

Article

Speciation of Trace Metals in the Bottom Sediments of the Mozhaisk Reservoir and the Moskva River

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Abstract: The speciation of heavy metal Geology, ls (Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in the bottom sediments of the Mozhaisk Reservoir and the Moskva River is described. They were characterized using the Tessier sequential selective extraction procedure trace element concentrations determined by inductively coupled plasma–mass spectrometry (ICP-MS). The bottom sediments of the Mozhaisk Reservoir are characterized by higher concentrations of the examined metals compared to the channel alluvium of the Moskva River. In this case, the most widespread metal compounds in the bottom sediments of the Mozhaisk Reservoir are firmly bound (stable form) to the mineral matrix. High concentrations of the firmly bound forms of metals (Co, Ni, Cu, Zn, Cd, Pb, and Fe) in the bottom sediments are due to an increased proportion of the silt fraction (0.1–0.01 mm) entering the reservoir due to abrasion of its shores. The only exceptions are Mn and Cd, which are present in labile compounds with carbonates and hydroxides of iron and manganese. In the bottom sediments of the Moskva River, strongly bound forms prevail for most metals—for Ni, Zn, and Cd, they are complex compounds with Fe and Mn hydroxides; for Co, Cu, Pb, and Fe, they are compounds with stable silicate minerals. The proportion of labile bioavailable forms of metals in the bottom sediments of the Moskva River is higher than in the reservoir due to anthropogenic input. Among the labile forms of the metal compounds, carbonates predominate. The proportion of elements in the most mobile exchange form and in compounds with organic matter is not large and does not exceed 14% for most elements. The only exceptions are Co and Cd, for which the concentration of the exchange form reaches 25%.

Keywords: bottom sediments; heavy metal speciation; sequential extraction procedure; ICP-MS; the Mozhaisk Reservoir; Moskva River



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1. Introduction

Bodies of water aggregate the natural and anthropogenic dispersion of chemical elements. On the one hand, surface bodies of water, especially those with slow water exchange, are transit systems for the general circulation of matter in nature. On the other hand, they are specific systems for purifying and burying chemical elements in bottom sediments [1]. Heavy metal microelements are among the most critical pollutants in the aquatic environment. At the same time, the main long-term depositary in aquatic ecosystems is bottom sediments. In these sediments, elements that are toxic for aquatic

ecosystems can be accumulated, which may have a negative impact on aquatic organisms stored within them and be transferred into food chains, thereby posing a potential threat to human health [2].

The heavy metals that enter surface waters migrate and are redistributed in the water-deposit system, which can include changes in their form [3]. The migration capacity, toxicity, and bioavailability of metals for aquatic organisms depend upon the physicochemical form in the water and bottom sediments rather than upon their total content [4]. Several studies have shown that anthropogenic pollution leads to increases in bioavailability [5,6]. Changes in the physicochemical environmental conditions, including pH, oxidation–reduction potential, and organic matter concentration, can transform metals from the solid phase to the liquid phase in surface and pore water, leading to environmental pollution [6–8]. In the course of hydrobiological (production–destruction), hydrodynamic (wind and waves), and hydrochemical processes, heavy metals are redistributed between aquatic ecosystem components (water-suspended matter, aquatic organisms, and bottom sediments) and change their forms [9]. The form of metals in bottom sediments determines their effect on the ecological conditions of an aquatic ecosystem. Sequential extraction techniques using various analytical protocols are widely used to quickly obtain information on the mobility and chemical forms of metals in bottom sediments [6,10–13].

In the processes of sorption, cation exchange, and sedimentation, heavy metals accumulate in bottom sediments. When the oxidation–reduction and acid–base conditions change because of the activity of living organisms (e.g., microbiota, benthos, and macrophytes), the destruction of organic matter can be released into the bottom water masses, affecting the quality of the water in the reservoir and leading to secondary pollution [14].

During normal operation of the Mozhaisk Reservoir, a large amount of bottom sediment accumulates. The first studies of the bottom sediments in the Mozhaisk Reservoir were performed in 1969 and focused on the particle size distribution and the total concentrations of some elements. In addition, the accumulation coefficients of microelements in bottom sediments were calculated relative to soils and rocks in the catchment area, as well as the coefficients of biological absorption of the microelements from water and bottom sediments by fish [15,16]. In a study conducted in 1975, M.V. Martynova collected data on manganese concentrations in the pore solutions and solid phase of silts in the Mozhaisk Reservoir and revealed patterns in manganese redistribution in deposits from the upper parts of the reservoir to the dam [17]. However, the published modern data on the particle size distribution and the accumulated amounts and forms of heavy metals in these deposits are incomplete.

This work aims to obtain new data on the specific features of the chemical forms of microelements from the heavy metal group in the bottom sediments of the Moskva River and the Mozhaisk Reservoir constructed in its valley. The resulting data on the heavy metal speciation in the bottom sediments of the Mozhaisk Reservoir and the Moskva River, as well as their particle size distribution, can be used to forecast the behavior of chemical elements in migration processes and to assess the toxicity and bioavailability of their compounds.

The main focus is the study of the features of total concentration and content of chemical forms of various metals in the bottom sediments of the Moskva River before the Reservoir, below the dam, in the central and near-dam zones of the Reservoir, and below the Moscow City agglomeration, as well as the analysis of the connections of these concentrations with the granulometric composition of bottom sediments. Such river–reservoir systems are typical for many small valley reservoirs in the central European part of Russia; therefore, the identified features can be extended to such reservoirs to a certain extent.

2. Objects of the Study

To study the chemical forms of heavy metals in the bottom deposits of the Moskva River and the Mozhaik Reservoir, bottom sediments were sampled in the Moskva River upstream of its inflow into the reservoir, 4 km downstream of it, and 18 km downstream of Moscow City (Figure 1, schematic map).

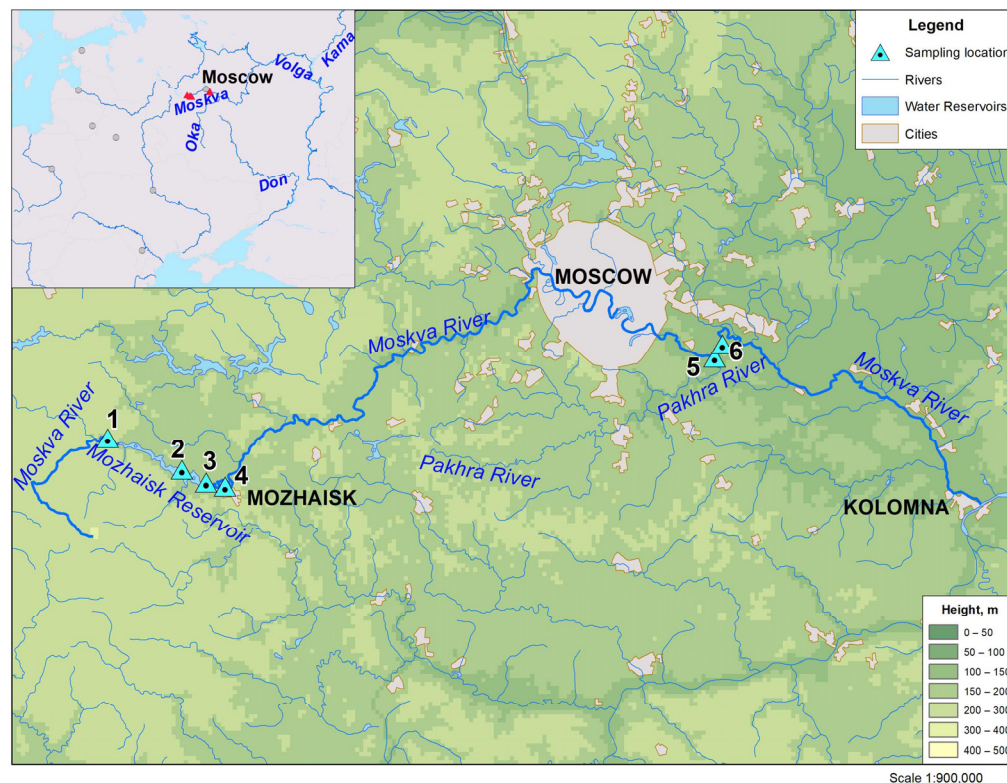


Figure 1. Bottom sediment sampling sites in the Moskva River and the Mozhaik Reservoir.

The length of the Moskva River is 473 km, and its drainage area is 17.6 thousand km². It flows almost entirely in the Moscow region. It is an eastern European type of lowland river predominantly fed by snow. The dominant part of the annual runoff is the spring flood (up to 60%) due to the melting of the snow cover accumulated in the cold season. The other part of the annual runoff is due to rain and groundwater recharge. The average long-term discharge of the Moskva River in its upper reaches (at Barsuki V. gauge, with a catchment area of 755 km²) is about 6 m³/s, that at Zvenigorod Town (catchment area of 5 thousand km²) is about 40 m³/s, and that at the outlet section at Kolomna C. is 150 m³/s [18]. Since the late 1930s, the river flow has increased considerably in its middle and lower reaches due to water transfer from the Volga River. Many ponds exist in the river basin, and reservoirs have been constructed on the major remaining tributaries of the Moskva River to regulate the annual flow distribution.

In its upper reaches, the Moskva River flows in a relatively narrow valley between moraine ridges and hills, with relatively high and steep banks. Upstream of the Mozhaik Reservoir, a wide floodplain and incised riverbed sections alternate. The width of the Moskva River channel in this segment is 5–20 m [19]. The Mozhaik Reservoir is in a widening of the Moskva River valley, which can be seen a short distance downstream of the reservoir. The river channel meanders frequently. The rate of floodplain bank erosion is about 0.5 m/year. The channel deposits consist of silt; sand; and, in sections of incised channel, pebbles. In the middle reaches, the concave banks of the bands are

eroded at a rate of 5 m/year. Within the boundaries of Moscow City, many bends have been straightened artificially.

The Mozhaisk Reservoir was constructed in 1960 in the upper reaches of the Moskva River (Figure 1). The reservoir is used for long-term and seasonal regulation of the hydrological regime. It is used for drinking water, electric power production, and recreation. The reservoir water area at the flood-control storage level is 30.68 km², its length is 28 km, the average depth is 7.66 m, the maximal depth is 22.6 m, and its volume is 0.235 km³.

The bottom sediments of the reservoir are secondary inorganic soils, represented in the channel trough by gray silt and by sandy silt and silted sand on the flooded right-bank floodplain and terrace slope, respectively [20]. According to their particle size distribution, the silt deposits are classified as fine-aleurite silts with an average content of 52.4% of 0.05–0.01 mm particles. The concentration of organic matter is not high, amounting, on average, to 6–7% for silts, 2–5% for silty sands, and less than 2% for sands [21].

The bottom sediments form because of three processes. The principal one is the erosion of the reservoir shores and bed (50%), followed by the sedimentation of some of the suspended matter delivered by river flow. The third source is the biological production–destruction processes within the body of water [22]. The Mozhaisk Reservoir contributes substantially to sediment settling. The solid runoff through the Mozhaisk Hydropower System is slightly greater than 2% of the suspended matter in the reservoir or 10% of the annual volume of suspended sediment inflow [23]. D.I. Sokolov [24] showed that the retention of sediments in the Mozhaisk Reservoir decreased from 90% to 70–85% from 1968 to 2016. Retention is now partially recovering due to the outflow of suspended organic substances formed within the reservoir. Bottom sediments accumulate most rapidly in the channel trough and in the mouths of inundated creeks and gullies, where bottom sediments are represented mainly by gray silts up to 20–35 cm thick. The bed of the channel sections subject to wave impact is covered by silty sands, and the narrow band along abrasion shores is covered by sand that is sometimes silty, with pebble, gravel, and boulder inclusions. The composition of the soils in the catchment area and bottom sediments of the reservoir bed determines the hydrochemical regime of the reservoir [23,24].

During field studies conducted on 26–27 July 2022, the air temperature was 21–24 °C. In the Mozhaisk Reservoir region, 11 to 16 mm of rain fell on 18, 20, and 21 July. Heavy rain fell in Moscow on 25 July, with total precipitation of about 45 mm. The inflow of water into the reservoir from the Moskva River on 26–27 July 2022, was about 2.5 m³/s, which is typical of the summer low-water season, while the discharge was 5 m³/s. After the spring filling of the reservoir, which ended in May, its gradual drawdown began in June, decreasing the water level. The water flow rate measured during field studies in the lower reaches of the Moskva River with the use of a Teledyne RDI RiverRay Doppler flow meter and a SonTek RiverSurveyor M9 was 70 m³/s.

3. Materials and Methods of Laboratory Analysis of Bottom Sediments

Bottom sediment samples were taken on 26–27 July 2022 at six sites, four of which were located on the Moskva River and two in the Mozhaisk Reservoir—in the central Krasnovidovskii Pool, where the depth is 3–6 m, and in the downstream, near-dam area at the Mozhaisk Hydrosystem near Blaznovo Village, where depths reach 14–16 m (Figure 1, Table 1).

Bottom sediment samples were taken from the top (0–10 cm) layer using a stainless-steel dredger and placed in plastic containers. The sample volume was about 1000 cm³ to ensure the selection of representative samples. The samples were dried at room temperature in the laboratory. The granulometric composition was determined according to GOST-12536-2014 [25], and the concentration of organic matter in bottom sediments

was determined according to GOST-26213 [26] in the test laboratory center of the V. V. Dokuchaev Soil Institute.

Table 1. General characteristics of the sampling sites.

Sample No.	Sampling Site	River/Reservoir Width, m
1	Moskva River at Barsuki Village	30
2	Mozhaisk Reservoir, Krasnovidovo Village	1500
3	Mozhaisk Reservoir, Blaznovo Village, near the dam	1500
4	Moskva River at Isavitsy Village	40
5	Moskva River, upstream of the Pakhra River inflow, Nizhnee Myachkovo Village	150
6	Moskva River, downstream of the Pakhra River inflow, Telman Settlement	150

For microelement analysis, an average sample weighing 10 g was dried at room temperature and ground to powder (particle size: 30–45 μm). To decompose bottom sediments by sintering [27], a 100 mg sample of bottom sediments was taken, mixed with 300 mg of soda Na_2CO_3 , stirred, and placed in corundum crucibles. The crucibles were heated in a muffle furnace at a temperature of 800 $^{\circ}\text{C}$ for 2–2.5 h. The sintered preparation was transferred to disposable test tubes with a volume of 50 cm^3 , and 1–2 mL of deionized water was poured in; then, concentrated acids were added: 0.5 mL of HCl and 3.5 mL of a mixture of HNO_3 and HF acids (10:1, *v/v*). After intense gas evolution, HNO_3 (0.5 N) was added into the test tube up to 50 mL, and the tablet dissolved completely. The solution obtained after decomposition was filtered through 0.45 μm glass fiber filters and stored at 4 $^{\circ}\text{C}$.

To ensure analytical quality, geochemical standard bottom sediment, calcareous silt (GSO SDO-3, Research Institute of Applied Physics at Irkutsk University, Irkutsk, Russia) was used for validation [28]. The recoveries of the standard samples ranged from 90% to 110%.

Element concentrations in bottom sediments were measured using an ELAN 6100 DRC Perkin–Elmer, Wellesley, United States inductively coupled plasma mass spectrometer. Instrument sensitivity calibration and mass calibration were performed using a standard multi-element calibration solution, TUNE F-X-SERIES (OEM N TUNE F50, Inorganic Ventures, Christiansburg, VA, USA). To control and account for the sensitivity drift of the device, an internal In standard was added to the samples and calibration solutions before measurement so that its amount in all measured samples was 10 ng/g. The detection limits of the elements ranged from 0.1 ng/g for heavy and medium elements, with an increase to 1 ng/g for light elements. The relative error of the analysis was 1–3 percent. To calculate the contents of the elements, a series of calibration solutions with concentrations of 0.03, 0.3, 3, and 10 ng/g was used, prepared from a standard solution, ICP-MS-68 (A, B, High-Purity Standards, Charleston, SC, USA).

Speciation of the bottom sediment samples was performed by a widely used scheme for analyzing group composition, the sequential Tessier extraction procedure [29]. This procedure separates and identifies five groups of metal compounds (5 geochemical fractions), which have different migration capacities, i.e., exchangeable, bound to carbonates, bound to iron and manganese oxides and hydroxides, bound to organic matter, and strongly bound or included in the crystalline structure of minerals (residual). These microelemental forms were leached with the use of the following reagents: (1) exchange forms were extracted for 1 h with 1 M MgCl_2 pH 7.0; (2) the metal forms, specifically those bound to calcium and magnesium carbonates, were extracted from residue (1) at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc) stirring for 1 h; (3) microelement

complexes with iron and manganese oxides and hydroxides were extracted from residue (2) by 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (*v/v*) HOAc for 6 h; and (4) the forms bound with organic matter were extracted from the residue (3) added by 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3 , and the mixture was heated to 85 °C for two hours with occasional agitation. Thereafter, an additional 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) was added, and the sample was heated again to 85 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4OAc in 20% (*v/v*) HNO_3 was added, and the sample was diluted to 20 mL and agitated continuously for 30 min. The addition of NH_4OAc is designed to prevent absorption of extracted metals onto the oxidized sediment.

After each extraction step, the solid and liquid phases were separated by centrifugation, followed by filtration of the liquid phase through 0.45 μm glass fiber filters, and stored at a temperature of 4 °C, then analyzed by ICP-MS. The residual fraction after extracting all migratory forms was decomposed using the method of sintering with soda and dissolving in a mixture of acids, as described above, to determine the proportions of the trace elements, which are embedded in the silicate crystalline structures of bottom sediment particles.

To obtain the mass balance of heavy metals in the bottom sediments, the residual fraction was measured after acid digestion using the procedure described above for total metal determination. Microelement concentrations in the solid and liquid phases after extraction were determined by ICP-MS.

4. Results and Discussion

4.1. Particle Size Distribution in the Bottom Sediments

The particle size distributions of bottom sediments in the Moskva River and the Mozhaik Reservoir are given in Table 2, which also gives the names of soils in accordance with the classification by Kachinsky [30]. The study of the particle size distribution in the channel deposits of the Moskva River at sections near Nizhnee Myachkovo Village, Telman Settlement, and Isavitsy Village shows that the physical sand fraction dominates (97.79%, 98.19%, and 98.27%, respectively), while the fraction of clay particles is 2.21%, 1.81%, and 1.73%, respectively, which is typical of the channel alluvium of rivers in this region. However, the sediments in the Mozhaik Reservoir at Krasnovidovo and Blaznovo St. are represented by medium and heavy loams with physical clay fractions of 39.02% and 44.68%, respectively, which are particle size distributions typical of reservoirs.

Table 2. Particle size distribution in the bottom sediments of the Moskva River and the Mozhaik Reservoir.

No.	W %	OM %	The Concentration of Particles (Diameter, mm), % Dry Weight										Ground Type
			>2	2–1	1–0.5	0.5–0.25	0.25–0.1	0.1–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	
1	1.78	3.4	0.08	0.34	2.92	6.33	17.18	29.67	27.46	4.88	5.65	5.49	clay sand
2	4.93	5.2	n.a.	n.a.	0.27	1.22	1.3	17.28	40.91	11.34	15.25	12.43	medium clay loam
3	4.71	6.4	20.67	n.a.	0.12	0.86	0.17	8.48	25.02	11.46	17.39	15.83	heavy clay loam
4	0.72	5	22.62	10.34	35.21	18.62	7.46	0.88	3.14	0.44	0.41	0.88	loose sand
5	0.66	0.8	8.59	6.22	16.3	19.84	39.77	6.01	1.06	0.18	0.51	1.52	loose sand
6	0.38	0.4	0.57	0.5	4.84	39.11	59.11	0.98	0.08	0.08	0.51	1.22	loose sand

Note: W is hygroscopic moisture content, and OM is organic matter mass fraction; n.a. means “The sample has no particles of this size, i.e., not available”.

This distribution is associated with the specific hydrodynamic conditions favorable for sedimentation and the accumulation of dust and clay particles in bottom sediments. Such a

particle size distribution in bottom sediments is typical of the valley reservoirs in central Russia. Thus, in the near-dam part of the Ivan'kovo Reservoir (located in the Upper Volga watershed 153 km NNE from Mozhaishk), the concentration of fractions smaller than 0.001 mm is 9.4%, and that of fractions smaller than 0.01 mm is 30.9% [31]. In the river section at the village of Barsuki, the Moskva River lies in the reservoir backwater and has low flow rates, which lead to the formation of sandy loam (or sandy loam deposits), a decrease compared to other sections on the Moskva River in the proportion of physical sand to 83.98%, and an increase in the proportion of physical clay to 16.02%. An important feature of the particle size distribution in the bottom sediments in this section and in the Mozhaishk Reservoir is that, in addition to a considerable increase in the concentration of particles less than 0.01 mm in size (physical clay), elevated concentrations of fine sand (0.1–0.05 mm) and coarse silt particles (0.05–0.01 mm) several times greater than in other sections in the Moskva River are observed. Thus, the share of the 0.1–0.01 mm fraction is 57.13% in the Barsuki Village section and 58.19% and 33.5% in the sections of the Mozhaishk Reservoir.

In the process of sedimentation of suspended matter and accumulation of bottom sediments in the Mozhaishk Reservoir, as in other valley-type reservoirs of the Central Zone of Russia, differentiation of particles of different fractions is observed, leading to the formation of differences in the particle size distribution in bottom sediments from the backwater zone to the dam. According to our data, the proportion of the <0.01 mm fraction in bottom sediments in the central part of the reservoir (Krasnovidovo gauge) is higher than in the upstream part (Barsuki gauge): 97.21% compared with 73.15%. In the near-dam part of the reservoir (Blaznovo gauge), the percentage content of this fraction decreases to 78.18%.

The concentration of organic matter in the bottom sediments of the Mozhaishk Reservoir is relatively high and equals 5.2–6.4%. It is close to the organic matter concentration of the Ivan'kovo Reservoir bottom sediments, which is 6% [32]. The high concentration of organic matter in the bottom sediments in the Isavitsy section (sample 4), 4 km downstream of the reservoir dam, can be explained by the inflow from the reservoir that is enriched by autochthonous organic matter, which forms in the reservoir as the result of phytoplankton photosynthesis. As shown earlier [18], the solid runoff from the Mozhaishk Reservoir is 2.7 times richer in organic matter than the inflow. This explains the increase in organic matter concentration in bottom sediments in sections further downstream found in our data. Therefore, the inflow of organic matter is the main factor affecting the accumulation of organic matter in the bottom sediments of the Moskva River sections downstream of the reservoir. The concentration of organic matter in the channel alluvium of the Moskva River upstream of the reservoir is very low and amounts to 0.4–0.8%. Changes in the particle size distribution of bottom sediments are accompanied not only by changes in their organic matter contents but also by an increase in their hygroscopic moisture content (Table 2).

4.2. The Accumulation and Chemical Forms of Metals

The accumulation and chemical forms of metals in bottom sediments are closely related to the particle size distribution. The channel deposits in the Moskva River are characterized by low contents of the examined elements (Samples 1, 4, 5, and 6) because they are represented by sandy alluvium. An exception is the section downstream of the Pakhra River inflow (sample 6), where the highest lead concentration was recorded. This high value is due to the permanent anthropogenic input of this element from the polluted waters of this river [33]. The bottom sediments of the Mozhaishk Reservoir show a high concentration of metals—several times greater than concentration in the Moskva River channel alluvium (Table 3). The concentrations of Co and Fe are 5 times higher; Ni and Mn are almost 4 times higher; and Cd, Cu, and Zn are 2–2.6 times higher.

The studied elements (except Pb) are characterized by a close relationship between their total concentrations in bottom sediments and the content of the clay fraction (<0.001 mm), which also is confirmed by rather high values of the coefficients of determination (0.82 for Mn, 0.97 for Fe, 0.99 for Co, 0.99 for Ni, 0.88 for Cu, 0.82 for Zn, and 0.95 for Cd). Examples of such dependencies are shown in Figure 2.

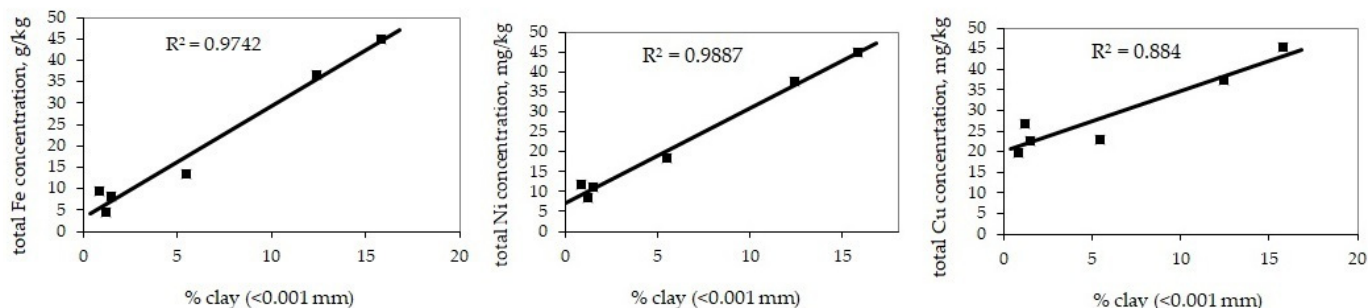


Figure 2. Typical relationships between total metal concentration (<0.001 mm) and share of clay fraction (in %).

The relationship between the total metal content and the proportion of the aleurite fraction (0.1–0.001 mm) is rather weak. This is confirmed by low values of the coefficient of determination for Mn, Fe, Ni, Cu, and Zn ($R^2 = 0.17$ – 0.42). At the same time, E.P. Yanin [32] has shown that the main carriers of almost all elements in the Pakhra River silt are aleurite particles (0.1–0.01 mm), which account for up to 50–70% of their total contents. As has been noted, the bottom sediments of the Mozhaisk Reservoir and the Moskva River at the site subject to the reservoir backwater effect (Sample 1) show the highest concentration of this fraction. This suggests that the high metal concentration in these sections is due to the large proportion of this granulometric fraction. It has also been shown previously [32] that the amount of many metals in finer fractions correlates with the high contents of iron and aluminum in these fractions, which indicates a major role in falling out metals from the water flow of the processes of sorption by colloidal iron and aluminum hydroxides.

Table 3. Forms of metal occurrence in the bottom sediments of the Moskva River and the Mozhaisk Reservoir.

Proportion of Compounds in the Total Content, %							
Loosely Bound (LB)				Strongly Bound (SB)			LB/SB, %
Sampling Site	Total Con- centration, mg/kg	Exchange Forms	Bound with Carbonates	Associated with Hydromorphic Hydroxides and Fe–Mn	Associated with Organic Matter	Strongly Bound with Silicates	
Manganese							
1	444	3	44	20	4	29	47/53
2	1115	3	47	28	3	19	50/50
3	1832	14	44	24	4.5	13.5	58/42
4	702	4	63	20	4	9	67/33
5	267	7	38	31	5	19	45/55
6	173	6	27	23	3	41	33/67
Iron							
1	13528	0.1	0.8	17	1.5	80.6	0.9/99.1
2	36481	0	0.7	15	0.8	83.5	0.7/99.3
3	45043	0	0.8	14	1	84.2	0.8/99.2
4	9380	0.2	2	35	1.5	61.3	2.2/97.8
5	8142	0.2	1.2	25	1	72.6	1.4/98.6
6	4351	0.4	0.9	24	0.7	74	1.3/98.7

Table 3. Cont.

Proportion of Compounds in the Total Content, %							
Loosely Bound (LB)				Strongly Bound (SB)			
Sampling Site	Total Con- centration, mg/kg	Exchange Forms	Bound with Carbonates	Associated with Hydromorphic Hydroxides and Fe–Mn	Associated with Organic Matter	Strongly Bound with Silicates	LB/SB, %
Cobalt							
1	6.92	8.7	13.4	29.6	10.7	37.6	22/78
2	12.54	4	6	28	8	54	10/90
3	15.8	4	9	26	8	53	13/87
4	3.51	14	9.7	33	11	32.3	24/76
5	2.98	20	7.4	33	6	33.6	27/73
6	1.97	25	5.6	29	4.6	35.8	31/69
Nickel							
1	18.3	3.8	11	29.5	12	43.7	15/85
2	37.5	1.9	5.3	19.2	10.4	63.2	7/93
3	44.8	2	6.3	15	9.3	67.4	8/92
4	11.8	6	15.5	37	13	28.5	22/78
5	11.1	6.3	12.6	42	11.7	27.4	19/81
6	8.5	8.2	11.8	47	14	19	20/80
Copper							
1	22.9	1.3	8.7	4.3	8.7	77	10/90
2	37.5	1	8	2.7	8	80.3	9/91
3	45.2	0.9	6.6	2.2	6.6	83.7	8/92
4	19.8	1.5	15	5	10	68.5	17/83
5	22.5	1.8	13.3	22	9	53.7	15/85
6	26.8	1.5	11.2	18.7	3.7	64.9	13/87
Zinc							
1	62.6	1.6	9.7	37	7	44.7	11/89
2	114	0.9	4.6	24.6	4	65.9	5/95
3	125.8	0.8	0.5	21	4	73.7	1/99
4	30.9	3.2	12	35.6	10	39.2	15/85
5	79.8	1.3	21	55	7.7	15	22/78
6	49.1	2	18	55	7	18	20/80
Cadmium							
1	0.29	6.9	31	52	3.4	6.7	38/62
2	0.46	8.7	24	54	4.3	9	33/67
3	0.47	8.5	21	51	8.5	11	30/70
4	0.14	14	36	28	7	15	50/50
5	0.23	22	35	35	4	4	57/43
6	0.16	25	25	37.5	6.3	6.2	50/50
Lead							
1	17.5	1	9	23	5.7	61.3	10/90
2	29.94	0.1	4.7	24	5	66.2	5/95
3	32	0.3	5.6	24	5.6	64.5	6/94
4	13.9	0.8	6.5	29	5.8	57.9	7/93
5	20.61	0	8.7	40	6.8	44.5	9/91
6	63.23	0.5	28	55	5.2	11.3	29/71

Fe, Mn, Co, Ni, Cu, Zn, and Cd concentrations in bottom sediments of the Mozhaisk Reservoir are much higher than those from the Moskva River. A comparison of the metals in the bottom sediments of the Mozhaisk Reservoir and the Uglich and Ivan'kovo Reservoirs in the Upper Volga [33,34] shows them to be very similar.

The proportions of metal compounds in the bottom sediments were used to assess their migration capacity, which can be characterized by the mobility index (Km) [35], which is equal to the ratio of the concentration of loosely bound (LB), labile forms to the concentration of strongly bound (SB) metal compounds: $K_m = LB/SB$.

The results were used to establish relationships between groups of metal compounds in the bottom sediments of the Mozhaisk Reservoir and the Moskva River (Table 3).

The total percentage of LB metals in bottom sediments ranged from 33% to 67% for Mn, from 0.7% to 2.2% for Fe, from 10% to 30.6% for Co, from 7.2% to 21.5% for Ni, from 9% to 16.5% for Cu, from 1.3% to 22.3% for Zn, from 29.5% to 57% for Cd, and from 4.8% to 28.5% for Pb. Sizeable fractions of labile forms of these metals indicate their high bioavailability in bottom sediments, with a potential for negative impact on the water ecosystem.

For the bottom sediments of the reservoir, the average values of metal bioavailability decrease in the following order: Mn (54%) > Cd (31%) > Co (11%) > Cu (9%) > Ni (8%) > Pb (5%) > Zn (3%) > Fe (0.8%). For river bottom sediments, the series of average bioavailability values looks different: Cd (49%) > Mn (48%) > Co (26%) > Ni (19%) > Zn (17%) > Cu (14%) > Pb (14%) > Fe (1.5%). The bioavailability of metals in bottom sediments can be strongly related to the presence of a pollution source, with lower availability usually observed when metals come from natural sources compared to anthropogenic ones [5,6].

Both in the reservoir sediments and the riverbed alluvium, the SB forms of metals prevail for most elements. However, the relative proportion of labile forms of metals is higher in the channel alluvium compared to the reservoir sediments. Fe and Cu are mainly found in mineral phases strongly bound to silicates. Among the labile forms of Mn and Cd in channel alluvium and SB forms with oxides and hydroxides of iron and manganese, compounds with carbonates predominate.

For migratory forms of Co, Ni, Zn, and Pb, compounds associated with oxide and hydroxide forms of Fe and Mn also predominate. N.M. Strakhov [36] established that in bottom sediments, the mobile forms of Fe and Mn and associated metals of secondary, authigenic origin are presented mainly in colloidal form. During eutrophication and high hypoxia in the summer and winter, when oxidizing conditions change to reducing conditions, metals associated with this form pass into solution, and their bioavailability increases.

Although the major portion of Fe and Cu is part of the poorly soluble residue, freshly precipitated Fe and Mn hydroxides comprise 20–25% of the compounds containing these elements. We explain the high metal concentration in aleurite fraction (0.1–0.01 mm) of bottom sediments by their volumetric surface absorption in the $\text{Fe}(\text{OH})_3$ structure, which covers the surface in a thin layer of large pieces of solid-phase of sediments. The deposition of metals on its surface occurs due to both sorption and coprecipitation, as described in [37]. For Cu, unlike other elements, these sediments typically occur in the Moskva River in the form of complex compounds with organic matter; the proportion of these compounds is 3.7–10%.

For the bottom sediments of the Mozhaisk Reservoir, most of the elements (53–84% of the total content) are found in hard-to-dissolve silicates in an SB form. The exceptions are Mn and Cd (44–47% and 21–24%, respectively), which are associated with carbonates, i.e., they are in a potentially mobile state, and 24–28% and 51–54% are firmly fixed by particles of oxides and hydroxides of Fe and Mn, respectively.

The source of the carbonate forms of Mn and Cd in these sediments are the limestones of the Middle Carboniferous that underlie the moraine loams in the Mozhaisk Reservoir region. In compounds with carbonates, Mn and Cd are found not only in sorbed form but mainly in the form of an isomorphic impurity. The high contents of SB forms of metals (Co, Ni, Cu, Zn, Cd, Pb, and Fe) in the bottom sediments of the Mozhaisk Reservoir are due to an increase in the share of the aleurite fraction (0.1–0.01 mm), which accumulates under no or low flow rates in the reservoir. The determination coefficient between the concentration of the 0.1–0.01 mm fraction and the concentration of elements in the poorly soluble residue for Fe ($R^2 = 0.58$), Co ($R^2 = 0.43$), Pb ($R^2 = 0.45$), Zn ($R^2 = 0.5$), Cu ($R^2 = 0.56$), and Ni

($R^2 = 0.6$) also confirms a close relationship between these indicators. This fraction is a carrier of many heavy metals that can be included in the crystal lattice of poorly soluble minerals and is represented by SB compounds. This is because, as mentioned above, the main source of soil-forming material in the reservoir is the material entering due to coastal abrasion and represented by silt particles. The source of minerals stable in the hypergenesis zone in bottom sediments is the Quaternary glacial deposits in the catchment area of the Mozhaisk Reservoir, which are represented by loams. The main minerals typical for the alluvium of the central regions of Russia are hornblende, epidote, garnets, magnetite, and zircon, and the composition of the crystal lattices includes the studied metals.

Heavy metals enter the absorbing complex of the solid phase of the sediments in their most mobile form as mass exchange processes connect them with the liquid phase of the bottom sediments (pore water) and water. The percentage of elements in the solid phase of sediment in the exchangeable form, in both the sediments of the channel alluvium of the Moscow River and the bottom sediments of the reservoir, is insignificant, amounting to 1–8% for most elements. It is only for Co and Cd that the percentage of exchangeable forms in the sediments of the Moscow River reaches 7–25%.

The bottom sediments of the Reservoir are enriched in organic matter to a greater extent than the sediments of the Moskva River. However, no significant differences were found between the relative contents of the organic–metal complexes in the channel alluvium and the sediments of the Reservoir. The proportion of forms represented by complexes with organic matter for most elements is 3–8%, increasing to 4–14% for Co, Ni, Cu, and Zn.

Given the large number of publications on the determination of the chemical forms of microelements in the bottom sediments of reservoirs in the central zone of Russia, for example [31,34,38], comparing the data is very difficult due to the different approaches and methods used. Table 4 compares the results of this study with the data for the bottom sediments of the Ivan'kovo Reservoir, which were also obtained using the Tessier sequential fractionation scheme. The relative contents (percentage of the gross content) of the migratory forms of elements in these reservoirs were very similar. An exception is Cu, for which higher relative contents of the forms associated with organic matter were found in the Ivan'kovo Reservoir (on average 82%); for the Mozhaisk Reservoir, the share of these forms, is on, average 43%. For Zn, Cd, and Pb in the Mozhaisk Reservoir, the percentages of sorption–carbonate forms were lower than in the Ivan'kovo Reservoir because, in that work [38], this fraction also included the exchangeable forms of the metals. In the present work, the exchangeable and sorption–carbonate forms were isolated for the sediments of the Mozhaisk Reservoir through separate extractions.

Except for Pb, the highest total concentration of the examined metals is observed in the bottom sediments of the Mozhaisk Reservoir. At the same time, the proportion of the labile forms of metals in these sediments is lower than in the Moskva River. The bottom sediments of the Moskva River in the sections upstream and downstream of the Pakhra River (18 km downstream of Moscow City) and in the lower pool of the reservoir are characterized by the highest relative concentrations of the labile forms of most of the considered metals. The concentration of labile metal forms in bottom sediments is relatively low due to the incorporation of metals into the exchange complex and sorption on calcium and magnesium carbonates. It varies from 1% to 2% for Fe, from 33% to 67% for Mn, from 29% to 57% for Cd, from 10% to 30% for Co, from 10% to 30% for Cu, from 7% to 21% for Ni, from 5% to 28% for Pb, and from 1% to 22% for Zn.

The mobility of all studied elements in the bottom sediments of the Moskva River, except for Co, is mainly due to their association with carbonates (their relative proportion is 0.7–63% of the total content). The mobile Co in the bottom sediments of the Moskva River is present in the exchange forms, the proportion of which is 8.7–25%. For Mn, Ni, Zn, and Cd,

the main SB forms in the bottom sediments of the Moskva River are complex compounds with Fe and Mn hydroxides, which have a relative proportion of 35–50%. For Fe, Cu, and Pb, the strongly bonded forms are compounds with silicates. For Co, the content of the mobile and strongly bonded forms is almost the same. In the bottom sediments of the Mozhaisk Reservoir, the main labile form of metals is also associated with carbonate, but the relative content of these compounds is lower: 0.5–47%. In the strongly bonded compounds in the sediments of the Mozhaisk Reservoir, compounds with Fe and Mn hydroxides predominate for Mn and Cd, and compounds containing silicates prevail for the remaining elements. The highest relative content of compounds associated with Fe and Mn hydroxides in the sediments of the Mozhaisk Reservoir is obtained for Cd (54%). Complexes with organic matter, the proportion of which is about 10%, are also important for Cu, Co, and Ni. The proportion of metal compounds in the exchangeable form in the bottom sediments of the Moskva River is low and amounts to less than 3% for Fe, Cu, Zn, and Pb and 3–25% for Mn, Co, Ni, and Cd. In the bottom sediments of the Mozhaisk Reservoir, the content of the exchange forms of Pb, Cu, Zn, and Fe is also negligible (less than 1%). For the other elements, the content of the exchange forms is also not high, ranging from 2% to 14%. The relative concentration of metal forms in complexes with organic matter is the same for the bottom sediments of the Moskva River and the Mozhaisk Reservoir and varies from 3% to 10%.

Table 4. Geochemical fractions of metals in the bottom sediments of the Mozhaisk and Ivan'kovo Reservoirs.

Element	The Share of the Total Content of Migratory Forms, %					
	Bound with Carbonates		Bound with Hydroxides Fe–Mn		Bound with Organic Matter	
	Mozhaisk Reservoir	Ivan'kovo Reservoir [38]	Mozhaisk Reservoir	Ivan'kovo Reservoir [38]	Mozhaisk Reservoir	Ivan'kovo Reservoir [38]
Mn	<u>60–61</u> 61	<u>47–77</u> 71	<u>33–36</u> 34	<u>19–50</u> 25	<u>4–6</u> 5	<u>2–6</u> 4
Fe	<u>4–5</u> 4.5	<u>10–30</u> 20	<u>89–91</u> 90	<u>42–80</u> 62	<u>5–6</u> 5.5	<u>9–48</u> 18
Co	<u>14–21</u> 17	<u>10–35</u> 22	<u>60–67</u> 64	<u>35–77</u> 49	19	<u>13–51</u> 29
Ni	<u>15–21</u> 18	<u>9–22</u> 15	<u>49–55</u> 52	<u>28–43</u> 39	30	<u>37–63</u> 46
Cu	43	<u>2–34</u> 12	14	<u>2–18</u> 6	43	<u>54–96</u> 82
Zn	<u>2–14</u> 8	<u>23–47</u> 38	<u>74–82</u> 78	<u>31–52</u> 46	<u>12–16</u> 14	<u>10–46</u> 16
Cd	<u>26–29</u> 27	<u>28–88</u> 52	<u>63–66</u> 65	<u>8–56</u> 38	<u>5–11</u> 8	<u>3–34</u> 10
Pb	<u>14–16</u> 15	<u>16–37</u> 29	<u>68–71</u> 70	<u>22–59</u> 44	<u>15–16</u> 15	<u>15–61</u> 27

Notes: the numbers above the line are the minimum and maximum values, and the number below is the mean value.

Two factors control the distributions of metal forms in bottom sediments: lithogenic and anthropogenic factors. The lithogenic factor is responsible for the high content of the aleurite granulometric fraction in sediments. This results in high total metal concentrations in reservoir sediments. The anthropogenic impact on the formation of metal compounds in bottom sediments of the Moskva River below large, industrial cities manifests itself in two pathways: firstly, in increased content of labile metal compounds and, secondly, in

changes in the balance of forms of some metals. Anthropogenic factors dominate in the formation of unstable metal compounds in unpure sediments that have a high migration ability and bioavailability. The migration ability and bioavailability of polluted sediments of the Moskva River increase mostly due to increases in metal compounds bound with carbonates. The relative contents of such compound forms for Ni, Pb, and Zn increased by 2.7 to 8 times, and for Cd, Zn, Ni, and Co, the fraction of exchangeable forms increases by 3 to 6 times. At the same time, for Mn, Ni, Cu, Zn, Cd, and Pb, carbonate compounds dominate over exchangeable forms, and in polluted sediments, for Co, exchangeable forms also dominate.

5. Conclusions

1. The bottom sediments of the Mozhaik Reservoir are characterized by much higher total concentrations of the examined metals compared with the deposits in the Moskva River due to the higher relative share of clay (<0.001 mm) and organic matter in the Mozhaik Reservoir bottom sediments. In addition, due to the significantly higher proportion of aleurite (0.1–0.01 mm), the total metal content in the sediments of the reservoir is also higher than in the river due to a significantly higher concentration of metals in strongly bounded forms.
2. Most metals in the Mozhaik Reservoir bottom sediments are in strongly bound compounds. The high percentage of tightly bound metals (Co, Ni, Cu, Zn, Cd, Pb, and Fe) in the Mozhaik Reservoir deposits is due to an increased aleurite (0.1–0.01 mm) fraction due to shore abrasion. The aleurite fraction carries these metals and is represented by poorly soluble primary and secondary minerals containing metals in their crystalline structures. The only exceptions are Mn and Cd, which are present in their labile forms, i.e., compounds with carbonates and hydroxides of iron and manganese.
3. In the bottom sediments of the Moscow River, the strongly bound forms of silicate compounds containing Fe, Cu, Pb, and Co and Fe and Mn hydroxides containing Ni, Zn, and Cd predominate, which, together, account for 29% to 98% of the total content. However, the proportion of mobile, bioavailable forms of metals in the bottom sediments of the Moskva River is higher than in the reservoir due to their anthropogenic input. Among the loosely bonded metal compounds, there is a higher proportion of metal compounds with carbonates.
4. The proportion of metals in the most mobile exchange form in the bottom sediments of the channel alluvium of the Moskva River and the reservoir bottom sediments is insignificant (1–14%). The only exceptions are Co and Cd, for which the concentration of exchange forms in the Moskva River sediments is somewhat higher and reaches 7–25%.
5. Although the bottom sediments of the Mozhaik Reservoir are richer in organic matter, the proportion of the complexes of the examined metals with organic matter is the same for the bottom sediments of both the Moskva River and the reservoir and varies from 3% to 10%.
6. The Mozhaik reservoir plays the role of a natural and anthropogenic geochemical sorption and sedimentation barrier, where the balance of granulometric fractions in bottom sediments changes and a large proportion of metals transported by the Moskva River accumulates, which is accompanied by a change in the forms of their presence in bottom sediments.
7. It looks like the discovered patterns in the microelement distributions in their chemical forms in the Mozhaik Reservoir bottom sediments are typical of the valley reservoirs of central Russia.

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