NH_4^+ + 3H_2O$	+0.87
$NO_3^- + 7H_2O$	+8e	$NH_4OH + 9OH^-$	–0.12
$SO_4^{2-} + 10H^+$	+8e	$H_2S\uparrow + 4H_2O$	+0.31

Table 8 Dissociation constants of acids most common in natural waters (t = 25 °C)[a]

Name		Formula	Ka	pKa
Amber	K_1	$HOOCCH_2CH_2COOH$	1.6×10^{-5}	4.80
	K_2		2.3×10^{-6}	5.64
Valeric (com.)		$CH_3(CH_2)_3COOH$	1.4×10^{-5}	4.85
Valeric (iso)		$(CH_3)_2CHCH_2COOH$	1.7×10^{-5}	4.77
Tartaric (H_2Tart)	K_1	$HOOCCH(OH)_xH(OH)$	1.3×10^{-3}	2.89
	K_2		3.0×10^{-5}	4.52
Carbonic	K_1	$CO_2+H_2O(H_2CO_3)$	4.3×10^{-7}	6.37
	K_2		4.7×10^{-11}	10.33
Glycolic		$CH_2(OH)COOH$	1.5×10^{-4}	3.82
Glutaric	K_1	$HOOC(CH_2)_3COOH$	4.6×10^{-5}	4.34
	K_2		5.4×10^{-6}	5.27
Gluconic		$CH_2OH(CHOH)_4COOH$	1.4×10^{-4}	3.85
Citric (H_3Cit)	K_1	$HOOCCH_2C(OH)\,(COOH)CH_2COOH$	7.4×10^{-4}	3.13
	K_2		2.2×10^{-5}	4.66
	K_3		4.0×10^{-7}	6.40
Malonic	K_1	$HOOCCH_2COOH$	4.2×10^{-2}	1.38
	K_2		2.1×10^{-6}	5.68
Butanoic (com.)		$CH_3CH_2CH_2COOH$	1.5×10^{-5}	4.82
Butanoic (iso)		$(CH_3)_2CHCOOH$	1.4×10^{-5}	4.85
Lactic		$CH_3CH(OH)COOH$	1.5×10^{-4}	3.82
Formic		$HCOOH$	1.8×10^{-4}	3.74
Acetic		CH_3COOH	1.74×10^{-5}	4.76
Propionic		CH_3CH_2COOH	1.35×10^{-5}	4.87

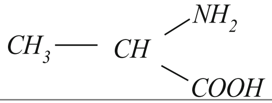
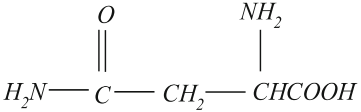
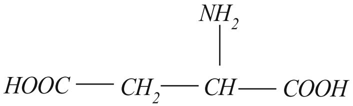
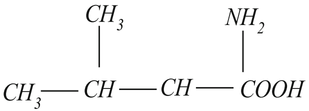
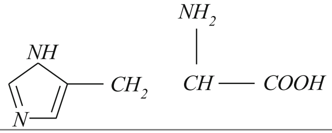
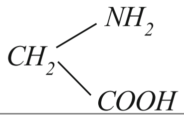
(continued)

Table 8 (continued)

Name		Formula	Ka	pKa
Hydrosulphuric	K_1	H_2S	1.0×10^{-7}	7.00
	K_2		2.5×10^{-13}	12.60
Silicic (orto)	K_1	H_4SiO_4	1.3×10^{-10}	9.9
	K_2		1.6×10^{-12}	11.8
	K_3		2.0×10^{-14}	13.7
Carbolic		C_6H_5OH	1.0×10^{-10}	10.0
Phosphorus (orto)	K_1	H_3PO_4	7.1×10^{-3}	2.15
	K_2		6.2×10^{-8}	7.21
	K_3		5.0×10^{-13}	12.3
Fluorhydric		HF	6.2×10^{-4}	3.21
Chromic	K_1	H_2CrO_4	1.6×10^{-1}	0.80
	K_2		3.2×10^{-7}	6.50
Oxalic	K_1	$H_2C_2O_4$	5.6×10^{-2}	1.25
	K_2		5.4×10^{-5}	4.27
Apple	K_1	$HOOCCH(OH)CH_2COOH$	3.5×10^{-4}	3.46
	K_2		8.9×10^{-6}	5.05

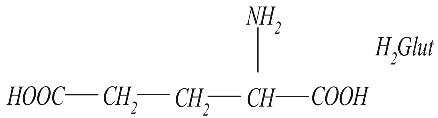
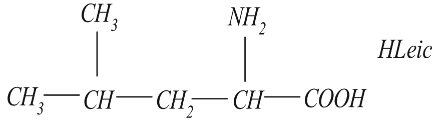
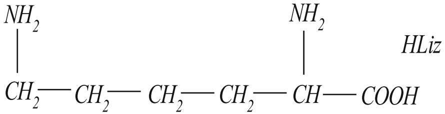
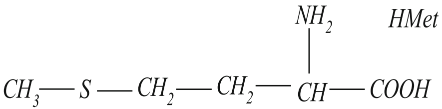
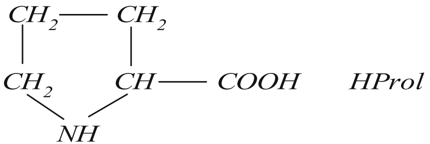
Humic and fulvic acids dissociation constants see Table 11

Table 9 Amino acids dissociation constants

Назва	Формула та позначення з урахуванням іонів H^+ карбоксильних груп	K_a	pK_a
α⁻Alanine	K_1 K_N  HAl	4.57×10^{-3} 1.35×10^{-10}	2.34 9.87
Asparagine	K_1 K_N  $H_2N-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{NH_2}{\vert}}{CHCOOH}$ HAsp	5.96×10^{-3} 9.46×10^{-10}	2.22 9.02
Asparagine acid	K_1 K_2 K_N  $HOOC-CH_2-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ H_2Asp	8.51×10^{-3} 7.08×10^{-5} 4.27×10^{-11}	2.07 4.15 10.37
Valine	K_1 K_N  $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ HVal	4.79×10^{-3} 2.40×10^{-10}	2.32 9.20
Histidine	K_{N1} K_{N2}  HGis	1.25×10^{-2} 6.10×10^{-7} 3.74×10^{-10}	1.90 6.21 9.43
Glycine (aminoacetic acid)	K_1 K_N  HGlic	4.47×10^{-3} 1.66×10^{-10}	2.35 9.78

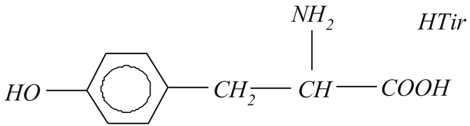
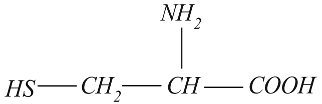
(continued)

Table 9 (continued)

Назва	Формула та позначення з урахуванням іонів H^+ карбоксильних груп	K_a	pK_a
Glutaminic acid	K_1 K_2 K_N $HOOC-CH_2-CH_2-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ H_2Glut	3.16×10^{-3} 2.06×10^{-5} 4.68×10^{-11}	2.50 4.69 10.33
Leucine	K_1 K_N $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ $HLeic$	2.57×10^{-3} 7.66×10^{-11}	2.59 10.12
Lysins	K_1 K_{N1} K_{N2} $\overset{\overset{NH_2}{\vert}}{CH_2}-CH_2-CH_2-CH_2-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ $HLiz$	5.43×10^{-3} 4.43×10^{-10} 1.03×10^{-11}	2.26 9.35 10.99
Methionine	K_1 K_N $CH_3-S-CH_2-CH_2-\overset{\overset{NH_2}{\vert}}{CH}-COOH$ $HMet$	5.19×10^{-3} 3.06×10^{-10}	2.28 9.51
Proline	K_1 K_N 	6.02×10^{-3} 1.30×10^{-11}	2.22 10.89

(continued)

Table 9 (continued)

Назва	Формула та позначення з урахуванням іонів H^+ карбоксильних груп	K_a	pK_a
Tyrosine	K_1  $HTir$	5.28×10^{-3}	2.28
	$K_{(HO-)}$	4.26×10^{-10}	9.37
	K_N	2.22×10^{-11}	10.65
Cysteine	K_1  $HS—CH_2—\overset{NH_2}{\overset{\vert}{CH}}—COOH$ H_2Cis	9.02×10^{-3}	2.04
	$K_{2(HS-)}$	2.93×10^{-9}	8.53
	K_N	2.83×10^{-11}	10.55

K_1, K_2—carboxy group ionization constants; K_N—amine group proton ionization constant
Almost exclusively carboxy groups dissociate in the natural waters ($pH \leq 10$)

Table 10 Dissociation constants of bases most common in natural waters (t = 25 °C)

Name	Formula	K_b	pK_b
Ammonium hydroxide	$NH_3 + H_2O$ (NH_4OH)		
	25 °C	1.76×10^{-5}	4.75
	15 °C	3.65×10^{-5}	4.44
	5 °C	7.80×10^{-5}	4.11
Aniline	$C_6H_5NH_2 + H_2O$ $(C_6H_5NH_3OH)$	4.3×10^{-10}	9.37
Hydroxylamine	$NH_2OH + H_2O$ $(OHNH_3OH)$	8.9×10^{-9}	8.05
Diethylamine	$(C_2H_5)_2NH + H_2O$ $[(C_2H_5)_2NH_3OH]$	1.2×10^{-3}	2.92
Dimethylamine	$(CH_3)_2NH + H_2O$ $[(CH_3)_2NH_3OH]$	5.4×10^{-4}	3.27
Diphenylamine	$(C_6H_5)_2NH + H_2O$ $[(C_6H_5)_2NH_3OH]$	6.2×10^{-14}	13.21
Ethanolamine	$H_2NCH_2CH_2OH + H_2O$ $(HOH_3NCH_2CH_2OH)$	1.8×10^{-5}	4.74
Ethylamine	$CH_3CH_2NH_2 + H_2O$ $(CH_3CH_2NH_3OH)$	6.5×10^{-4}	3.19
Methylamine	$CH_3NH_2 + H_2O$ (CH_3NH_3OH)	4.6×10^{-3}	2.34
Urea	$CO(NH_2)_2 + H_2O$ $(CONH_2NH_3OH)$	1.5×10^{-14}	13.82
Trimethylamine	$(CH_3)_3N + H_2O$ $[(CH_3)_3NHOH]$	6.5×10^{-5}	4.19

Table 11 Humic and fulvic acid dissociation constants

Acids	Counter ion	Carboxyl groups				Phenolic hydroxyl		References
		$Ka_{(1)}$	$pKa_{(1)}$	$Ka_{(2)}$	$pKa_{(2)}$	Ka	pKa	
Humic acids (peat extract)	Li+	–	–	1.58×10^{-5}	4.80	5.62×10^{-10}	9.25	[1]
	Na+	–	–	1.12×10^{-5}	4.95	3.39×10^{-10}	9.47	
	K+	–	–	9.55×10^{-6}	5.02	5.75×10^{-10}	9.24	
Fulvic acids, molecular mass 300 Da (isolated from the waters of the Moscow River at different times)	Na+ K+	2.5×10^{-3}	2.62	4×10^{-3}–6×10^{-6}	4.4–5.2	2×10^{9}–1×10^{9}	8.7–9.0	[3]
Fulvic acids, eq. weight 90–160 Da	Na+	2×10^{-3}	2.7	5×10^{-5}	4.3	–	–	[4]
Fulvic acids	Na+	1.6×10^{-3}–4×10^{-4}	2.8–3.4	1.3×10^{-5}–7.9×10^{-6}	4.9–5.1	–	–	[2]

1. Lishtvan II., Kudritskiy NN, Tretinnik VYu (1976) Phisiko-khimicheskaya mekhanika humusovykh veshchestv (Physico-chemical mechanics of humic substances). Nauka i technika, Minsk
2. Reuter JH, Perdue EM (1977) Interaction of metals with organic matter. Geochim et cosmochim acta 41(2) : 325–334
3. Varshal GM, Bugaevsky AA, Kholin YuYu. (1990) Modelirovanie ravnovesiy v rastvorakh fulvokislot prirodnykh vod (Modelling of equilibriums in fulvic acid solutions of natural waters). J Water Chem. Technology 12 (11) : 979–986
4. Varshal GM, Koscheeva IYa, Sirotkina IS Velyuhanova TK, Intskirveli LL et al. (1979) Izuchenie organicheskikh veschestv poverkhnostnykh vod i ikh vzaimodeystviya s ionamy metallov (The study of surface water organic substances and their interaction with metal ions). Geochemistry 4 : 598–607

Table 12 Carbonic acid dissociation constants and $CaCO_3$ solubility product depending on water temperature

Water t °C	$K_1 \times 10^6$	$K_2 \times 10^{10}$	$SP \times 10^9$	Water t °C	$K_1 \times 10^6$	$K_2 \times 10^{10}$	$SP \times 10^9$
0	0.26	0.23	5.50	16	0.38	0.38	4.44
2	0.28	0.25	5.37	18	0.39	0.40	4.31
4	0.29	0.27	5.24	20	0.40	0.42	4.17
5	0.30	0.28	5.18	22	0.42	0.44	4.04
6	0.31	0.29	5.11	24	0.43	0.46	3.90
8	0.32	0.30	4.98	25	0.43	0.47	3.84
10	0.34	0.32	4.84	26	0.44	0.48	3.77
12	0.35	0.34	4.71	28	0.44	0.50	3.64
14	0.37	0.36	4.57	30	0.45	0.51	3.51

Table 13 Stability constants of complex compounds most common in natural waters

Metal	Complex compound	β_n	Metal	Complex compound	β_n
Al^{3+}	$AlOH^{2+}$	$1{,}00 \cdot 10^{9}$	Al^{3+}	AlF_6^{3-}	$4{,}68 \cdot 10^{20}$
	$Al(OH)_2^{+}$	$7{,}94 \cdot 10^{17}$		$AlC_2O_4^{+}$	$2{,}00 \cdot 10^{7}$
	$Al(OH)_3^{0}$	$1{,}58 \cdot 10^{25}$		$Al(C_2O_4)_2^{-}$	$1{,}00 \cdot 10^{13}$
	$Al(OH)_4^{-}$	$2{,}00 \cdot 10^{33}$		$Al(C_2O_4)_3^{3-}$	$2{,}00 \cdot 10^{16}$
	$AlSO_4^{+}$	$3{,}16 \cdot 10^{3}$		$AlCit^{0}$	$2{,}25 \cdot 10^{9}$
	$Al(SO_4)_2^{-}$	$1{,}00 \cdot 10^{5}$		$Al(Cit)_2^{3-}$	$9{,}55 \cdot 10^{14}$
	$AlPO_4^{0}$	$5{,}75 \cdot 10^{16}$		$AlHCit^{+}$	$1{,}10 \cdot 10^{12}$
	AlF^{2+}	$1{,}26 \cdot 10^{7}$		$AlAsp^{2+}$	$1{,}21 \cdot 10^{7}$
	AlF_2^{+}	$9{,}55 \cdot 10^{11}$		$Al(Asp)_2^{+}$	$1{,}46 \cdot 10^{11}$
	AlF_3^{0}	$6{,}76 \cdot 10^{15}$		$AlAsk^{+}$	$2{,}23 \cdot 10^{17}$
	AlF_4^{-}	$3{,}39 \cdot 10^{18}$		$Al(Ask)_2^{-}$	$1{,}56 \cdot 10^{32}$
	AlF_5^{2-}	$1{,}58 \cdot 10^{20}$		$Al(Ask)_3^{3-}$	$1{,}71 \cdot 10^{43}$
Al^{3+}	$AlGlic^{2+}$	$1{,}75 \cdot 10^{8}$	Cd^{2+}	$CdAl^{+}$	$3{,}16 \cdot 10^{4}$
	$AlGlut^{+}$	$1{,}29 \cdot 10^{16}$		$Cd(Al)_2^{0}$	$1{,}05 \cdot 10^{8}$

(continued)

Table 13 (continued)

	$Al(Glut)_2^-$	$8{,}00\cdot10^{30}$		$Cd(Asp)_2^0$	$1{,}16\cdot10^{7}$
	$Al(Glut)_3^{3-}$	$4{,}40\cdot10^{39}$		$CdAsk^0$	$6{,}46\cdot10^{4}$
Ca^{2+}	$CaCO_3^0$	$1{,}58\cdot10^{3}$		$Cd(Ask)_2^{2-}$	$1{,}38\cdot10^{8}$
	$CaHCO_3^+$	$1{,}82\cdot10^{1}$		$CdGis^+$	$6{,}76\cdot10^{5}$
	$CaSO_4^0$	$2{,}04\cdot10^{2}$		$Cd(Gis)_2^0$	$1{,}14\cdot10^{10}$
	$CaPO_4^-$	$2{,}88\cdot10^{6}$		$CdGlic^+$	$6{,}31\cdot10^{4}$
	$CaHPO_4^0$	$5{,}89\cdot10^{2}$		$Cd(Glic)_2^0$	$6{,}76\cdot10^{8}$
	$CaH_2PO_4^+$	$2{,}57\cdot10^{1}$		$CdGlut^0$	$7{,}24\cdot10^{4}$
	$CaC_2O_4^0$	$4{,}57\cdot10^{1}$		$Cd(Glut)_2^{2-}$	$1{,}20\cdot10^{8}$
	$Ca(C_2O_4)_2^{2-}$	$4{,}89\cdot10^{2}$		$CdLeic^+$	$1{,}48\cdot10^{4}$
	$CaTart^0$	$9{,}55\cdot10^{2}$		$Cd(Leic)_2^0$	$4{,}32\cdot10^{7}$
	$Ca(Tart)_2^{2-}$	$1{,}02\cdot10^{9}$		$Cd(Liz)_2^0$	$9{,}89\cdot10^{5}$
	$CaCit^-$	$4{,}79\cdot10^{4}$		$CdMet^+$	$2{,}09\cdot10^{4}$
	$CaHCit^0$	$1{,}12\cdot10^{3}$		$Cd(Met)_2^0$	$1{,}53\cdot10^{7}$
	CaH_2Cit^+	$1{,}41\cdot10^{1}$		$CdProl^+$	$6{,}92\cdot10^{4}$
	$CaAl^+$	$1{,}74\cdot10^{1}$		$Cd(Prol)_2^0$	$5{,}42\cdot10^{7}$
	$CaAsk^0$	$1{,}10\cdot10^{2}$		$CdTir^+$	$1{,}37\cdot10^{3}$
	$CaGlic^+$	$2{,}40\cdot10^{1}$		$Cd(Tir)_2$	$3{,}64\cdot10^{5}$
	$CaGlut^0$	$7{,}41\cdot10^{1}$		$Cd(Cis)_2^{2-}$	$1{,}30\cdot10^{9}$
	$CaTir^+$	$3{,}02\cdot10^{1}$	Co^{2+}	CoOH+	$2{,}51\cdot10^{4}$
Cd^{2+}	$CdOH^+$	$1{,}20\cdot10^{6}$		$Co(OH)_2^0$	$1{,}58\cdot10^{9}$
	$Cd(OH)_2^0$	$5{,}01\cdot10^{8}$		$CoCO_3^0$	$8{,}13\cdot10^{4}$
	$CdCl^+$	$1{,}12\cdot10^{2}$		$CoHCO_3^+$	$1{,}00\cdot10^{3}$
	$CdSO_4^0$	$1{,}29\cdot10^{2}$		$CoSO_4^0$	$1{,}51\cdot10^{3}$
	$CdC_2O_4^0$	$1{,}00\cdot10^{4}$		$CoHPO_4^0$	$5{,}25\cdot10^{2}$
	$Cd(C_2O_4)_2^{2-}$	$5{,}89\cdot10^{5}$		$CoC2O_4^0$	$5{,}01\cdot10^{5}$
	$CdCit^-$	$2{,}29\cdot10^{5}$		$Co(C2O4)_2^{2-}$	$6{,}31\cdot10^{6}$

(continued)

Table 13 (continued)

	$CdHCit^0$	$1{,}58 \cdot 10^2$		$CoTart^0$	$1{,}20 \cdot 10^3$
Co^{2+}	CoCit-	$1{,}00 \cdot 10^5$	Cr^{3+}	CrF^{2+}	$1{,}58 \cdot 10^5$
	CoHCit0	$1{,}05 \cdot 10^3$		CrF_2^+	$3{,}47 \cdot 10^8$
	CoAl+	$6{,}61 \cdot 10^4$		CrF_3^0	$1{,}05 \cdot 10^{11}$
	$Co(Al)_2^0$	$3{,}02 \cdot 10^8$		$CrC_2O_4^+$	$2{,}19 \cdot 10^5$
	CoAsp+	$1{,}12 \cdot 10^5$		$Cr(C_2O_4)_2^-$	$3{,}24 \cdot 10^{10}$
	$Co(Asp)_2^0$	$5{,}14 \cdot 10^8$		$Cr(C_2O_4)_3^{3-}$	$2{,}75 \cdot 10^{15}$
	$CoAsk^0$	$2{,}19 \cdot 10^6$		$CrAl^{2+}$	$1{,}00 \cdot 10^9$
	$Co(Ask)_2^{2-}$	$1{,}11 \cdot 10^{11}$		$Cr(Al)_2^+$	$6{,}82 \cdot 10^{16}$
	$CoGis^+$	$1{,}26 \cdot 10^7$		$CrAsp^{2+}$	$1{,}42 \cdot 10^8$
	$Co(Gis)_2^0$	$5{,}04 \cdot 10^{12}$		$Cr(Asp)_2^+$	$1{,}34 \cdot 10^{14}$
	$CoGlic^+$	$1{,}05 \cdot 10^5$		$Cr(Asp)_3^0$	$2{,}54 \cdot 10^{19}$
	$Co(Glic)_2^0$	$9{,}77 \cdot 10^8$		$CrVal^{2+}$	$5{,}66 \cdot 10^8$
	CoGlut0	$1{,}45 \cdot 10^5$		$Cr(Val)_2^+$	$2{,}84 \cdot 10^{15}$
	$Co(Glut)_2^{2-}$	$9{,}28 \cdot 10^8$		$Cr(Val)_3^0$	$1{,}01 \cdot 10^{21}$
	CoLeic+	$4{,}68 \cdot 10^4$		$CrGlic^{2+}$	$7{,}12 \cdot 10^8$
	$Co(Leic)_2^0$	$2{,}15 \cdot 10^8$		$Cr(Glic)_2^+$	$3{,}58 \cdot 10^{15}$
	$CoLiz^+$	$4{,}34 \cdot 10^3$		$Cr(Glic)_3^0$	$2{,}54 \cdot 10^{21}$
	$Co(Liz)_2^0$	$5{,}09 \cdot 10^6$		$CrLeic^{2+}$	$1{,}79 \cdot 10^9$
	$CoMet^+$	$3{,}63 \cdot 10^4$		$Cr(Leic)_2^+$	$2{,}26 \cdot 10^{16}$
	$Co(Met)_2^0$	$5{,}77 \cdot 10^7$		$Cr(Lei)_3^0$	$2{,}54 \cdot 10^{22}$
	$CoProl^+$	$2{,}14 \cdot 10^5$		$CrMet^{2+}$	$7{,}04 \cdot 10^7$
	$CoTir^+$	$3{,}30 \cdot 10^3$		$Cr(Met)_2^+$	$5{,}58 \cdot 10^{13}$
	$CoCis^0$	$8{,}90 \cdot 10^8$		$Cr(Met)_3^0$	$7{,}85 \cdot 10^{18}$
	$Co(Cis)_2^{2-}$	$3{,}54 \cdot 10^{16}$	Cu^{2+}	$CuOH^+$	$2{,}19 \cdot 10^7$
Cr^{3+}	$CrOH^{2+}$	$1{,}26 \cdot 10^{10}$		$Cu(OH)_2^0$	$5{,}01 \cdot 10^{13}$

(continued)

Table 13 (continued)

	$Cr(OH)_2^+$	$6{,}31 \cdot 10^{17}$		$Cu(OH)_3^-$	$2{,}63 \cdot 10^{14}$
	$Cr(OH)_3^0$	$5{,}74 \cdot 10^{23}$		$CuCO_3^0$	$5{,}89 \cdot 10^{6}$
	$Cr(OH)_4^-$	$7{,}94 \cdot 10^{29}$		$Cu(CO3)_2^{2-}$	$1{,}02 \cdot 10^{10}$
	$CrSO_4^+$	$3{,}98 \cdot 10^{1}$		$CuHCO_3^+$	$5{,}01 \cdot 10^{2}$
	$CrHPO_4^+$	$2{,}82 \cdot 10^{9}$		$CuCl^+$	$1{,}51 \cdot 10^{1}$
Cu^{2+}	$CuSO_4^0$	$2{,}29 \cdot 10^{2}$	Cu^{2+}	$Cu(Prol)_2^0$	$8{,}33 \cdot 10^{15}$
	$CuHPO_4^0$	$1{,}58 \cdot 10^{3}$		$CuTir^+$	$1{,}16 \cdot 10^{8}$
	$CuC_2O_4^0$	$5{,}01 \cdot 10^{6}$		$Cu(Tir)_2^0$	$1{,}17 \cdot 10^{15}$
	$Cu(C_2O_4)_2^{2-}$	$2{,}00 \cdot 10^{10}$		$CuCis_2^{2-}$	$1{,}56 \cdot 10^{16}$
	CuTart0	$1{,}00 \cdot 10^{3}$	Fe^{2+}	$FeOH^+$	$3{,}63 \cdot 10^{5}$
	$Cu(Tart)_2^{2-}$	$1{,}29 \cdot 10^{5}$		$Fe(OH)_2^0$	$5{,}89 \cdot 10^{9}$
	$CuCit^-$	$7{,}94 \cdot 10^{5}$		$FeCO_3^0$	$5{,}37 \cdot 10^{4}$
	$CuHCit^0$	$2{,}64 \cdot 10^{3}$		$FeHCO_3^+$	$\sim 1 \cdot 10^{3}$
	CuH_2Cit^+	$1{,}82 \cdot 10^{2}$		$FeSO_4^0$	$1{,}58 \cdot 10^{2}$
	$CuAl^+$	$3{,}24 \cdot 10^{8}$		$FeHPO_4^0$	$1{,}58 \cdot 10^{7}$
	$Cu(Al)_2^0$	$2{,}34 \cdot 10^{15}$		$FeH_2PO_4^+$	$5{,}01 \cdot 10^{2}$
	$CuAsp^+$	$1{,}95 \cdot 10^{8}$		$FeC_2O_4^0$	$1{,}12 \cdot 10^{3}$
	$Cu(Asp)_2^0$	$5{,}14 \cdot 10^{14}$		$Fe(C_2O_4)_2^{2-}$	$3{,}31 \cdot 10^{4}$
	$CuAsk^0$	$2{,}63 \cdot 10^{9}$		$FeCit^-$	$2{,}51 \cdot 10^{4}$
	$Cu(Ask)_2^{2-}$	$5{,}34 \cdot 10^{16}$		$FeHCit^0$	$1{,}32 \cdot 10^{2}$
	$CuVal^+$	$1{,}26 \cdot 10^{8}$		$FeAl^+$	$3{,}61 \cdot 10^{3}$
	$Cu(Val)_2^0$	$5{,}92 \cdot 10^{14}$		$Fe(Al)_2^0$	$3{,}65 \cdot 10^{7}$
	$CuGis^+$	$9{,}71 \cdot 10^{10}$		$FeAsp^+$	$2{,}62 \cdot 10^{3}$
	$Cu(Gis)_2^0$	$1{,}52 \cdot 10^{19}$		$FeAsk^0$	$2{,}37 \cdot 10^{4}$
	$CuGlic^+$	$4{,}17 \cdot 10^{8}$		$Fe(Ask)_2^{2-}$	$7{,}15 \cdot 10^{8}$
	$Cu(Glic)_2^0$	$3{,}89 \cdot 10^{15}$		$FeVal^+$	$2{,}56 \cdot 10^{3}$

(continued)

Table 13 (continued)

	$CuGlut^{0}$	$8{,}91\cdot10^{7}$		$FeGis^{+}$	$1{,}66\cdot10^{6}$
	$Cu(Glut)_{2}^{2-}$	$8{,}09\cdot10^{14}$		$Fe(Gis)_{2}^{0}$	$4{,}44\cdot10^{10}$
	$CuLeic^{+}$	$1{,}17\cdot10^{8}$		$FeGlic^{+}$	$3{,}02\cdot10^{4}$
	$Cu(Leic)_{2}^{0}$	$4{,}00\cdot10^{14}$		$Fe(Glic)_{2}^{0}$	$1{,}15\cdot10^{8}$
	$CuLiz^{+}$	$8{,}85\cdot10^{7}$		$FeGlut^{0}$	$4{,}79\cdot10^{4}$
	$Cu(Liz)_{2}^{0}$	$4{,}48\cdot10^{14}$		$Fe(Glut)_{2}^{2-}$	$1{,}82\cdot10^{7}$
	$CuMet^{+}$	$2{,}04\cdot10^{8}$		$FeLeic^{+}$	$2{,}74\cdot10^{3}$
	$Cu(Met)_{2}^{0}$	$2{,}24\cdot10^{15}$		$FeLiz^{+}$	$4{,}79\cdot10^{4}$
	$CuProl^{+}$	$5{,}89\cdot10^{8}$		$FeMet^{+}$	$1{,}81\cdot10^{3}$
Fe^{2+}	$Fe(Met)_{2}^{0}$	$9{,}17\cdot10^{6}$	Fe^{3+}	$FeAsk^{+}$	$2{,}85\cdot10^{11}$
	$FeProl^{+}$	$1{,}22\cdot10^{4}$		$FeVal^{2+}$	$4{,}24\cdot10^{9}$
	$Fe(Prol)_{2}^{0}$	$4{,}84\cdot10^{8}$		$FeGis^{2+}$	$5{,}34\cdot10^{4}$
	FeGis	$3{,}02\cdot10^{4}$		$FeGlic^{2+}$	$1{,}07\cdot10^{10}$
	$Fe(Gis)_{2}^{0}$	$1{,}15\cdot10^{8}$		$FeGlut^{+}$	$1{,}43\cdot10^{12}$
	$Fe(Cis)_{2}^{2-}$	$5{,}89\cdot10^{11}$		$FeLeic^{2+}$	$8{,}46\cdot10^{9}$
Fe^{3+}	$FeOH^{2+}$	$7{,}41\cdot10^{11}$		$FeMet^{2+}$	$1{,}34\cdot10^{9}$
	$Fe(OH)_{2}^{+}$	$1{,}48\cdot10^{21}$		$FeProl^{+}$	$1{,}10\cdot10^{10}$
	$Fe(OH)_{3}^{0}$	$4{,}68\cdot10^{30}$		$Fe(Cis)_{3}^{3-}$	$1{,}26\cdot10^{32}$
	$FeCO_{3}^{+}$	$5{,}23\cdot10^{9}$	Hg^{2+}	$HgOH^{+}$	$2{,}00\cdot10^{10}$
	$FeHCO_{3}^{2+}$	$1{,}00\cdot10^{5}$		$Hg(OH)_{2}^{0}$	$5{,}01\cdot10^{21}$
	$FeCl^{2+}$	$2{,}81\cdot10^{1}$		$HgCO_{3}^{0}$	$3{,}24\cdot10^{7}$
	$FeCl_{2}^{+}$	$1{,}26\cdot10^{2}$		$HgCl^{+}$	$5{,}01\cdot10^{6}$
	$FeSO_{4}^{+}$	$1{,}10\cdot10^{4}$		$HgCl_{2}^{0}$	$1{,}70\cdot10^{13}$
	$Fe(SO4)_{2}^{-}$	$2{,}40\cdot10^{5}$		$HgCl_{3}^{-}$	$1{,}70\cdot10^{14}$
	$FeHPO_{4}^{+}$	$5{,}62\cdot10^{9}$		$HgCl_{4}^{2-}$	$1{,}66\cdot10^{15}$
	$FeH_{2}PO_{4}^{2+}$	$3{,}16\cdot10^{3}$		$HgSO_{4}^{0}$	$2{,}19\cdot10^{1}$
	FeF^{2+}	$1{,}10\cdot10^{6}$		$Hg(SO_{4})_{2}^{2-}$	$2{,}75\cdot10^{2}$

(continued)

Table 13 (continued)

	FeF_2^+	$5{,}50 \cdot 10^{10}$		$HgCit^-$	$7{,}94 \cdot 10^{10}$
	FeF_3^0	$5{,}50 \cdot 10^{13}$		$Hg(Al)_2^0$	$8{,}11 \cdot 10^{18}$
	FeF_4^-	$5{,}50 \cdot 10^{15}$		$Hg(Gis)_2^0$	$2{,}92 \cdot 10^{21}$
	$FeC_2O_4^+$	$2{,}51 \cdot 10^{9}$		$Hg(HGis)^{2+}$	$3{,}75 \cdot 10^{18}$
	$Fe(C_2O_4)_2^-$	$1{,}58 \cdot 10^{16}$		$Hg(HGis)_2^{2+}$	$1{,}84 \cdot 10^{15}$
	$Fe(C_2O_4)_3^{3-}$	$1{,}58 \cdot 10^{20}$		$HgGlic^+$	$3{,}99 \cdot 10^{10}$
	$FeTart^+$	$3{,}09 \cdot 10^{7}$		$Hg(Glic)_2^0$	$4{,}49 \cdot 10^{19}$
	$Fe(Tart)_2^-$	$7{,}24 \cdot 10^{11}$		$HgMet^+$	$9{,}12 \cdot 10^{6}$
	$FeCit^0$	$2{,}51 \cdot 10^{11}$		$Hg(Met)_2^0$	$1{,}28 \cdot 10^{12}$
	$FeHCit^+$	$2{,}00 \cdot 10^{6}$		$Hg(Prol)_2^0$	$5{,}83 \cdot 10^{20}$
	$FeAl^{2+}$	$1{,}02 \cdot 10^{11}$		$Hg(Tir)_2^0$	$1{,}75 \cdot 10^{17}$
	$FeAsp^{2+}$	$4{,}24 \cdot 10^{8}$		$HgCis^0$	$5{,}62 \cdot 10^{14}$
Hg^{2+}	$Hg(Cis)_2^{2-}$	$3{,}53 \cdot 10^{20}$	Mn^{2+}	$MnAsk^0$	$1{,}83 \cdot 10^{4}$
Mg^{2+}	$MgCO_3^0$	$2{,}51 \cdot 10^{3}$		$MnVal^+$	$1{,}05 \cdot 10^{3}$
	$MgHCO_3^+$	$1{,}45 \cdot 10^{1}$		$Mn(Val)_2^0$	$6{,}64 \cdot 10^{5}$
	$MgSO_4^0$	$2{,}29 \cdot 10^{2}$		$MnGis^+$	$1{,}05 \cdot 10^{4}$
	$MgHPO_4^0$	$7{,}59 \cdot 10^{2}$		$MnGlic^+$	$2{,}34 \cdot 10^{3}$
	$MgH_2PO_4^+$	$1{,}48 \cdot 10^{1}$		$Mn(Glic)_2^0$	$15{,}78 \cdot 10^{5}$
	$MgC_2O_4^0$	$3{,}55 \cdot 10^{2}$		$MnGlut^0$	$2{,}51 \cdot 10^{3}$
	$Mg(C_2O_4)_2^{2-}$	$2{,}40 \cdot 10^{4}$		$MnLeic^+$	$9{,}12 \cdot 10^{2}$
	$MgTart^0$	$8{,}13 \cdot 10^{1}$		$Mn(Leic)_2^0$	$5{,}15 \cdot 10^{5}$
	$MgCit^-$	$9{,}12 \cdot 10^{3}$		$MnLiz^+$	$1{,}48 \cdot 10^{2}$
	$MgHCit^0$	$6{,}92 \cdot 10^{1}$		$MnMet^+$	$1{,}62 \cdot 10^{3}$
	$MgAl^+$	$9{,}12 \cdot 10^{1}$		$Mn(Met)_2^0$	$1{,}59 \cdot 10^{5}$
	$Mg(Asp)_2^0$	$1{,}79 \cdot 10^{4}$		$MnProl^+$	$6{,}03 \cdot 10^{3}$
	$MgAsk^0$	$7{,}41 \cdot 10^{2}$		$MnTir^+$	$6{,}52 \cdot 10^{1}$

(continued)

Table 13 (continued)

	MgGlic	$4,27\cdot 10^{2}$		$Mn(Tir)_2^0$	$9,94\cdot 10^{3}$
	$MgGlut^0$	$2,19\cdot 10^{2}$		$MnCis^0$	$1,00\cdot 10^{5}$
Mn^{2+}	$MnOH^+$	$7,94\cdot 10^{3}$	Ni^{2+}	$NiOH^+$	$9,33\cdot 10^{4}$
	$Mn(OH)_2^0$	$6,68\cdot 10^{6}$		$Ni(OH)_2^0$	$3,55\cdot 10^{8}$
	$Mn(OH)_3^-$	$2\cdot 10^{8}$		$NiCO_3^0$	$2,34\cdot 10^{5}$
	$MnCO_3^0$	$7,94\cdot 10^{4}$		$NiHCO_3^+$	$5,01\cdot 10^{3}$
	$MnHCO_3^+$	$8,91\cdot 10^{1}$		$NiSO_4^0$	$2,09\cdot 10^{2}$
	$MnSO_4^0$	$1,86\cdot 10^{2}$		$Ni(SO_4)_2^{2-}$	$1,58\cdot 10^{3}$
	$MnHPO_4^0$	$3,80\cdot 10^{2}$		$NiHPO_4^0$	$1,20\cdot 10^{2}$
	$MnC_2O_4^0$	$6,61\cdot 10^{3}$		$NiC_2O_4^0$	$2,00\cdot 10^{5}$
	$Mn(C_2O_4)_2^{2-}$	$1,78\cdot 10^{5}$		$Ni(C_2O_4)_2^{2-}$	$3,24\cdot 10^{6}$
	$MnTart^0$	$2,75\cdot 10^{1}$		$NiTart^0$	$4,07\cdot 10^{3}$
	$MnCit^-$	$5,25\cdot 10^{3}$		$Ni(Tart)_2^0$	$2,63\cdot 10^{5}$
	$MnHCit^0$	$1,20\cdot 10^{2}$		$NiCit^-$	$2,51\cdot 10^{5}$
	$MnAl^+$	$1,05\cdot 10^{3}$		$NiHCit^0$	$2,00\cdot 10^{3}$
	$Mn(Asp)_2^0$	$5,78\cdot 10^{4}$		$NiAl^+$	$9,12\cdot 10^{5}$
Ni^{2+}	$Ni(Al)_2^0$	$4,57\cdot 10^{10}$	Pb^{2+}	$PbCO_3^0$	$2,51\cdot 10^{6}$
	$NiAsp^+$	$1,23\cdot 10^{6}$		$Pb(CO_3)_2^{2-}$	$1,23\cdot 10^{9}$
	$Ni(Asp)_2^0$	$3,90\cdot 10^{10}$		$PbHCO_3^+$	$5,32\cdot 10^{2}$
	$NiAsk^0$	$1,20\cdot 10^{7}$		$Pb(HCO_3)_2^0$	$5,89\cdot 10^{4}$
	$Ni(Ask)_2^{2-}$	$2,70\cdot 10^{12}$		$Pb(HCO_3)_3^-$	$1,55\cdot 10^{5}$
	$NiVal^+$	$7,41\cdot 10^{5}$		$PbCl^+$	$4,14\cdot 10^{1}$
	$Ni(Val)_2^0$	$1,45\cdot 10^{10}$		$PbCl_2^0$	$2,75\cdot 10^{2}$
	$NiGis^+$	$7,41\cdot 10^{8}$		$PbSO_4^0$	$4,17\cdot 10^{2}$
	$Ni(Gis)_2^0$	$6,06\cdot 10^{15}$		$Pb(SO_4)_2^{2-}$	$2,95\cdot 10^{3}$
	$NiGlic^+$	$1,51\cdot 10^{6}$		$PbC_2O_4^0$	$7,94\cdot 10^{4}$
	$Ni(Glic)_2^0$	$1,38\cdot 10^{11}$		$Pb(C_2O_4)_2^{2-}$	$3,47\cdot 10^{6}$

(continued)

Table 13 (continued)

	$NiGlut^0$	$6{,}92\cdot10^5$		$PbTart^0$	$8{,}32\cdot10^2$
	$Ni(Glut)_2^{2-}$	$3{,}37\cdot10^9$		$PbCit^-$	$3{,}16\cdot10^6$
	$NiLeic^+$	$1{,}27\cdot10^6$		$PbHCit^0$	$5{,}25\cdot10^5$
	$Ni(Leic)_2^0$	$7{,}78\cdot10^{10}$		$PbAl^+$	$1{,}00\cdot10^5$
	$Ni(Leic)_3^-$	$4{,}00\cdot10^{15}$		$Pb(Al)_2^0$	$1{,}74\cdot10^8$
	$NiLiz^+$	$3{,}07\cdot10^5$		$PbAsp^+$	$2{,}37\cdot10^4$
	$Ni(Liz)_2^0$	$1{,}06\cdot10^9$		$Pb(Asp)_2^0$	$1{,}80\cdot10^6$
	$Ni(Liz)_3^-$	$1{,}01\cdot10^{11}$		$PbAsk^0$	$7{,}90\cdot10^5$
	$NiMet^+$	$4{,}27\cdot10^5$		$Pb(Ask)_2^0$	$2{,}55\cdot10^7$
	$Ni(Met)_2^0$	$2{,}96\cdot10^{10}$		$PbVal^+$	$1{,}09\cdot10^4$
	$NiProl^+$	$3{,}89\cdot10^6$		$Pb(Val)_2^0$	$8{,}64\cdot10^9$
	$Ni(Prol)_2^0$	$8{,}15\cdot10^{11}$		$PbGis^+$	$1{,}87\cdot10^7$
	$NiTir^+$	$2{,}16\cdot10^5$		$PbGlic^+$	$5{,}95\cdot10^5$
	$Ni(Tir)_2^0$	$5{,}85\cdot10^9$		$Pb(Glic)_2^0$	$7{,}24\cdot10^8$
	$NiCis^0$	$6{,}86\cdot10^9$		$PbGlut^0$	$4{,}32\cdot10^4$
	$Ni(Cis)_2^{2-}$	$9{,}91\cdot10^{20}$		$Pb(Glut)_2^{2-}$	$1{,}80\cdot10^6$
Pb^{2+}	$PbOH^+$	$3{,}31\cdot10^7$		$PbMet^+$	$6{,}60\cdot10^4$
	$Pb(OH)_2^0$	$3{,}47\cdot10^{10}$		$Pb(Met)_2^0$	$1{,}95\cdot10^9$
	$Pb(OH)_3^-$	$8{,}91\cdot10^{13}$		$PbTir^+$	$3{,}07\cdot10^4$
Pb^{2+}	$Pb(Tir)_2^0$	$1{,}15\cdot10^9$	Zn^{2+}	$Zn(Ask)_2^{2-}$	$9{,}69\cdot10^{10}$
	$PbCis^0$	$8{,}73\cdot10^{11}$		$ZnVal^+$	$1{,}51\cdot10^5$
Zn^{2+}	$ZnOH^+$	$2{,}04\cdot10^6$		$Zn(Val)_2^0$	$2{,}30\cdot10^9$
	$Zn(OH)_2^0$	$1{,}55\cdot10^{11}$		$ZnGis^+$	$1{,}13\cdot10^7$
	$Zn(OH)_3^-$	$2{,}04\cdot10^{14}$		$Zn(Cis)_2^0$	$9{,}02\cdot10^{12}$
	$ZnCO_3^0$	$2{,}00\cdot10^5$		$ZnGlic^+$	$3{,}31\cdot10^5$
	$ZnHCO_3^+$	$1{,}26\cdot10^2$		$Zn(Glic)_2^0$	$9{,}12\cdot10^5$
	$ZnSO_4^0$	$2{,}19\cdot10^2$		$ZnGlut^0$	$3{,}55\cdot10^5$

(continued)

Table 13 (continued)

$ZnHPO_4^0$	$2{,}51\cdot10^2$	$Zn(Glut)_2^{2-}$	$9{,}28\cdot10^9$
$ZnC_2O_4^0$	$7{,}08\cdot10^4$	$ZnLeic^+$	$1{,}23\cdot10^5$
$Zn(C_2O_4)_2^{2-}$	$3{,}55\cdot10^7$	$Zn(Leic)_2^0$	$1{,}56\cdot10^9$
$ZnTart^0$	$2{,}04\cdot10^3$	$Zn(Liz)_2^0$	$7{,}28\cdot10^7$
$Zn(Tart)_2^{2-}$	$1{,}45\cdot10^5$	$ZnMet^+$	$6{,}46\cdot10^4$
$ZnCit^-$	$9{,}55\cdot10^4$	$Zn(Met)_2^0$	$6{,}52\cdot10^8$
$ZnHCit^0$	$9{,}55\cdot10^2$	$ZnProl^+$	$6{,}31\cdot10^5$
$ZnAl^+$	$1{,}62\cdot10^5$	$ZnTir^+$	$2{,}91\cdot10^4$
$Zn(Al)_2^0$	$3{,}47\cdot10^9$	$Zn(Tir)_2^0$	$5{,}71\cdot10^8$
$Zn(Asp)_2^0$	$9{,}17\cdot10^8$	$ZnCis^0$	$3{,}02\cdot10^9$
$ZnAsk^0$	$1{,}91\cdot10^6$	$Zn(Cis)_2^{2-}$	$1{,}48\cdot10^{18}$

Table 14 Conditional stability constants of fulvic (FA) and humate (HA) metal complexes Expressions of constants are presented according to the original literature. Sign "–" means that the origin of FA and HA is not specified

Metal	Expression of a constant	β	pH	Ionic strength μ	Other conditions	References
Al(III)	$[AlFA]/[Al]\cdot[FA]$	4.68×10^4	4.0	0.1	FA isolated from water	[6]
	– ″ –	2.88×10^6	5.0	0.1	– ″ –	[6]
Au(III)	$[AuFA]/[Au^{3+}]\cdot[FA^{2-}]$	2.57×10^6	3.5	0.1	FA isolated from water	[26]
	– ″ –	5.62×10^8	5.8	0.1	– ″ –	[26]
	– ″ –	8.91×10^9	7.5	0.1	– ″ –	[26]
Ca(II)	$[CaFA]/[Ca^{2+}]\cdot[FA^{2-}]$	4.37×10^3	5.0	0.1	FA isolated from water	[26]
	– ″ –	1.00×10^3	5.0	0.05	FA isolated from soil	[9]
	$[CaFA]/[Ca^{2+}]\cdot[FA]$	1.32×10^3	5.0	0.1	–	[22]

(continued)

Table 14 (continued)

Metal	Expression of a constant	β	pH	Ionic strength μ	Other conditions	References
Cd(II)	$[CdFA]/[Cd^{2+}] \cdot [HFA^{-}]$	1.38×10^3	4.0	0.1	FA isolated from water	[18]
	– ″ –	3.02×10^3	5.0	0.1	– ″ –	[18]
	– ″ –	4.79×10^3	6.0	0.1	– ″ –	[18]
	$[CdFA]/[Cd^{2+}] \cdot [HFA^{-}]$	8.13×10^3	7.0	0.1	FA isolated from water	[18]
	– ″ –	1.20×10^4	8.0	0.1	– ″ –	[18]
	$[CdFA]/[Cd^{2+}] \cdot [HFA^{-}]$	1.70×10^3	4.0	0.1	FA isolated from soil	[18]
	– ″ –	6.31×10^3	5.0	0.1	– ″ –	[18]
	– ″ –	1.20×10^4	6.0	0.1	– ″ –	[18]
	– ″ –	2.09×10^4	7.0	0.1	– ″ –	[18]
	– ″ –	4.27×10^4	8.0	0.1	– ″ –	[18]
	$[CdFA]/[Cd^{2+}] \cdot [H_xFA^{-}]$	2.0×10^5	5.7	0.01	FA isolated from soil	[2]
	– ″ –	4.0×10^5	6.7	0.01	– ″ –	[2]
	– ″ –	1.0×10^6	7.7	0.01	– ″ –	[2]
	$[CdFA]/[Cd^{2+}] \cdot [FA]$	1.10×10^3	5.0	0.1	–	[22]
	$[CdHA]/[Cd^{2+}] \cdot [HA^{2-}]$	$(0.2-1.0) \times 10^4$	4.0−−6.0	0.1	HA isolated from soil	[20]
	$[CdHA^{(m-n)-}]/ / [Cd^{n+}] \cdot [HA^{m-}]$	1.10×10^5	6.8	0.1	HA isolated from soil	[10]
Co(II)	$[CoFA]/[Co^{2+}] \cdot [FA^{2-}]$	5.0×10^3	6.0	0.1	FA isolated from soil	[16]
	$[CoFA]/[Co] \cdot [FA]$	9.33×10^6	7.6	0.01	FA isolated from water	[14]
Cr(III)	$[CrFA]/[Cr(OH)^{2+}] \cdot [FA^{2-}]$	6.3×10^5	4.8	0.1	FA isolated from peat soil	[13]
	– ″ –	1.6×10^5	4.8	0.1	FA isolated from forest soil	[13]
Cu(II)	$[CuFA]/[Cu^{2+}] \cdot [FA^{2-}]$	5.0×10^3	5.0	0.05	FA isolated from soil	[9]
	– ″ –	1.0×10^5	6.0	0.1	– ″ –	[16]
	– ″ –	5.50×10^5	7.5	0.1	FA isolated from water	[26]
	$[CuFA^{+}]/[Cu^{2+}] \cdot [FA^{-}]$	7.9×10^5	3.9	0.1	Aqueous acetone extract from peat	[23]

(continued)

Table 14 (continued)

Metal	Expression of a constant	β	pH	Ionic strength μ	Other conditions	References
Cu(II)	$[Cu(FA)^0]/[Cu^{2+}] \cdot [FA^-]_2$	4.0×10^{12}	3.9	0.1	– ″ –	[23]
	– ″ –	1.3×10^{13}	3.9	0.1	Ammonium hydroxide extract from peat	[23]
	$[Cu(FA)]/[Cu^{2+}] \cdot [FA]$	2.75×10^5	4.8	0.1	Aqueous extract from peat soil	[13]
	– ″ –	7.76×10^4	4.8	0.1	Aqueous extract from forest soil	[13]
	– ″ –	3.72×10^2	4.0	0.1	FA isolated from soil	[1]
	– ″ –	8.51×10^3	5.5	0.1	– ″ –	[1]
	– ″ –	3.2×10^5	4.0	0.1	FA isolated from water	[3]
	$[Cu(FA)]/[Cu^{2+}] \cdot [FA]$	1.0×10^6	5.0	0.1	FA isolated from water	[3]
	– ″ –	1.3×10^6	6.0	0.1	– ″ –	[3]
	– ″ –	4.0×10^5	4.0	0.1	FA isolated from soil	[3]
	– ″ –	1.0×10^6	5.0	0.1	– ″ –	[3]
	– ″ –	2.0×10^6	6.0	0.1	– ″ –	[3]
	$[Cu(FA)]/[Cu] \cdot [FA]$	4.79×10^4	5.0	0.1	FA isolated from soil	[17]
	– ″ –	1.03×10^5	6.0	0.1	– ″ –	[17]
	– ″ –	2.82×10^5	7.0	0.1	– ″ –	[17]
	– ″ –	5.0×10^5	7.0	–	FA of lake waters	[21]
	– ″ –	6.3×10^7	7.6	0.01	– ″ –	[24]
	– ″ –	$(0.4-1.0) \times 10^7$	8.0	0.01	FA isolated from bottom sediments	[11]
	$[CuHA^0)]/[Cu^{2+}] \cdot [HA^{2-}]$	6.3×10^7	6.8	–	HAcommercial formulation	[7]
	$[Cu(HA)^{2-}]/[Cu^{2+}] \cdot [HA^{2-}]^2$	6.3×10^{16}	6.8	–	– ″ –	[7]
	$[CuHA)]/[Cu] \cdot [HA]$	1.0×10^6	7.0	–	HA of lake waters	[21]
	– ″ –	$(0.3-6.3) \times 10^9$	8.0	0.02	HA of river and lake waters	[15]
	$[CuHA^{(m-n)-}] / [Cu^{n+}] \cdot [HA^{m-}]$	1.6×10^6	6.8	0.1	HA isolated from soil	[10]
Fe(II)	$[FeFA]/[Fe^{2+}] \cdot [FA^{2-}]$	4.68×10^4	5.0	0.1	FA isolated from water	[26]

(continued)

Table 14 (continued)

Metal	Expression of a constant	β	pH	Ionic strength μ	Other conditions	References
Fe(III)	$[FeFA]/[Fe^{3+}] \cdot [FA^{2-}]$	1.41×10^{7}	5.0	0.1	– ″ –	[26]
	$[Fe(FA)_2]/[Fe^{3+}] \cdot [FA^{2-}]^2$	3.16×10^{12}	5.0	0.1	– ″ –	[12]
	$[FeFAOH]/[Fe^{3+}] \cdot [FA^{2-}] \cdot [OH^-]$	1.3×10^{20}	5.0	0.1	– ″ –	[12]
	$[FeFA(OH)_2^-]/[Fe^{3+}] \cdot [FA^{2-}] \cdot [OH^-]^2$	3.2×10^{30}	5.0	0.1	– ″ –	[12]
Hg(II)	$[HgFA]/[Hg^{2+}] \cdot [FA^{2-}]$	1.70×10^{11}	6.4	0.1	FA isolated from water	[26]
	– ″ –	$(1.3-2.5) \times 10^{11}$	6.5	0.1	– ″ –	[25]
	$[HgFA]/[Hg] \cdot [FA]$	7.24×10^{4}	3.0	0.1	FA isolated from soil	[5]
	– ″ –	1.22×10^{5}	4.0	0.1	– ″ –	[5]
Mg(II)	$[MgFA]/[Mg^{2+}] \cdot [FA^{2-}]$	6.3×10^{2}	5.0	0.05	FA isolated from soil	[9]
	$[MgFA]/[Mg^{2+}] \cdot [FA]$	5.0×10^{2}	5.0	0.1	–	[22]
	$[MgFA]/[Mg^{2+}] \cdot [FA^{2-}]$	7.1×10^{3}	8.0	0.1	–	[22]
Mn(II)	$[MnFA]/[Mn^{2+}] \cdot [FA^{2-}]$	5.0×10^{3}	5.0	0.05	FA isolated from soil	[9]
	– ″ –	4.0×10^{3}	6.0	0.1	– ″ –	[16]
	$[MnFA]/[Mn] \cdot [FA]$	1.0×10^{3}	4.62 − 4.68	0.01	FA isolated from bottom sediments	[11]
Ni(II)	$[NiFA]/[Ni^{2+}] \cdot [FA^{2-}]$	$(1.4\text{-}1.6) \cdot 10^{7}$	4.0−6.5	0.05	FA isolated from soil	[9]
	$[NiFA^{2-x}]/[Ni^{2+}] \cdot [FA^{x-}]$	$6.3 \cdot 10^{3}$	5.7−6.5	0.05	Ammonium hydroxide extract from peat	[8]
	$[NiFA]/[Ni^{2+}] \cdot [FA]$	1.55×10^{3}	4.0	0.1	FA isolated from soil	[1]
	– ″ –	1.70×10^{3}	5.5	0.1	– ″ –	[1]
	– ″ –	2.24×10^{4}	4.0−5.0	0.1	– ″ –	[5]
	– ″ –	6.46×10^{3}	5.0	0.1	–	[22]
	$[NiFA]/[Ni] \cdot [FA]$	$(0.5-1.3) \times 10^{7}$	6.5−7.6	0.01	FA isolated from water	[14]
	$[NiHA)]/[Ni] \cdot [HA]$	9.55×10^{4}	8.0	0.02	HA isolated from peat	[15]
	– ″ –	$(1.4-1.8) \times 10^{5}$	8.0	0.02	HA isolated from water	[15]

(continued)

Table 14 (continued)

Metal	Expression of a constant	β	pH	Ionic strength μ	Other conditions	References
Pb(II)	$[PbFA^0]/[Pb^{2+}] \cdot [FA]$	1.66×10^4	5.0	0.1	–	[22]
	$[Pb(FA)_2]/[Pb^{2+}] \cdot [FA]^2$	6.92×10^6	5.0	0.1	–	[22]
	$[PbFA]/[Pb^{2+}] \cdot [FA]$	$(0.5-1.3) \times 10^5$	5.0–6.0	–	–	[19]
	$[Pb(FA)_2]/[Pb^{2+}] \cdot [FA]^2$	$(0.2-1.3) \times 10^{10}$	5.0–6.0	–	–	[19]
	$[PbFA]/[Pb^{2+}] \cdot [FA]$	1.3×10^5	6.0	–	–	[4]
	$[Pb(FA)_2]/[Pb^{2+}] \cdot [FA]^2$	5.0×10^9	6.0	–	–	[4]
	$[PbHA^0)]/[Pb^{2+}] \cdot [HA^{2-}]$	1.3×10^6	6.8	–	Commercial formulation	[7]
	$[Pb(HA)^{2-}]/[Pb^{2+}] \cdot$ $\cdot [HA^{2-}]^2$	6.3×10^{14}	6.8	–	– ″ –	[7]
	$[PbHA^{(m-n)-}]/[Pb^{n+}] \cdot [HA^{m-}]$	2.82×10^6	6.8	0.1	HA isolated from soil	[10]
Sb(III)	$[SbFA]/[Sb^{3+}] \cdot [FA^{2-}]$	8.71×10^7	5.8	0.1	FA isolated from water	[26]
Sr(II)	$[SrFA]/[Sr^{2+}] \cdot [FA^{2-}]$	3.72×10^3	5.0	0.1	FA isolated from water	[26]
Zn(II)	$[ZnFA]/[Zn^{2+}] \cdot [FA^{2-}]$	2.0×10^2	5.0	0.05	FA isolated from soil	[9]
	$[ZnFA]/[Zn^{2+}] \cdot [FA]$	2.82×10^3	5.0	0.1	–	[22]
	– ″ –	9.77×10^2	4.0	0.1	FA isolated from soil	[1]
	– ″ –	1.45×10^4	5.5	0.1	– ″ –	[1]
	$[ZnFA]/[Zn] \cdot [FA]$	$(1.1-2.6) \times 10^5$	8.0	0.02	FA isolated from water	[15]
Zn(II)	– ″ –	$(4.7-6.3) \times 10^5$	8.0	0.01	FA isolated from bottom sediments	[11]
	$[ZnHA]/[Zn^{2+}] \cdot [HA^{2-}]$	$(0.4\text{-}5.1) \times 10^4$	4.0–6.0	0.1	HA isolated from soil	[20]
	$[ZnHA^{(m-n)-}]/$ $/ [Zn^{n+}] \cdot [HA^{m-}]$	1.0×10^5	6.8	0.1	– ″ –	[10]

1. Adhikari M, Hazra GC (1972) Stability constants of Cu^{2+}, Ni^{2+} and Zn^{2+} fulvic acid metal complexes. J Indian Chem Soc 49(10): 947–951

2. Brady B, Pagenkopf GK (1978) Cadmium complexation by soil fulvic acid. Can J Chem 56(17): 331–233

3. Bresnahan WT, Grant CL, Weber JH (1978) Stability Constants of the Complexation of Copper (II) Ions with Water and Soil Fulvic Acids Mesaumered by an Ion Selective Electrode. Anal Chem 50 (12): 1675–1679

4. Buble Y, Greter F-L (1979) Voltammetric study of humic and fulvic substances. Part II: Mechanism of reaction of the fulvic complexes on the mercury electrode. J Elektroanal Chem 101(2): 231–25

5. Cheam V, Gamble DS (1974) Metal-fulvic chelation equilibrium in aqueos $NaNO_3$ solution. Hg(II), Cd(II) and Cu(II) fulvate complexes. Can J Soil Sci 54(4): 413–418

6. Elkins KM, Nelson DJ (2002) Spectroscopic approaches to the study of the interaction of aluminium with humic substances. Coordination chemistry Rewiews 228: 205–225

7. Ernst R, Allen HE, Mancy KH (1975) Characterization of trace metal species and measurement of trace metal stability constants by electrochemical techniques. Water Res 9(11): 969–979

8. Goncharova TO, Kolosov IV, Kaplin VT (1978) Hydroliz i kompleksoobrazovanie ionov Ni^{2+} v rastvorakh fulvokisloy (Hydrolysis and complexing Ni^{2+} ions in fulvic acids solutions). Hydrochemical materials 71: 64–71

9. Goncharova TO, Kolosov IV, Kaplin VT (1989) O formakh nakhozhdenia metallov v poverkhnostnykh vodakh (Coexisting forms of metals in surface water). Hydrochemical materials (77): 16–26

10. Guy RD, Chakrabarty CL (1976) Studies of metal-organik interaction in model system pertaining to natural waters. Can J Chem 54(16): 2600–2611

11. Hirata Sh. (1981) Stability constants for the complexes of transition—metal ions with fulvic and humic acids in sediments measumered by gel filtration. Talanta 28(11): 809−815

12. Intskirveli LN (1975) Issledovanie i opredelenie form zheleza v pryrodnykh vodakh (The study and determination of iron forms in natural water). Dissertation, Vernadsky Institute of Geochemistry and Analytical chemistry of Russian Academy of Sciences

13. Kraync M, Stupar J, Milicev S (1995) Characterization of chromium and copper complexes with fulvic acidc isolated from soils Slovenia. Sci Total Environ 159: 23–31

14. Lee J (1983) Complexation analysis of fresh water by equilibrium diafiltration. Water Res 17(5): 501–510

15. Mantoura RFC, Riley JP (1975) The use of gel filtration in the study of metal binding by humic acids related compounds. Analyt Chem Acta 78(1): 193–200

16. Ryan DK, Thompson CP, Weber JH (1983) Comparison of Mn^{2+}, Co^{2+} and Cu^{2+} binding to fulvic acid as measured by fluorescence quenching. Can J Chem 61(7): 1505–1509

17. Ryan DK, Weber JH (1982) Fluorescence Quenching Titration for Determination of Complexing Capacities and Stability Constants of Fulvic Acid. Anal Chem 54(6): 986–990

18. Saar RA, Weber JH (1979) Complexation of cadmium (II) with water and soil derived fulvic acids: effect of pH and fulvic acid concentration. Canadian J Chem 57(11): 1263–1268

19. Saar RA, Weber JH (1980) Lead (II) fulvic acid complexes. Conditional stability constants solubility and implications for lead (II) mobility. Environ Sci Technol 14(7): 877–880

20. Saha SK, Dutta SL, Chakravarti SK (1979) Polagrographic study of metal–humic acid interaction. Determination of stability constants of $Cd-$ and $Zn-$ humic acid complexes at different pH. J Indian Chem Soc 56(11): 1128–1134

21. Shuman MS, Cromer JL (1979) Copper association with aquatic fulvic and humic acid. Estimation of conditional formation constants with a titrimetic anodic stripping voltammetry procedure. Environ Sci Technol 13(5): 543–545

22. Sposito G (1981) Trace metals in contaminated waters. Environ Sci Technol 15(14): 396–403

23. Tokareva GI, Kolosova IV, Goncharova TO (1983) Vzaimodeystvie ionov Cu(II) s hyminovymi kislotami i razlichnymi tractsiyami fulvokislot (Interaction of Cu^{2+} ions with humic acids and fulvic acids different factions). Hydrochemical materials (58): 88–101

24. Van der Berg CMG, Kramer JR (1979) Determination of complexing capacities of ligands in natural waters and conditional stability constants of the copper complexes by means of manganes dioxide. Analyt Chim Acta 106(1): 113–120

25. Varshal GM, Buachidze NS (1983) Issledovanie sosushchestvuyushchikh form rtuti (II) v poverkhnostnych vodakh (Study coexisting forms of mercury (II) in surface water). Anal Chem J 38 (12): 2155–2167

26. Varshal GM, Velukhanova TK, Koshcheeva IYa at all (1983) Izuchenie khimicheskikh form elementov v poverkhnostnykh vodakh (Study of chemical forms of elements in surface water). Ana Chem J 38(9): 1590–1600

Table 15 Dependence of normal oxygen concentration (C_0) in water upon temperature

Temperature °C	Normal oxygen concentration C_0, mg O_2/L									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	14.65	14.61	14.57	14.53	14.49	14.45	14.41	14.37	14.33	14.29
1	14.25	14.21	14.17	14.13	14.09	14.05	14.02	13.98	13.94	13.90
2	13.86	13.82	13.79	13.75	13.71	13.68	13.64	13.60	13.56	13.53
3	13.49	13.46	13.42	13.38	13.35	13.31	13.28	13.24	13.20	13.17
4	13.13	13.10	13.06	13.03	13.00	12.96	12.93	12.89	12.86	12.82
5	12.79	12.76	12.72	12.69	12.66	12.52	12.59	12.56	12.53	12.49
6	12.46	12.43	12.40	12.36	12.33	12.30	12.27	12.24	12.21	12.18
7	12.14	12.11	12.08	12.05	12.02	11.99	11.96	11.93	11.90	11.87
8	11.84	11.81	11.78	11.75	11.72	11.70	11.67	11.64	11.61	11.58
9	11.55	11.52	11.49	11.47	11.44	11.41	11.38	11.35	11.33	11.30
10	11.27	11.24	11.22	11.19	11.16	11.14	11.11	11.08	11.06	11.03
11	11.00	10.98	10.95	10.93	10.90	10.87	10.85	10.82	10.80	10.77
12	10.75	10.72	10.70	10.67	10.65	10.62	10.60	10.57	10.55	10.52
13	10.50	10.48	10.45	10.43	10.40	10.38	10.36	10.33	10.31	10.28
14	10.26	10.24	10.22	10.19	10.17	10.15	10.12	10.10	10.08	10.06
15	10.03	10.01	10.09	9.97	9.95	9.92	9.90	9.88	9.86	9.84
16	9.82	9.79	9.77	9.75	9.73	9.71	9.69	9.67	9.65	9.63
17	9.61	9.58	9.56	9.54	9.52	9.50	9.48	9.46	9.44	9.42
18	9.40	9.38	9.36	9.34	9.32	9.30	9.29	9.27	9.25	9.23
19	9.21	9.19	9.17	9.15	9.13	9.12	9.10	9.08	9.06	9.04
20	9.02	9.00	8.98	8.97	8.95	8.93	8.91	8.90	8.88	8.86
21	8.84	8.82	8.81	8.79	8.77	8.75	8.74	8.72	8.70	8.68
22	8.67	8.65	8.63	8.62	8.60	8.58	8.56	8.55	8.53	8.52

(continued)

Table 15 (continued)

Temperature °C	Normal oxygen concentration C_0, mg O_2/L									
23	8.50	8.48	8.46	8.45	8.43	8.42	8.40	8.38	8.37	8.35
24	8.33	8.32	8.30	8.29	8.27	8.25	8.24	8.22	8.21	8.19
25	8.18	8.16	8.14	8.13	8.11	8.11	8.08	8.07	8.05	8.04
26	8.02	8.01	7.99	7.98	7.96	7.95	7.93	7.92	7.90	7.89
27	7.87	7.86	7.84	7.83	7.81	7.80	7.78	7.77	7.75	7.74
28	7.72	7.71	7.69	7.68	7.66	7.65	7.64	7.62	7.61	7.59
29	7.58	7.56	7.55	7.54	7.52	7.51	7.49	7.48	7.47	7.45
30	7.44	7.42	7.41	7.40	7.38	7.37	7.35	7.34	7.32	7.31

Atmospheric pressure 760 Mmhg; O_2 (%) = Cx · 100 · 760/ C0 · p; Cx—oxygen concentration found experimentally, mg O_2/L; p—atmospheric pressure during water sampling, Mmhg

Table 16 Maximum permissible concentrations (MPC) of harmful substances for fishery water reservoirs

Sr. No.	Substance	MPC, mg/L
1	Alkamon OS-2 (a mixture of quaternary ammonium salts of high molecular fatty compounds)	0.012
2	Monoalkyl sulfate Al surfactant	0.2
3	Aluminum potassium sulphates	0.63 (0.04 as per Al)
4	Ammonium	0.05
5	Ammonium dichromate	0.05
6	Ammoniacals (NH_4^+)	0.5 (0.39 as per N)
7	Acetaldehyde	0.25
8	Acetate ion (sodium acetate)	0.4
9	Benzene	0.5
10	Bromo-benzene	0.0001
11	Vanadium	0.001
12	Hexane	0.5
13	Hexachlorane	None
14	Hydroquinone	0.001
15	Humic acids	0.2
16	Technical DDT	None
17	N_I N-Diethylaniline	0.0005
18	4-nitro-N_I N-Diethylaniline	0.001
19	Dimethylamine	0.005
20	2,6-Dimethylaniline	0.03
21	Dinitrometylfenol	0.002
22	3,5-Anilotic acid	0.2
23	2,4-Dinitrophenol	0.0001
24	2,4-Dinitrochlorobenzene	0.01
25	3,4−Dichloraniline	0.001
26	2,5−Dichloronitrobenzene	0.01
27	Sodium dichromate	0.05
28	Diethanolamine	0.01
29	Diethylamine	0.01
30	Iron (Fe^{2+})	0.005
31	Isopropylbenzene	0.1
32	IKN-4 (synthetic surfactant's aqueous emulsion)	0.05
33	Cadmium (Cd^{2+})	0.005
34	Potassium (K^+)	50
35	Potassium phosphate monobasic KH_2PO_4	5.0 (1.1 as per P)
36	Calcium (Ca^{2+})	180
37	Calcium phosphate monobasic $Ca(HPO_4)_2$	7.5 (2.0 as per P)
38	Karbofos	None

(continued)

Table 16 (continued)

Sr. No.	Substance	MPC, mg/L
39	Cobalt (Co^{2+})	0.01
40	Ammonium lignosulfonate	1.0
41	Magnesium (Mg^{2+})	50
42	Mangan (Mn^{2+})	0.01
43	n-Butyraldehyde	0.24
44	Metaphos	None
44	O, O-dimethyl−O−thiophosphate	None
46	Copper sulfate	0.004 (0.001 per Cu)
47	Copper (Cu^{2+})	0.001
48	Molybdenum (MoO_4^{2-})	0.0012
49	Monoethanolamine	0.01
50	Monoethylaniline	0.0001
51	Formic acid	1.0
52	Sodium phosphate $Na_3PO_4 \cdot 12H_2O$	12.5 (1.0 as per P)
53	Sodium (Na^+)	120
54	Sodium sulfide Na_2S	0.001
55	Crude oil and petroleum products	0.05
56	Nefras AR 120/200 (mixture of aromatic hydrocarbons)	0.25
57	Nickel (Ni^{2+})	0.01
58	Nitrate ion (NO_3^{-})	40 (9.1 as per N)
59	Nitrite ion (NO_2^{-})	0.08 (0.02 as per N)
60	Nitrobenzene	0.01
61	o-Cresol	0.003
62	OM-84 (synthetic surfactants mixture)	0.25
63	OP-7 (synthetic surfactant)	0.3
64	OP-10 (synthetic surfactant)	0.5
65	Polyethylene glycol (PEG-35)	0.001
66	Polyethylene glycol-115	10.0
67	Progalit DEM 15/100 (non-ionic surfactant in methanol)	0.5
68	Propanide (herbicide)	0.0003
69	Propionic acid	0.6
70	Resorcin	0.004
71	Mercury (Hg^{2+})	0.00001
72	Lead (Pb^{2+})	0.1
73	Urea	80
74	Potassium silicate	2.0
75	Synthanol ALM-7	0.002
76	Synthanol DS-10	0.0005

(continued)

Table 16 (continued)

Sr. No.	Substance	MPC, mg/L
77	Aluminum sulphate	0.5 (0.08 as per Al)
78	Solvasol O (non-ionic surfactant)	0.01
79	Sulphanol NP-5 (sodium sulphonate with alkyl residues)	0.5
80	Sulphates (SO_4^{2-})	1000
81	Sulphonate kerosene-type (sodium sulphonate)	0.5
82	Triethanolamine	0.01
83	Triethylamine	1.0
84	Triethylenetetramine	0.1
85	Trimethylamine	0.01
86	Phenols (carbolic acid)	0.001
87	Phosalone (toxic chemical)	None
88	Formalin	0.25 (0.1 as per formaldehyde)
89	Fluoride ion (F^-)	0.75
90	Chlorides (Cl^-)	300
91	Organochlorine contaminants (DDT, aldrin, etc.)	None
92	Chlorophos and its derivatives	None
93	Chromium (Cr^{6+})	0.001
94	Zink (Zn^{2+})	0.01
95	Cyanides	0.05