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BIOAVAILABILITY AND MIGRATION FEATURES OF METALS IN "BOTTOM SEDIMENTS – WATER" SYSTEM UNDER THE ACTION OF DIFFERENT ENVIRONMENTAL FACTORS

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Abstract. This review considers and summarizes findings of the studies on metals' coexisting forms in bottom sediments of surface water bodies. This makes it possible to assess metals' migration ability in the "bottom sediments – water" system and their potential bioavailability for hydrobionts. The coexisting forms of metals in bottom sediments depend on their chemical properties and the component composition of the solid phase. Metals are distributed among exchangeable, carbonate, oxide, organic and residual fractions of bottom sediments. The highest migration ability is observed for metals contained in the first three fractions. Metals migration from organic and residual fractions hardly ever takes place. The oxygen regime, pH and redox potential, total dissolved solids and water temperature, concentration and component composition of organic substances affect the exchange of metals between bottom sediments and overlying water. The metal mobility in the "bottom sediments – water" system will increase under conditions of climate change. This is because cases of dissolved oxygen deficiency become more common, the total dissolved solids get higher in concentration, and pH and redox potential is reduced. Therefore, the development of methods to reduce metals migration from bottom sediments is a relevant task, which is discussed in the present paper.

Keywords: water body, bottom sediment, metal speciation, metal mobility, environmental factor.

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Introduction

Metal compounds are an integral component of surface waters' chemical composition, which has a noticeable effect on plants and animals' development and functioning. The metal concentration in reservoirs and rivers has risen dramatically due to human impact during the last decades. This poses a hazard to aquatic organisms and to humans as well [1–7]. Under present conditions, most surface water bodies are subjected to anthropogenic pollution by various chemical substances, including metal compounds. It is important to note that metals undergo transformation under environmental factors and accumulate in various components of aquatic ecosystems, especially in the biotic component and bottom sediments, but metals do not undergo degradation like organic substances [6,8–10].

The behaviour of metals in the environment, including in surface water bodies, depends on the coexisting forms of the metals (metal speciation). In turn, the distribution of metals among the abiotic components (water, suspended matter, bottom sediments), as well as their mobility, bioavailability and toxicity for aquatic organisms, depends to a great extent on the coexisting forms of metals [9,11–19]. Therefore, information on the total metals concentration in water and bottom sediments is insufficient to understand their hazard to the hydrobionts' functioning [16]. It is generally known that the metals bioavailability and toxicity are primarily related to such an important property as lability [20]. The results of numerous studies indicate that metals assimilation by hydrobionts is largely related to the activity of free metal ions or its labile fraction, and not its total concentration in water [11,21,22]. The labile fraction of metals includes free (hydrated) ions, complexes with inorganic ligands and, possibly, some part of weakly bound metals in the composition of organic complexes that dissociate when the equilibrium is disturbed [20,21,23]. It is believed that stable complexes of metals with organic ligands belong to the non-labile fraction.

In their majority, they are usually not bioavailable, in particular, this applies to high-molecular weight organic complexes.

Bottom sediments are an important part of surface water bodies, that significantly affect the ecological state of aquatic systems and, in particular, the quality of the aquatic environment as a habitat for hydrobionts [1,19]. Bottom sediments facilitate the aquatic environment's self-purification from various pollutants, including metal compounds. Suspended particles with chemical compounds adsorbed on their surface continually precipitate onto bottom sediments and are deposited there. At the same time, iron and manganese oxyhydroxides, which are part of the suspended substances, play a significant role in the adsorption of chemicals, including metals [24–26]. However, one cannot consider self-purification of the aquatic ecosystem as a whole, since one of its links (components) remains polluted. Bottom sediments are marked by much higher metal concentrations compared to the water phase. Many researchers for good reason consider bottom sediments to be an indicator of surface water bodies contamination with metal compounds [17,27]. Metal binding in the bottom sediments occurs primarily due to precipitation, ion exchange or adsorption [28,29]. Precipitation, in its turn, is associated with hydroxides, carbonates, silicates, phosphates, and sulphides (in anoxic conditions). Ion exchange involves clay substances present in bottom sediments. Metals are adsorbed on the surface of finely dispersed particles of oxides and hydroxides, which are also found in suspended substances and bottom sediments.

Contaminated bottom sediments affect both the quality of the overlying water that comes into contact with them, and metal bioassimilation and bioaccumulation in aquatic organisms. This leads to long-term consequences for human and ecosystem health [30]. There is evidence that organisms in direct contact with bottom sediments, such as rooted macrophytes, are more affected by metals accumulated in bottom sediments than by the dissolved form thereof [31].

Bottom sediments should be considered as a serious source of secondary water pollution by chemicals, including metals, due to their migration into water under favourable conditions (factors and processes that affect their migration mobility) [25,32–37].

A number of papers state that metal mobility in bottom sediments usually varies [6,38,39]. Most metals in uncontaminated bottom sediments are part of their mineral (crystalline) structure, which is distinguished by low solubility, and therefore they are unavailable. In the case when bottom sediments are contaminated, a significant part of metals is in fractions which can desorb chemicals, as well as metals, thus leading to certain physicochemical changes [1,40]. Such metals have much higher mobility, and therefore they pose a certain hazard to aquatic organisms, as well as to humans using water for drinking purposes, because metals become bioavailable [4,41]. This is especially true for the exchangeable, carbonate and oxyhydroxides fractions of metals in bottom sediments [3,40–42].

Measuring the total metal content in the bottom sediments is usually not very informative, since without assessing their mobility and bioavailability, a correct determination of their hazard to aquatic organisms is not possible [9,43,44]. The chemical forms of metals in the bottom sediments of lakes, reservoirs and rivers are diverse and include a number of fractions [13,45,46].

– water-soluble fraction, which includes free ions, inorganic or organic complexes:

– exchangeable fraction;

– fraction consisting of inorganic compounds, including insoluble sulphides;

– fraction associated with high-molecular weight humic substances;

– fraction represented by amorphous and crystalline oxyhydroxides of iron and manganese;

– fraction represented by metals in the structure of crystal lattices of primary minerals.

Studying the metals share in each of these fractions is important for assessing their mobility in bottom sediments and the ability to exchange in the "bottom sediments – water" system, as well as their bioavailability [3,17,34,47]. Undoubtedly, these characteristics will differ depending on the metals' chemical properties, as well as the bottom sediments' composition and particle size distribution [17,26,34,48–50].

Research on the coexisting forms of metals in bottom sediments is becoming more and more relevant. The main goal is to establish the metal mobility and ability to pass from bottom sediments to overlying water [1,9,17,25,35,43,44,47,51–55]. There are various ways to extract metals from bottom sediments using different chemical reagents [25,26,35,51]. These methods can have five stages with modification [26,56] or four stages, as recommended by the General reference office of the European Commission (BCR - Bureau Commune de Reference of the European Commission), including modified ones

[15,35,57–62], or even six stages [63–65]. In most cases, exchangeable, carbonate, oxide (associated with Fe and Mn oxyhydroxides), organic/sulphide, and residual fractions are extracted [53,56]. Sometimes exchangeable and carbonate fractions are combined into one fraction (according to the BCR method). In this case, we have four factions [35,40,60]. There are also more detailed characteristics of metal fractions in bottom sediments, in particular, the oxide fraction of metals, divided into amorphous and crystalline components. The metal fraction in the composition of humic substances is also distinguished. It is known that metals of exchangeable, carbonate and oxide fractions have the greatest mobility, since changes in the bottom layer of overlying water (increased total dissolved solids, decrease in water pH and redox potential, anaerobic conditions, *etc.*) contribute to the release of metals from bottom sediments. At the same time, the mobility of metals in organic/sulphide and residual fractions is usually low [1,47].

Thus, the aim of this paper is to summarize and analyse the results of research on the metals forms in the bottom sediments of surface water bodies to assess their migration ability in the "bottom sediments - water" system and potential bioavailability for hydrobionts.

Background

Specifics of metals distribution among different fractions of bottom sediments of surface water body

The data on metal fractions shares in bottom sediments of reservoirs and rivers from different regions of the world are summarized below (Table 1). One can see that the ratio of the studied fractions of the same metal in bottom sediments of surface water bodies from different regions may have certain specifics. The distribution of copper among different fractions of bottom sediments can be a clear confirmation of this. In some cases, most of the copper is concentrated in the composition of oxide/sulphide and residual fractions, which is typical for Goretskie and some other lakes in Poland, reservoirs of the Dnipro Cascade (Ukraine), the Niger River Delta (Nigeria), Naivasha Lake (Kenya) and some other surface water bodies (see Table 1). The maximum share of copper in the organic/sulphide fraction of bottom sediments is most often around 50–55% of Cu_{total}. However, it may reach as much as 85% of Cu_{total} in the bottom sediments of some water bodies (see Table 1). It depends on the organic matter concentration and presence of sulphide ions in bottom sediments, since Cu(II) is actively bound by humic acids, and also forms sparingly soluble sulphides. The share of copper in the organic/sulphide fraction of the Dnipro reservoirs' bottom sediments (Ukraine) can vary within the range of 40–77% of Cu_{total} [33,66,67]. In this regard, it should be noted also that there is a high concentration of organic matter in silt sediments (approximately 6.5–12%) [68]. The residual fraction of bottom sediments is characterized by a fairly wide range of copper content – 27.2–89.6% of Cu_{total} (see Table 1).

There are some cases where a significant part of copper is concentrated in the oxide fraction (Buriganga River (Bangladesh), Po River (Italy), or the first three fractions (rivers of Spain, Canadian lakes, Tamagawa River (Japan), Roosevelt Lake (U.S.A.) and some others). To some extent, this also applies to lead, which is mainly found in the composition of the first three fractions (Goretski Lake in Poland, the Buriganga River (Bangladesh), Canadian lakes, the Tamagawa River (Japan), Chapala Lake (Mexico), the Niger River Delta (Nigeria), Yellow River (China), *etc.*) or in organic/sulphide and residual fractions (some reservoirs of the Dnipro Cascade (Ukraine), rivers of Spain, Naivasha Lake (Kenya), some lakes of Poland, Poxim River estuary (Brazil); see Table 1).

Table 1

Forms of metals found in bottom sediments (BS) of surface water bodies.

Water bodies, country	*The thickness of the BS layer, cm*	*M*	*C_{total}, mg/kg of dry weight*	*Share of metal fractions, % M_{total}*					*Lit. ref.*
				I	*II*	*III*	*IV*	*V*	
Goreckie Lake, Poland	0–10	Fe*	9150	×	×	14	40	46	[69]
		Mn*	350	11	41	31	6.1	9.9	
		Zn*	64	8.6	16	58	16	1.9	
		Ni*	13	×	3.8	20	12	66	
		Cu*	12	×	×	2.9	16	83	
		Pb*	47.5	0.8	21	34	10	34	
		Cd*	3.4	×	18	28	43	5.9	
		Cr*	9.7	×	×	7.2	38	56	

Continuation of Table 1

Water bodies, country	*The thickness of the BS layer, cm*	*M*	C_{total}*, mg/kg of dry weight*	*Share of metal fractions, %* M_{total}					*Lit. ref.*
				I	*II*	*III*	*IV*	*V*	
Reservoirs of the Dnipro (Upper Beif), Ukraine:									[47,67,70]
Kyivske	0–2	Cd*	0.8	42	16	26	×	16	
		Pb*	27.8	×	×	43	10	47	
		Mn*	360	10.5	18.4	50.5	1.0	19.6	
		Co*	8.1	0.0	0.0	14.7	14.7	70.6	
		Cu*	35.9	0.7	0.7	8.9	50.2	39.6	
		Zn*	69.2	0.0	10.3	65.9	6.9	16.9	
Kanivske	0–2	Cd*	1.6	10	10	25	25	30	
		Pb*	55.9	6	5	15	30	44	
		Mn*	1598	8.1	2.0	74.6	9.0	6.1	
		Co*	19.6	12.2	20.4	32.6	10.2	24.5	
		Cu*	38.4	1.8	1.2	4.9	44.0	47.5	
		Zn*	76.8	1.2	0.6	36.4	17.3	44.5	
Kremen-chukske	0–2	Cd*	1.8	60	5	×	×	35	
		Pb*	47.1	5	7	21	20	47	
		Mn*	1199	0.8	1.0	85.5	4.4	8.2	
		Co*	21.4	29.9	5.6	23.8	7.9	32.8	
		Cu*	26.4	1.5	0.0	7.2	24.6	66.7	
		Zn*	59.9	0.0	0.8	52.7	8.8	37.7	
Kamianske	0–2	Cd*	0.8	74	×	26	×	×	
		Pb*	40.4	0	11	25	30	34	
		Mn*	590.4	19.0	9.1	61.8	3.6	6.3	
		Co*	12.7	0.0	0.0	19.7	10.2	70.1	
		Cu*	68.0	1.9	0.3	19.1	51.5	27.2	
		Zn*	59.7	3.5	5.9	52.9	12.6	25.1	
Dniprovske	0–2	Cd*	3.6	50	×	36	×	14	
		Pb*	106.0	0	4	42	28	26	
		Mn*	2750	4.5	1.4	83.6	6.1	4.3	
		Co*	16.8	13.1	0.0	36.3	7.7	42.9	
		Cu*	70.8	1.8	0.3	12.4	40.0	45.5	
		Zn*	251.2	0.6	0.2	71.5	5.6	22.1	
Kakhovske	0–2	Cd*	1.7	29	5	36	×	30	
		Pb*	41.0	×	×	51	24	25	
		Mn*	1582	0.9	0.3	91.7	3.5	3.5	
		Co*	32.1	0.0	6.4	42.5	8.5	42.6	
		Cu*	48.7	1.6	0.8	8.2	22.6	66.7	
		Zn*	60.6	0.5	0.8	55.3	6.3	37.1	
Buriganga River, Dhaka, Bangla-desh	0–15	Cr*	105–4249	8**		65	16	11	[71]
		Pb*	56–1592	13**		80	5	3	
		Zn*	129–3002	54**		34	2	10	
		Cu*	30–459	9**		64	13	15	
		Ni*	56–244	24**		39	11	25	
		Co*	19–58	22**		46	18	13	
Pearl River Estuary, China	0–10	Cu*	46.8±17.0	0.4	5.2	10.8	19	64.6	[24]
		Pb*	47.9±13.7	0.6	9.9	37.9	15.4	36.2	
		Zn*	140±42	0.1	4.8	30.1	5.7	59.3	
Po River, Italy	Not indicated	Cd	1.25–3.70	33–58**		16–39	1–3	11–46	[58]
		Cu	31.7–187	1.2–8.5**		34–64	19–22	14–41	
		Zn	178–645	25–43**		16–27	7.5–14	19–46	
		Ni	52.3–161	13–27**		34–46	14–20	13–39	
		Pb	32.0–98.5	14–28**		29–45	18–29	7–19	

Continuation of Table 1

Water bodies, country	*The thickness of the BS layer, cm*	*M*	*C_{total}, mg/kg of dry weight*	*Share of metal fractions, % M_{total}*					*Lit. ref.*
				I	*II*	*III*	*IV*	*V*	
Tinto and Odiel rivers; Canal Padre Santo, Spain	2–20	Zn*	1233	46–64**		12–28	4–18	8–22	[30]
		Cd*	9.98	32–90**		4–16	5–20	1.5–18	
		Pb*	572	1.5–4**		5–40	6–60	16–84	
		Cu*	2074	15–44**		4–36	18–70	8–24	
		As*	351.3	1–12**		6–52	1.5–14	28–98	
Naivasha Lake, Kenya	Not indicated	Cu*	62.1	1.7	1.8	1.4	5.5	89.6	[72]
		Fe*	38919	×	0.8	0.8	6.2	92.2	
		Mn*	1619	12.2	28.0	7.0	7.9	45.0	
		Pb*	117.3	2.3	1.6	6.8	5.3	84.0	
		Zn*	247.4	0.7	5.6	1.6	21.5	79.5	
Lakes Diamond, Fairy, Peninsula, Canada	100 (with sampling every 10 cm)	Ni	There are no corresponding data for all metals	4–20^{+}		24–46	6–15	39–50	[48]
		Cr		3–23^{+}		5–29	13–20	32–68	
		Al		3–46^{+}		16–27	3–5	31–82	
		Fe		13–53^{+}		24–37	3–11	20–47	
		Mn		20–35^{+}		23–42	3–6	30–50	
		Cd		66–90^{+}		8–31	1	2–5	
		Hg		19–36^{+}		19–42	23–63	0–2	
		Pb		33–61^{+}		17–48	0–2	16–29	
		Cu		38–50^{+}		21–46	6–20	4–10	
		Zn		36–63^{+}		18–38	6–12	6–15	
Canal flowing into the Danube River, Serbia	30–500	Zn*	55.8	2.7	8.7	29.0	3.2	56.3	[26]
		Cu*	16.8	1.7	3.0	52.4	2.9	39.8	
		Pb*	11.6	3.7	25.0	28.0	6.9	36.8	
		Ni*	20.9	1.5	12.5	35.0	12.6	38.5	
		Cr*	12.5	2.1	2.5	23.0	5.9	66.6	
		Cd*	1.07	4.7	5.6	57.0	6.5	26.2	
		Fe*	17155	0.02	2.5	32.6	2.2	62.8	
		Mn*	395	4.2	59.0	13.1	3.5	20.1	
		Hg*	0.07	1.4	5.7	8.6	×	85.7	
		As*	0.24	×	41.7	28.8	×	29.2	
Tamagawa River, Japan	0–10	Cr	17.0–161	0–9		18–20	12–40	32–68	[44]
		Ni	10.2–71.2	2.5–3.5		20–39	23–58	20–36	
		Cu	9.8–160	69–74.5		16–22	5–7	3.5–4.0	
		Zn	36.4–298	11.5–15.0		47–53	15–20	19–23	
		Pb	6.9–71.4	7–23		54–57	5–9	17–29	
Chapala Lake, Mexico	0–10	Pb	11.9–59.7	×	3–10	50–70	2–46	23–62	[52]
		Cr	22.8–137	0.5–1.5	0.5–1.5	0.5–3.5	1.5–3.5	85–98	
		Mn	0.53–1.01"	×	3–25	18–45	7.5–26	14–60	
		Ni	29–42.2	0.5–3.0	0.5–1.5	3–19	1.5–15	80–86	
		Zn	122–164	0.5–3.0	0–0.5	14–32	1.5–21	60–70	
		Fe	31.6–42.2"	×	0.5–9.5	48–66	3–32	15–23	
Niger delta, Nigeria	0–10	Cd	7.5–46.6	32–48	20–35	10–19	3–6	6–20	[73]
		Cu	0.31–1.8	0.5–5.0	2.5–16	10–12	42–55	22–40	
		Cr	0.8–34.6	0–1.2	0.5–6.0	2.5–20	42–60	24–40	
		Mn	<0.002–1.7	0.5–36	2.5–15	29–52	2.5–20	20–30	
		Pb	4.7–47.5	0.5–4.0	12–52	20–56	1.5–15	17–31	
		Ni	<0.002–36.8	1.5–6.0	5–17	15–32	1.5–16	48–60	
		Zn	<0.002–40.7	1.5–9.5	20–44	20–40	8.5–18	20–36	
Lakes with different anthropogenic load, Poland	0–10	Cu*	4.0–17.4	1.9–2.6	4.4–7.8	7.8–17	37–42	34–46	[6]
		Fe*	1.9–24.4"	<0.09	0.9–1.7	22–30	8–10	58–66	
		Mn*	31.6–541	14–23	10–14	15–41	2.3–3.2	28–49	
		Ni*	5.1–21.9	1.9–4.3	11–15	29–30	10–16	40–41	
		Pb*	3.4–26.1	0.3–2.6	7.1–8.7	1.3–4.5	5–53	37–81	

Continuation of Table 1

Water bodies, country	*The thickness of the BS layer, cm*	*M*	*C_{total}, mg/kg of dry weight*	*Metal fractions shares, % M_{total}*					*Lit. ref.*
				I	*II*	*III*	*IV*	*V*	
Poxim River Estuary, Brazil	0–5	Cd*	0.23±0.17	17.4		13.0	34.8	34.8	[9]
		Cr*	7.98±4.99	16.9		22.2	21.3	40.2	
		Cu*	8.79±3.46	14.8		17.9	31.9	35.5	
		Ni*	1.71±1.44	9.4		21.6	33.3	36.3	
		Pb*	12.04±3.91	18.1		22.2	34.0	25.7	
		Zn*	19.02±11.57	36.3		16.1	12.7	31.8	
Roosevelt Lake, Columbia River, U.S.A.	0–10	Pb	9–1110	2–24		5–80	3–40	4–63	[74]
		Zn	54–26000	14–40		22–50	5–26	13–66	
		Cu	10–2800	5–24		10–36	2–80	6–82	
		Cd	0.2–7.7	18–66		18–46	5–56	3–20	
Yellow River, China	0–20	As*	13.7–48.1	0.42	1.33	8.72	24.04	65.49	[34]
		Pb*	26.4–77.7	0	7.52	63.25	10.62	18.61	
		Zn*	89.8–202	0.35	4.91	32.09	13.53	49.12	
		Cr*	41.5–128	0.40	0.55	9.88	3.69	85.48	
		Cu*	29.7–102	0.35	12.22	21.13	10.67	55.63	
		Mn*	773–1460	0.95	19.32	20.31	4.83	54.59	
Korle Lagoon, Ghana	0–15	Cd*	10.15±0.2	0.88		0.24	94.99	3.89	[75]
		Cu*	18.75±6.64	36.09		4.89	50.82	8.20	
		Cr*	44.85±2.33	12.73		12.72	61.96	12.59	
		Ni*	11.71±0.48	21.23		4.75	62.94	11.08	
		Pb*	29.95±9.16	50.80		24.73	19.14	5.33	
		Zn*	168.77±53	57.01		28.86	10.47	3.66	
		Hg*	0.20±0.01	1.35		19.17	30.11	49.38	
Rybnik Reservoir, Poland	0–15	Zn	902–1077	43–59		23–30	12–22	3–7	[1]
		Cu	110–681	1–41		2–12	51–85	7–18	
		Pb	73.7–125	0.37–0.68		11–37	51–78	8–13	
		Cd	5.0–16.8	18–46		21–40	16–49	2–3	
		Ni	28.6–47.3	19–34		14–19	27–33	21–33	
		Cr	125–197	0.89–1.0		7–8	60–61	30–31	

*Note: M – metal; * – data on the content of metals in BS and the proportion of their various forms are given as averaged values; ** – total weight portion of adsorbed, exchangeable and carbonate fractions; × – trace metal concentrations or determinations were not carried out; I, II, III, IV, V – respectively, exchangeable, carbonate, oxide, organic/sulphide and residual fractions of metals in bottom sediments. The share of each metal form is calculated to its total content (M_{total}) in bottom sediments. $^{+}$ – fraction of metals associated with humic substances. ″ – g/kg.*

A similar situation of distribution between different fractions of bottom sediments can be typical for other metals. Thus, iron is mainly concentrated in the organic/sulphide and residual fractions of bottom sediments, as can be seen in the case of lakes in Poland, alluvial bottom sediments of the Danube River (Serbia), Naivasha Lake (Kenya). This may be due to the fact that iron is actively bound by humic substances into complexes, and also forms poorly soluble sulphides. However, there is evidence that iron is mainly found in the first three fractions (lakes of Canada, Chapala Lake, Mexico). Manganese dominates the composition of the first three fractions, primarily the oxide fraction. That was predictable, because its significant part is contained in suspended particles and bottom sediments. This was confirmed by manganese distribution among different fractions of bottom sediments in Goretskie and some other lakes of Poland, reservoirs of the Dnipro Cascade (Ukraine), alluvial bottom sediments of the Danube River (Serbia), Canadian lakes, and the Niger River delta (Nigeria). Zinc usually predominates in the composition of the oxide fraction (Goretskie Lake, Poland; reservoirs of the Dnipro Cascade; Tamagawa River, Japan; Roosevelt Lake, U.S.A.) or the first two fractions (rivers of Spain, lakes of Canada, Buriganga River, Bangladesh). The prevalence of zinc in the composition of the oxide fraction is associated with its active adsorption by iron and manganese oxyhydroxides. There are cases when zinc dominates in the composition of the residual fraction (Pearl River estuary (China), Naivasha Lake (Kenya), alluvial bottom sediments of the Danube River (Serbia), Chapala Lake (Mexico), Yellow River (China).

However, there are certain general patterns of metals distribution among different fractions of bottom sediments. Let's consider some of them in more detail. For example, cadmium is mainly concentrated in exchangeable and carbonate fractions, or in exchangeable, carbonate and oxide fractions. Moreover, this is typical for surface water bodies located in different regions of the world (see Table 1). This means that this metal is mobile. An increase in total dissolved solids, a decrease in pH and redox potential are important factors that significantly affect the exchange of cadmium in the “bottom sediments - water” system. Due to the mentioned factors, the migration of cadmium from the bottom sediments is significantly increased. Therefore, its concentration and bioavailability in overlying water can increase, which poses a significant environmental risk for aquatic life. This is stated in a number of papers devoted to the problem of metal migration in the “bottom sediments - water” system [1,4,37,70]. Manganese is also referred to mobile metals, since this metal is most often found in exchangeable, carbonate and oxide fractions [35,47]. An intensive supply of manganese from the bottom sediments occurs due to prolonged anoxia and a decrease in redox potential and pH in the hypolimnion of lakes and reservoirs. As a result, the concentration of dissolved manganese in overlying water increases significantly, reaching milligram values per litter [76]. Such an increase in the surface waters of Ukraine was 25–50-fold [33,77]. Another example is copper. This metal is most often found in the organic/sulphide and residual fractions, so its mobility usually remains low.

A significant part of metals in river bottom sediments is concentrated mainly in the first three fractions (exchangeable, carbonate and oxide), as indicated by the research results (see Table 1). They are very often concentrated in the oxide fraction, which is explained by their adsorption on freshly formed iron and manganese oxides. The latter can then be deposited in the mouth of rivers or estuaries when the current slows down. This is how river bottom sediments differ from lake sediments, although this is not always evident. It is difficult to clearly answer the question about the metals’ migration ability in river bottom sediments. It can significantly increase, when oxygen is in deficiency and water pH shifts towards acid conditions, although this is less typical for river waters than for lakes and reservoirs, especially their deep-water areas (hypolimnion of lakes).

Therefore, it can be stated that the metal mobility in bottom sediments and their migration ability significantly depends on the distribution between different fractions of the bottom sediments’ solid phase [35,53]. Thus, metals from the exchangeable fraction of bottom sediments are released when the ionic strength of water (total dissolved solids value) changes. Metals from this fraction are available for plants. Metals of the carbonate fraction migrate from the bottom sediments when the water pH decreases. Metals associated with oxyhydroxides can change their mobility when the oxidizing conditions are increased or decreased at the bottom sediments – water phase interface. Metals of the organic/sulphide and residual fractions have the lowest mobility. Assessing bottom sediments toxicity based on metallic form concentrations alone is considered problematic and bioassays are required [1].

The most important factors and processes affecting metals migration in the “bottom sediments – water” system

The metals exchange in the “bottom sediments – water” system depends on some physical, chemical and biological factors and processes that are observed at the boundary of solid and liquid phases (Figure 1). Important chemical and biological processes include adsorption and desorption, precipitation and co-precipitation with iron and manganese oxides and hydroxides, complexation with organic substances, formation of sulphides and carbonates, as well as organic substances mineralization and immobilization [78,79]. The dissolved oxygen concentration, redox potential (Eh) and pH in the boundary of “bottom sediments – water" system are the most important factors governing the mentioned processes [68].

Effect of total dissolved solids on the migration of metals in the “bottom sediments – water” system

An increase in total dissolved solids concentration affects the migration mobility of metals from the exchangeable fraction of bottom sediments. This is due to the competition of Na^+, K^+, Ca^{2+} and Mg^{2+} ions for sorption centers, as well as ion exchange with heavy metals adsorbed on the surface of suspended substances and bottom sediments. They also reduce the complexing ability of humic substances with respect to metals [10,13,80].

An increase in fresh water salinity can enhance the metals bioavailability in bottom sediments due to metals removal from bottom sediments composition [78,79], concerning metals with pronounced toxic properties, their entry into overlying water should be considered as an undesirable phenomenon. It was experimentally proven that a rise in water salinity due to the addition of 0.5, 2.5, and 5.0 g of NaCl/L led to an increase in the cadmium concentration in water due to its migration from bottom sediments, and, accordingly, to an increase in the aquatic environment toxicity [80]. The concentration of cadmium increased significantly in overlying water, even at the lowest salinity (0.5 g NaCl/L). It is noted that the risk of increasing the concentration of cadmium can be significantly reduced due to its precipitation in the form of sulphide.

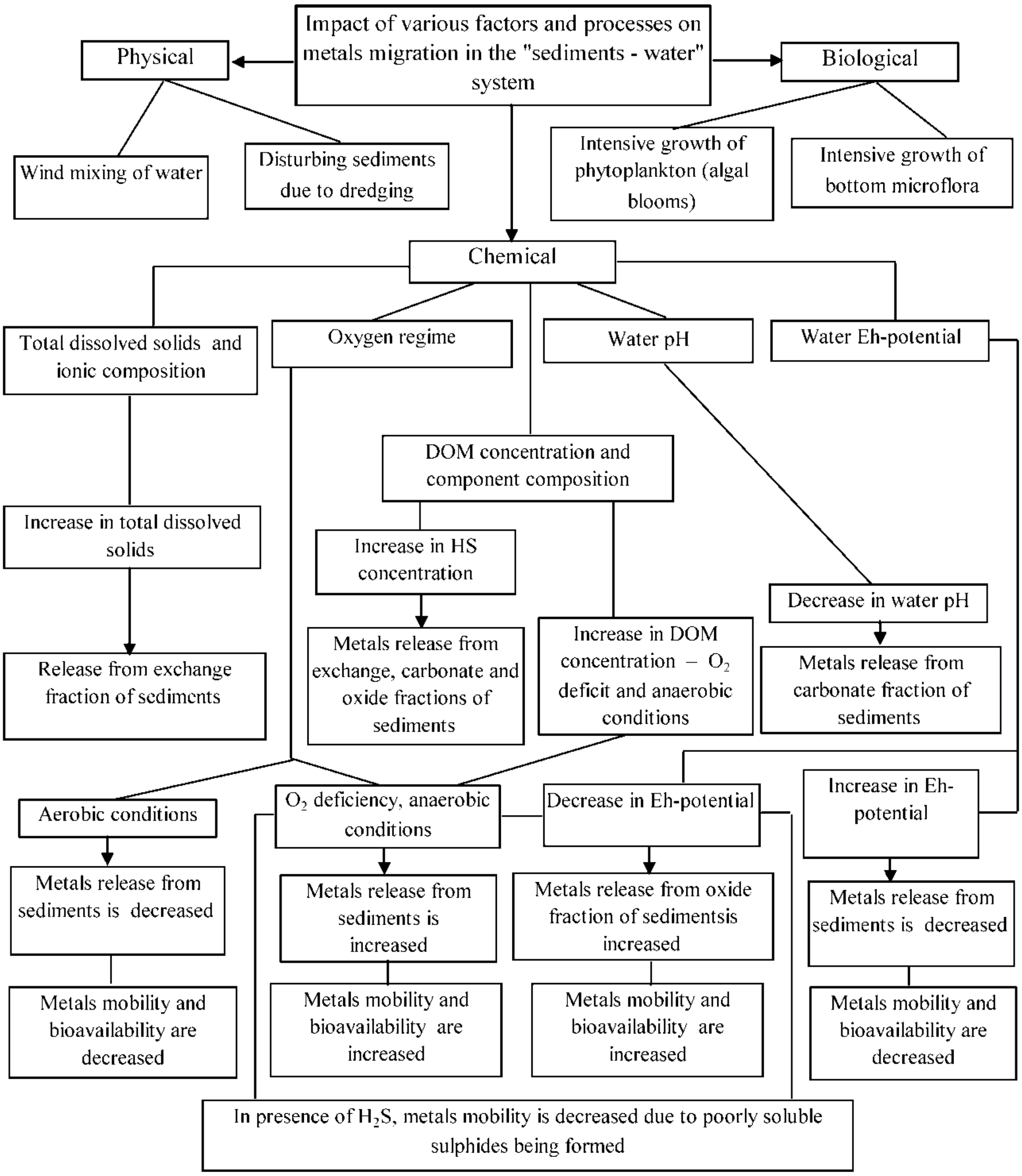
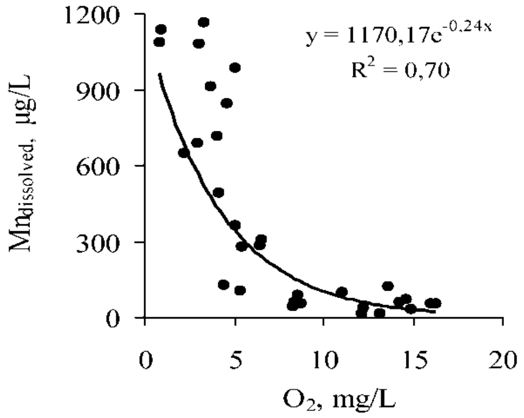


Figure 1. The most important factors and processes affecting the migration ability of metals in the system "bottom sediments – overlying water", their bioavailability and potential toxicity. (DOM– dissolved organic matter; HS– humic substances). Arrows indicate individual groups of factors and processes that affect the metals' migration in bottom sediments. Lines indicate the list of factors in each group, or the consequences of the influence of processes on the metals' migration mobility and bioavailability in bottom sediments, which can increase or, conversely, decrease.

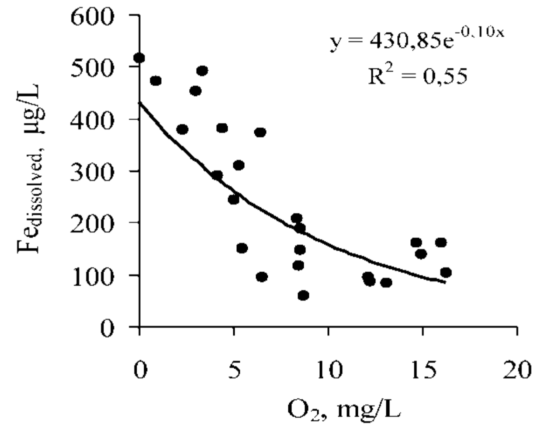
Effect of the oxygen regime and redox potential on the metals migration in the "bottom sediments – water" system

The migration of metals with different degrees of oxidation, primarily manganese and iron, at the bottom sediments – water interface depends on the dissolved oxygen concentration and the *Eh*-potential value. Metals can migrate from the overlying water towards the bottom sediments or vice versa, from the bottom sediments to the overlying water [5,7,25,32,35,68,81–85]. Therefore, under aerobic conditions, metals will migrate towards the bottom sediments, since finely dispersed oxyhydroxides of iron and manganese will be formed in the oxidizing environment, which will precipitate. It should be noted that under aerobic conditions Fe(II) is oxidized to Fe(III) much faster than Mn(II) to Mn(IV) [86]. In anaerobic conditions, on the contrary, Mn(IV) is reduced faster than Fe(III) [87,88]. At the same time, iron and manganese oxyhydroxides are marked by a high adsorption capacity for other metal ions, as well as organic substances, in particular humic substances, therefore, compound complexes (aggregates) capable of sedimentation will be formed [25]. A significant part of manganese and iron in the hypolimnion of lakes and reservoirs at the bottom sediments – water interface migrates into pore water, and then into overlying water under dissolved oxygen deficiency and anaerobic conditions. Under such conditions, Fe(III) and Mn(IV) are reduced to Fe(II) and Mn(II). The research in microcosms showed that that long-term hypoxia contributed to an increase in Pb, Cd, Cu and Cr concentrations in overlying water [45]. The unpublished findings of our studies also confirm the effect of dissolved oxygen content on the dissolved manganese and iron concentrations in surface waters (Figure 2).

It is necessary to pay considerable attention to measuring the value of the *Eh*-potential, since it governs whether oxidizing or reducing conditions are formed in the bottom horizon of water and on the surface of bottom sediments. The gradation of the *Eh*-potential indicators and the correspondence to these indicators of the redox conditions that are formed have been studied [35]. It is noted that oxidizing conditions dominate the water environment at *Eh*-potential values exceeding +414 mV, and therefore the metals migration from bottom sediments should be assessed as low. If the values of the *Eh*-potential are in the range between +414 mV and +120 mV, then moderate reducing conditions are formed. Noticeable migration of iron and manganese from the bottom sediments due to the dissolution of their oxyhydroxides should not be expected under these conditions.



(a)



(b)

Figure 2. The relationship between the concentration of dissolved Mn *(a)*, Fe *(b)* and the concentration of dissolved oxygen in the water of the Opechen' system lakes, Kyiv 2021 (unpublished research results).

At the same time, oxyhydroxides are unstable and begin to dissolve at *Eh*-potential values ranging from +250 to +100 mV. Consequently, iron and manganese migration should be expected to increase, as well as migration of other metals that were adsorbed on their oxyhydroxides surface. The metals migration from bottom sediments reaches maximum values when the *Eh*-potential value of water is -120 mV and below, which indicates that reducing conditions are formed.

Iron and manganese oxyhydroxides are known to regulate the migration of other metal cations adsorbed by them [25,82]. However, their migration significantly depends on the concentration of sulphides, which increases in conditions of prolonged hypoxia [45]. Since corresponding metal sulphides can form, their migration from bottom sediments is significantly reduced, in particular, this applies to cadmium, copper, zinc and some other metals [45,82,89]. Anaerobic conditions are favourable only for iron and manganese migration from bottom sediments, while the migration of other metals (Zn, Cu, Cr, Pb) occurs with greater intensity in aerobic conditions.

In the case when the metals are mainly in the composition of organic/sulphide and residual fractions, then the water pH (7, 8, 9), dissolved oxygen concentration (1.0 and 5.0 mg/L), Eh-potential and temperature (4, 16, 25°C) hardly make any impact upon the metals migration from bottom sediments. This was shown experimentally using river bottom sediments, in which most of Cr, Ni, Cu, Zn, Cd, and Pb were found in the residual fraction [90].

The effect of pH on the metals migration in the "bottom sediments – water" system

The metals migration in the system "bottom sediments – water" depends significantly on the pH value at the boundary between the water phase and bottom sediments [35,81,89–91]. The pH values affect the decrease or increase in the solubility of metals in the bottom sediments. A rise in pH values causes metals to adsorb and precipitate, while a decrease in pH values enhances metal migration due to metal bonds weakening in bottom sediments [10]. The negative charge on the surface of organic substances, in particular humic substances, clay particles, iron and manganese oxyhydroxides, as well as sulphides, which act as active adsorbents of metal ions, decreases at low pH values [13]. Ultimately, a decrease in pH leads to an increase in the rate of redox processes. First of all, this concerns the reduction of Fe(III) and Mn(IV) in oxyhydroxides to Fe(II) and Mn(II), respectively.

It was found that the rate of Zn, Cu, Cd, Cr and Pb migration was significantly greater at pH 4–7 than at pH 8–10 [89]. For example, the maximum Zn concentration in overlying water at pH 4.0 was 0.11 mg/L, and at pH 7.0 it was only 0.01 mg/L. The highest Zn concentration in alkaline medium at pH 8.0 and 10.0 was 0.02 and 0.03 mg/L respectively. The pH of natural water is unlikely to drop to 4.0, therefore no significant increase in the metals concentration with pH decrease should be expected. A considerable increase in the Cd, Pb, Zn, Mn and Fe concentration with a decrease in pH to 6.0±1.0 was shown in experimental conditions with the bottom sediments of Macquarie Lake (New South Wales, Australia), which are contaminated with heavy metals [81]. Thus, the Cd concentration in water increased from <3 μg/L to 40–50 μg/L on the 19th and 21st days of the experiment, Ni – to 100–370 μg/L on the 19th and 20th days of the experiment, and Zn – up to 1600 μg/L. A decrease in the pH of the overlying water contributes to the dissolution of mainly the carbonate fraction of bottom sediments and the outward migration of metals [89]. The migration of aluminium from the bottom sediments also increases significantly with a decrease in water pH [25,92]. Lakes acidification in northern countries is often accompanied by an increased dissolved aluminium content in water and its negative impact on hydrobionts [93,94].

The metals' migration ability in the "bottom sediments – water" system is influenced to a certain extent by seasonal fluctuations in the chemical composition of surface waters, in particular their pH. This impact is most relevant to lakes and reservoirs, because intense photosynthesis causes the surface water to have a much higher pH value than the bottom layer. If this applies to the lakes and reservoirs' hypolimnion, then the difference in water pH values of surface and bottom layers becomes very noticeable in the summer [95,96]. The water in the bottom layer quickly loses oxygen due to organic matter oxidation. It creates anaerobic conditions facilitating the migration of metals from the bottom sediments. This was mentioned above.

The effect of temperature on metals migration from bottom sediments

Temperature is one of the important factors that significantly affect the rate of chemical reactions. As the research results show, the migration of metals from the bottom sediments increases significantly when the water temperature rises [89]. Other researchers found that the effect of temperature had an indirect nature on the migration of metals from bottom sediments and could be insignificant [90]. This is due to the fact that temperature affects bacterial activity, the dissolved oxygen concentration, the rate of redox reactions and diffusion of molecules. Changing these parameters can impact the migration of metals from bottom sediments. Therefore, the effect of temperature on the migration of heavy metals is ambiguous and complex.

The influence of biological factors on the metal's migration from bottom sediments

Studies on the effects of biological factors on the release of metals from bottom sediments showed that an important role in this process was played by bacteria, in particular sulphur-oxidizing bacteria such as *Thiobacillus thiooxidans* and

Thiobacillus thioparus [97–99]. Cu and Zn were removed from the bottom sediments to the greatest extent among the studied metals (Cu, Zn, Pb, Cr), while Pb and Cr migration was insignificant [97]. This is due to the fact that at a high concentration of sulphate ions, a poorly soluble $PbSO_4$ precipitate was formed, and Cr was mainly in the inaccessible crystal lattice of minerals. Sulphur-oxidizing bacteria decrease the pH of the water environment by producing acid, which contributes to metals migration from bottom sediments. Sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* are able to oxidize sulphide minerals and therefore accelerate the release of metals from their composition [91]. Calcite ($CaCO_3$) was dissolved due to acid production by bacteria. However, the migration of various metals from the bottom sediments differed significantly. Due to the fact that copper was mainly in the organic fraction, its migration from bottom sediments was insignificant. Lead was not observed to migrate either, due to low solubility of $PbSO_4$. At the same time, the zinc and cadmium migration from bottom sediments was noticeable due to a pH drop.

Ways to reduce the migration of metals from bottom sediments into overlying water

There are various ways to reduce the flow of metals from bottom sediments [100]. It is important that their use does not cause additional negative consequences on aquatic ecosystems and is not expensive. It can be the covering of bottom sediments with materials that bind pollutants, including metals, and transform them into biota-inaccessible forms. However, in this case, the amount of bottom sediments may increase. Several methods are available for chemical treatment of bottom sediments, but in the authors' opinion they are mainly effective for small water bodies.

Artificial aeration should be considered as one of the effective ways to reduce the migration intensity of many chemicals, including nutrients and metal compounds, from bottom sediments [101–105]. The efficiency of artificial aeration was shown for the Camanche Reservoir (California, U.S.A.), Amisk Lake (Alberta province, Canada), Varese Lake (Italy) and the small Telbin Lake, which is located within the Kyiv city. Enriching the bottom aqueous layer with oxygen prevents the reduction of Fe(III) and Mn(IV) and the dissolution of their oxyhydroxides, and ultimately, the influx of other metals adsorbed by them. Self-purification of the aquatic environment in a natural way in the epilimnion of lakes and reservoirs occurs due to the oxidation of chemicals at high dissolved oxygen concentrations, at presence of free radicals that can be formed with the involvement of H_2O_2, metal ions, and solar radiation [106]. In the hypolimnion, activation of water self-purification can occur due to aeration.

Hypolimnetic oxygenation is one of the ways to reduce metals migration from bottom sediments. It consists in supplying pure oxygen to the hypolimnion zone [107–112]. Today, more than 30 hypolimnetic oxygenation systems are deployed in lakes and reservoirs around the world [108,110]. At the same time, there are different systems of hypolimnetic oxygenation, which provide for the supply of oxygen:

1) by direct injection *via* bubble plume diffusers that are either linear or circular;
2) through in situ contact chambers such as the Speece Cone;
3) by side-stream saturation, for which water is withdrawn from the hypolimnion, oxygenated, and then recirculated [108,113].

At the same time, the authors of the paper [114] state that hypolimnetic oxygenation is not always effective. This was proven on the example of five Danish eutrophic lakes. The various types of hypolimnetic aeration and oxygenation devices are discussed in detail earlier [115]. It is quite obvious that they are being improved over time. Circular bubble diffusers are used to improve the oxygen condition in the hypolimnion of lakes and reservoirs and reduce the flow of chemicals, including metals, from bottom sediments. They are considered an efficient technology for the improvement of water bodies [113,116].

Is is necessary to pay attention at bottom sediments mixing, as it ensures their oxidation after staying in anoxia [100]. On the one hand, as a result of sulphides oxidation, sulphates are formed, and this contributes to metals migration from bottom sediments. On the other hand, oxidation causes oxyhydroxides of iron and manganese to form, on the surface of which copper, lead and many other metals are actively adsorbed, and to a lesser extent cadmium [117]. Therefore, the migration of metals from bottom sediments is significantly reduced under such conditions. At the same time, it is noted that the extraction of metals under conditions of mixing of bottom sediments is usually insignificant. Addition of chemical reagents, in particular phosphates and calcification of bottom sediments is also considered as one of the ways to reduce metals migration from bottom sediments [7,118,119]. Metals form poorly soluble compounds with phosphates, which decreases their mobility. However, adding phosphates can induce negative effects due to increased eutrophication of water bodies.

It is also proposed to use new composite materials based on polonite (calcium silicate) with added activated carbon for a thin-layer coating of bottom sediments in order to reduce the release of chemicals from their composition, in particular nutrients and metals [120].

Different options for biological treatment are also used, which give positive results in reducing metals migration from bottom sediments [121]. Artificial aeration, eco-brick cover, biological packaging cover and low-sited plant floating beds were used for their treatment. Due to this treatment of bottom sediments, the rate of Cr, Zn, Cu and Pb migration from their composition decreased at an average by 59.3, 42.3, 55.3 and 41.2%, respectively.

Conclusions

Bottom sediments of surface water bodies are an important component of aquatic ecosystems, in which various chemicals, including metals, are accumulated. As a result, they fall out of circulation for a certain period of time, and the aquatic environment is dominated by self-purification. However, chemicals can migrate from bottom sediments to overlying water, causing secondary pollution of the aquatic environment.

Considering metals as a component of chemical contamination of surface water bodies' bottom sediments, it should be noted that the fractions of solid phase in which they are predominantly concentrated is important. It is believed that metals of anthropogenic origin are concentrated mainly in exchangeable, carbonate and oxide fractions, therefore they are estimated to be the most mobile when conditions change in the "bottom sediments - water" system. The type of bottom sediments plays a significant role in the distribution of metals of anthropogenic origin between fractions.

Secondary pollution of water bodies is observed with a significant decrease in the dissolved oxygen content in the bottom layer water up to its deficit, a decrease in the value of pH and redox potential, an increase in the total dissolved solids and temperature of the bottom water, activation of biological processes, *etc*. At the same time, the migration of many metals slows down or does not occur at all due to the formation of poorly soluble metal sulphides under the conditions of a long-term oxygen deficit and presence of sulphides. An increase in the concentration of organic substances in water can be one of the reasons for increasing the metals mobility in bottom sediments. This is especially true for humic substances, which are marked by pronounced complexation and resistance to degradation. At the same time, an increase in the organic substances' concentration is inevitably accompanied by an increase in the oxygen consumption for their oxidation and destruction, and therefore, an increase in its deficiency leads to negative consequences. The increase in total dissolved solids can affect metals migration from bottom sediments if they are mainly in the exchangeable fraction. An increase in the metals migration from the bottom sediments should be expected with a decrease in the pH of the overlying water. A change in water temperature has an ambiguous effect, since its increase accelerates both the chemical and biological transformation of metals in bottom sediments.

On the question of which type of bottom sediments (rivers or lakes) is marked by a greater mobility of metals, it must be said that much depends on a number of different factors. Negative phenomena such as anaerobic conditions, increased concentrations of organic compounds, decreased pH of water and redox potential (*Eh*) are observed in lakes and reservoirs to a greater extent and more often than in rivers. These factors have the greatest influence on the mobility of metals. Therefore, it is assumed that the metals' migration mobility in bottom sediments of lakes and reservoirs will be higher than in rivers.

Future prospective

Due to climate changes that have started recently and will be observed in the future as well, the effect of mentioned factors and processes on the metals migration mobility in bottom sediments is expected to become more intense. The probability of secondary pollution of the aquatic environment will increase due to metals migration from bottom sediments. This will create ecological risks in the functioning of aquatic ecosystems owing to increased toxicity of the aquatic environment for hydrobionts. This will have a significant impact on the quality of the drinking water supply, further treatment will require the improvement of existing treatment systems and development of new ones and additional financial costs for their implementation.

Therefore, in the view of the above, it is worth noting the importance to reduce metals migration ability in the "bottom sediments -

water” system, which can be achieved in different ways. In particular, by covering bottom sediments with materials that bind pollutants, including metals, transforming them into bio-inaccessible forms. Artificial aeration should be considered as an effective way to reduce metals migration from the bottom sediments to overlying water, because under oxidizing conditions, iron and manganese oxides and hydroxides are formed. On the surface of the latter many other metals are actively adsorbed and, ultimately, they precipitate. Attention should also be paid to oxygenation (supplying purified oxygen with the help of special devices), which makes it possible to improve the oxygen regime in reservoirs, in particular in their deep-water areas. The addition of nitrate ions, which contributes to the formation of oxidizing conditions in the bottom water horizon, as well as phosphate ions, is also proposed. Different options of biological treatment of bottom sediments also deserve attention. In our opinion, the specified methods of reducing the migration of metals from bottom sediments can be the most efficient for small water bodies in urbanized areas. However, it should be remembered that the application of materials to cover bottom sediments or the use of chemical reagents can be expensive or dangerous to the aquatic ecosystems functioning, since additional chemicals are introduced. The addition of nitrate and phosphate ions, which can increase eutrophication of surface water bodies, is of particular concern. This can cause intensive development of phytoplankton up to harmful algal blooms (cyanobacterial bloom), which can be the source of toxins dangerous for living organisms.

Nevertheless, these problems will arise in the future and will require their urgent solution by developing a number of scientifically based measures to improve the condition of surface water ecosystems.

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