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Accumulation of Heavy Metals in Bottom Sediment and Their Migration in the Water Ecosystem of Kapshagay Reservoir in Kazakhstan

Laura Ismukhanova [1], Temirbek Choduraev [2], Christian Opp [3,*] and Azamat Madibekov [1,*]

[1] Institute of Geography and Water Security, Almaty 050010, Kazakhstan
[2] Faculty of Geography, Ecology and Tourism, Kyrgyz State University Named after I. Arabaev, St. Razzakova, 51A, Bishkek 720026, Kyrgyzstan
[3] Faculty of Geography, Philipps-Universität Marburg, D-35032 Marburg, Germany
* Correspondence: opp@geo.uni-marburg.de (C.O.); madibekov@ingeo.kz (A.M.)

Abstract: The bottom sediment of reservoirs has many functions. Among them, matter sorption is a very important one, and results in many side-effects on the reservoir sediment forming the water–bottom sediment system. As a result, bottom sediment can also be an indicator of anthropogenic water pollution. There is only very little knowledge of this situation in the study area. The main objective was the analysis of heavy metal accumulation in bottom sediment, as well as their ability to migrate throughout the water–bottom sediment system and their spatial distribution in the Kapshagay Reservoir in Kazakhstan. Heavy metal concentrations, in the both water samples and the bottom sediment, were determined using the atomic absorption spectrophotometric method. Surfer software was used to visualize the processes of migration and accumulation. Another objective was the development of model maps of the spatial distribution of metals in the reservoir water area, which indicated significant anthropogenic loads. It is obvious that both the transboundary inflow of the Ili River and the inflow from small rivers in the territory of Kazakhstan are the reasons for the anthropogenic water and sediment load. The results of the spectrometric analysis verify the water pollution in the reservoir, revealing increased concentrations of zinc reaching up to 10.8 µg/L and lead up to 32.7 µg/L, transported by the transboundary runoff of the Ili River and by the small rivers on the left bank into the Kapshagay Reservoir. Sediment concentrations close to the central part and dam zone of the reservoir reached the following values: zinc up to 37.0 mg/kg and lead up to 8.8 mg/kg. The results of this study indicate a significant anthropogenic load of the ecological conditions of the Kapshagay Reservoir. This is discussed and compared with other relevant studies.

Keywords: sedimentation; accumulation; bottom sediment; reservoir; heavy metals; migration

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1. Introduction

Bottom sediment, due to their absorption capacity, play an important role in the self-purification processes of water bodies [1–4]. However, they can cause secondary pollution of the aquatic environment, which is facilitated by water turbulence caused by subsurface streams, wind mixing, involving the upper layer of bottom sediment into the water mass. Supplementary diffusion, sorption and desorption, complexation, ion exchange and dissolution influence physicochemical, biological and microbiological processes at the water–bottom sediment line (in Supplementary materials) [1,5–11].

Pollution of water systems by heavy metals has become a global problem in recent decades. Heavy metals can enter aquatic systems from a variety of anthropogenic and natural sources (Figure 1). These activities include industrial or domestic wastewater, the use of pesticides and inorganic fertilizers, landfill leaching, storm sewage, shipping, atmospheric deposition and geological respectively geomorphological erosion of the Earth's crust and land surfaces [2]. Metals, entering aquatic ecosystems, cannot decompose, thereby deposit, assimilate or be included in water, sediment and aquatic animals, leading to pollution of water bodies by heavy metals [4,12].

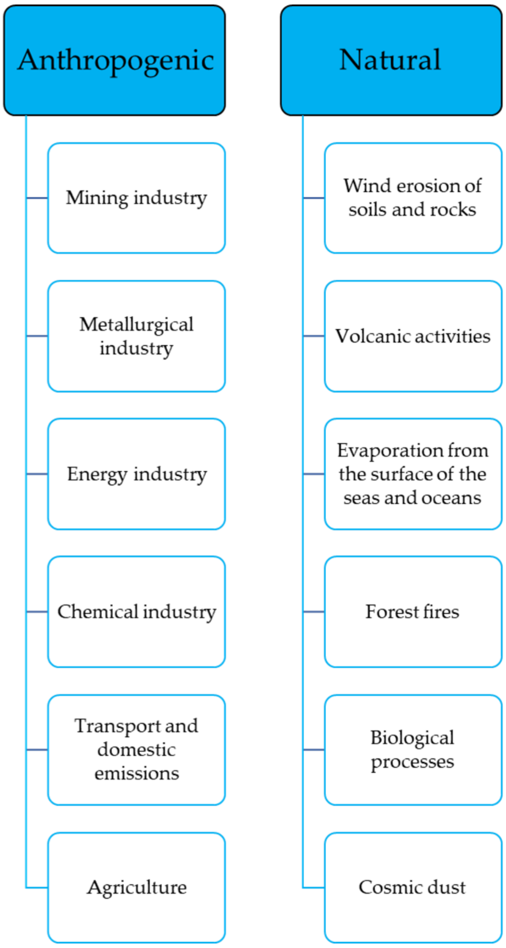

Figure 1. Anthropogenic and natural sources of heavy metals. (authors Ismukhanova L.T., Madibekov A.S.).

Bottom sediment can be considered an indicator of anthropogenic water pollution occurring during the process of sedimentation, depending mainly on the migration activity and sorption of toxic substances such as heavy metals as well as, to a large extent, on geochemical processes in the aquifers. By determining and monitoring the concentrations of toxicants in reservoir bottom sediment, it is possible to assess the anthropogenic load and follow the pollution dynamics in the long term [1,13–15].

The analysis of heavy metals in bottom sediment needs to consider their geogenic content and the form of compounds in the lithosphere of the study area [15]. Such information is of great importance when the specific elemental chemical composition of local soils needs to be taken into account [16]. In the case of significant differences between the regional background values and the global ones, one can either not notice the beginning of anthropogenic pollution of the local soil cover, or on the contrary, take the natural regional background as the result of anthropogenic impact [17,18].

Thus, the natural and anthropogenic factors accompanied by the processes of sedimentation and bioaccumulation are significant in water bodies ecosystems pollution by heavy metals, in both spatial and temporal aspects [19]. Research in this area has become widespread due to the toxicity, persistence, and biological accumulation of heavy metals [20–23]. When evaluating metal pollution of aquatic ecosystems, first of all, it is necessary to take into account the background values of heavy metals in the lithosphere or pre-anthropogenic impact concentrations of metals, which can be compared with the measured values of the region and catchment area under consideration [24]. For this reason, some researchers have used data of Earth's crust average concentrations as initial reference values [25–28].

All the main migration routes of heavy metals in the biosphere, including aquatic and biological systems, can be temporally fixed in bottom sediment. However, they can start as a result of lithosphere weathering and particle transport by land erosion and fluvial processes. Thus, Dobrovolskiy claims that the main masses of heavy metals are mobilized from, and their migration forms originate in, the soil. The huge reaction surface of mineral substances, the presence of soil solutions and dead organic substances in which significant amounts of metals are selectively concentrated, and the high saturation by microorganisms, mesofauna and roots of higher plants create a complex system of metal transformation in soils [29].

The mobility and accumulation of metals in soils and bottom sediment mainly depend on the absorption capacity, the grain size composition (sandy, clayey and silty particles), the humus content, the acidity and the amount of exchangeable cations and free surfaces for cation exchange. Due to the expressed cationic absorption capacity of the soil, due to the negative charge excess of humic substances, it retains positively charged heavy metal ions very well, and a constant supply, even in small quantities for a long time, can lead to significant accumulation of heavy metals in bottom sediment [28–30]. The ability of bottom sediment to accumulate toxicants, and their subsequent conversion into forms that are hardly soluble, but accessible to plants and aquatic organisms, is the main threat to ecological conditions from technogenic pollution of water bodies, creating a potential danger to public health [31,32].

Due to the fact that several heavy metals (Mo; Pd; Au; Ga; In; Tl; Ge; Co) have chalcophilic properties, that is, they have a high degree of mobility in the aquatic environment and bottom sediment (soils), they can be non-toxic, low, moderately or highly toxic in aquatic ecosystems [33]. Toxic to aquatic organisms, as a rule, are metals belonging to class B (chalcophilic, i.e., having a high affinity for non-metals of group 6 of the periodic table). These include metals present in natural sulfides in the form of cations Ag; Hg; Cu; Pb; Cd; Bi; Zn; Sb and non-metals present in the form of anions S; Se; Te; As. Chalcophilic properties are also possessed by several elements that are simultaneously assigned to several groups—Mo; Pd; Au; Ga; In; Tl; Ge; Co, etc.—on the scale of complex compounds. Among this class, the most toxic metals are those with the largest ionic radius and the highest degree of polarization and affinity for sulfide ions, and the lowest degree of oxidation and electronegativity, as has been reported by different authors [34–38]. An additional factor determining the degree of toxicological effects of heavy metals on aquatic organisms is the bioavailability of heavy metals [39–41]. Moreover, toxicological effects are expressed only when heavy metals are available for them, regardless of the concentration level of these metals in aquatic ecosystems [37–43]. It is also necessary to take into account the type of water body, i.e., whether it is of natural origin (lake) or artificial (reservoir), and the impact of river waters on the ecological conditions of the water body for the assessment of the pollution origin [25,44,45].

Accurate assessments of heavy metal pollution of the bottom sediment of water bodies requires the consideration of both natural and anthropogenic factors, as well as the chemical properties of metals (activity, toxicity), their background concentrations in nature (in the lithosphere of the study area) [1,15], their impact on aquatic organisms and plants (bioaccumulation), and the toxic hazards along the food chain [41].

This work did not consider the chemical activity of metals and their mobility by accumulation in the surface levels of the reservoir bottom sediment, because the lack of data for a long period did not allow the solution of these tasks. In the future, it would be interesting to consider the long-term dynamics of sedimentation–sorption processes occurring in reservoir aquatic ecosystems—not only those of an anthropogenic nature, but also those desorption processes occurring as a result of climate change.

In the works of Sokolov ("Natural zones of Kazakhstan") and Durasov ("Soils of Kazakhstan"), it was indicated that the soil cover of the Kapshagay Reservoir catchment area is formed mainly of gray-brown desert soils, among which alkaline, non-saline and takyr-like soils are widespread [46,47]. Kurmangaliyev attributed such soils to the foothills and foothill plains, which are cut by numerous riverbeds, such as Ili River and its tributaries [48]. On the left bank of the reservoir, where the main deltas of the inflowing rivers are located, there are meadow–marsh soils and alkaline soils, which are characterized by the accumulation of metals over a long period of time [46–48].

Thus, the processes of heavy metal migration in the water–bottom sediment system are relevant for river waters, where resuspension processes occur constantly, leading to secondary pollution. In the water area of a reservoir, desorption processes are possible under changing weather conditions (wind, wave regime) in shallow areas, such as on the left bank of the Kapshagay Reservoir.

Due to the expected metal accumulation in the sediment of the Kapshagay Reservoir and the multiple functions of this reservoir besides energy production, such as water storage, appropriation of irrigation water, recreation, aquatic sport, as a habitat for fishes and other aquatic organisms, fishery, surface water purification, as a sediment sink, and sorption of pollutants in reservoir sediments, the purpose of this study is to assess the pollution of the Kapshagay Reservoir bottom sediment by heavy metals, their accumulation in terms of spatial differentiation, and their migration ability in the aquatic ecosystem.

The main objective of this investigation is to analyze the accumulation of heavy metals in bottom sediment, as well as their migration ability in the water–bottom sediment system and their spatial distribution in the Kapshagay Reservoir in Kazakhstan. Due to the fact that only a single small data set was available before our investigation, it represents a special challenge to analyze, evaluate and determine the origin, the spatial distribution and the potential risk of the heavy metal load of the Kapshagay Reservoir with respect to water quality and living organisms.

2. Materials and Methods

2.1. Research Object

The object of the study is the Kapshagay Reservoir, a 140-km-long lake fixed by a dam of the Ili River, ca. 80 km north of Almaty. It is the largest artificial water body in Kazakhstan and one of the biggest in Central Asia. It is of great socioeconomic importance. Its main functions are hydroenergy production and irrigation. Its resources are also widely used for fisheries and recreational purposes. In combination with the construction (1965–1980) of the Kapshagay Reservoir, large irrigation systems were also formed: the Akdala and Karatal rice growing fields and Shengeldy irrigation area (more than 65.0 thousand hectares) [49–51]. These authors already have noted that the reservoir is subject to significant anthropogenic load, caused not only by the influence of the transboundary (Chinese–Kazakh) Ili River, but also by the waters of its tributaries (Kaskelen, Talgar, Yesik, etc.) within the territory of Kazakhstan. They flow through the city Almaty, the small towns Yesik, Talgar, and Kaskelen and the large rural settlements Turgen, Zhetigen, Baiserke, and Shengeldy, and also carry toxicants in washout from irrigation areas, agricultural land and from atmospheric transport [52–58].

Pollution analyses, including those related to heavy metals, are becoming more relevant at present, under the conditions of increasing anthropogenic impact on the aquatic ecosystem of the reservoir. Since metals have high stability and cumulative effects, they can accumulate in bottom sediment to concentrations hundreds or thousands of times higher than their inflow concentration, which can cause significant disturbances to physiological and biochemical processes of aquatic organisms [41].

2.2. Samples Selection

Sediment sampling was carried out at 10 constant points at different depths ranging from 1.0 m in the upper reaches to 40 m in the dam zone of the reservoir, considering the location of fishery areas and reservoir spatial differentiation. Zones identified throughout the water area (upper, central and dam zones) generally characterize ecological and toxicological features of the certain parts of reservoir subjected to the influence of natural and anthropogenic factors (Figure 2).

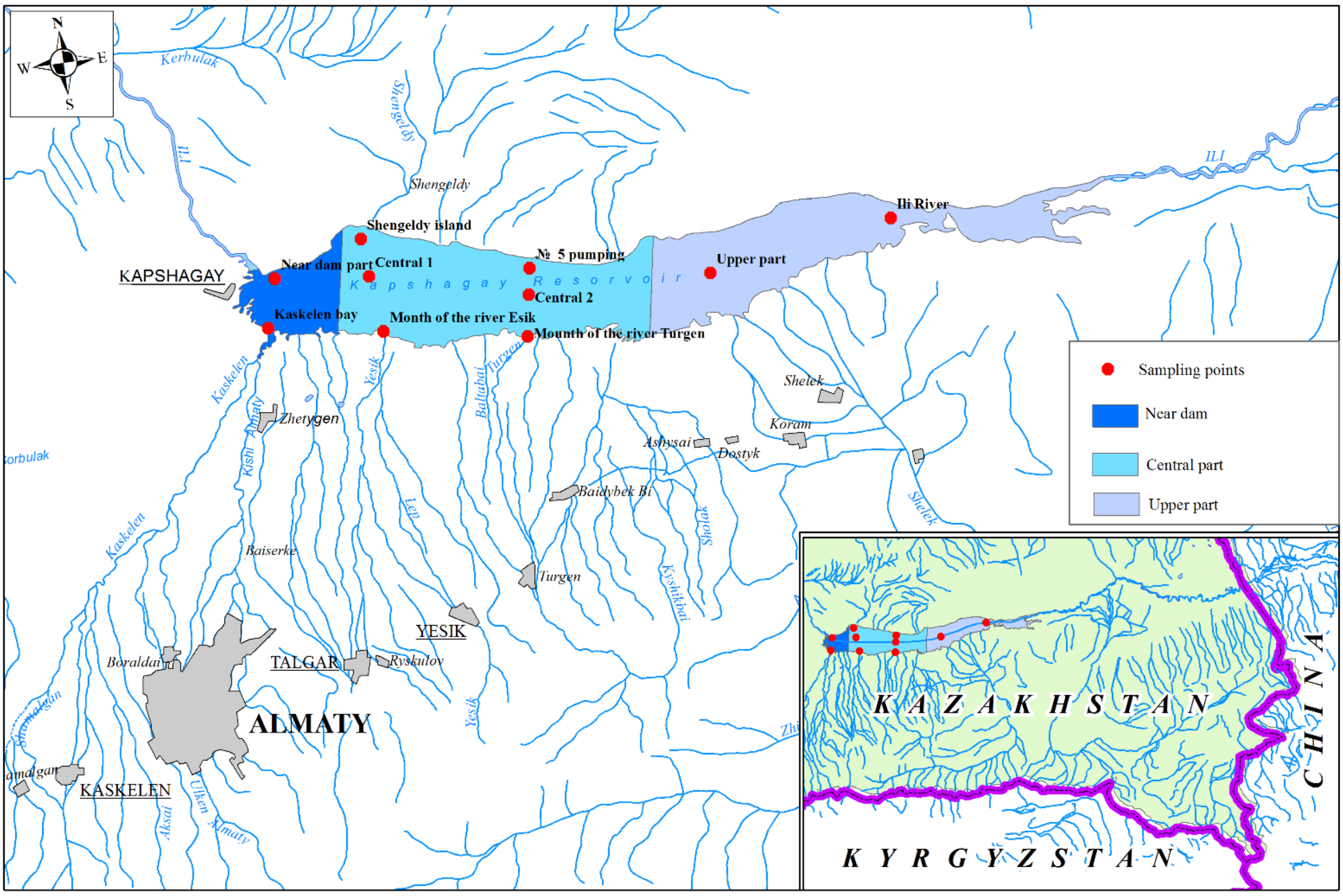

Figure 2. Scheme of the Kapshagay Reservoir with sampling points for bottom sediment in South-East Kazakhstan. (authors Ismukhanova L.T., Madibekov A.S.).

2.3. Sampling Methods

Bottom sediment samples were taken from the upper (5 cm) layer using a Petersen dredge with a small capture area in order to characterize the current level of metal accumulation [59]. Sampling by the bottom dredge was carried out using a motor boat. The bottom dredger descends smoothly when open [S 1]. The moment at which it reaches the bottom is detected by the weakening of the cable tension. Depending on the design of the bottom dredge, the device is closed, and a certain volume of sediment is captured. Then, the device is lifted. The bottom dredge with the sampled sediment is placed in a neutral container, where it is opened and a sample is taken for toxicological analysis of the bottom sediment.

2.4. Spectrometric Analysis Methods of Atomic Absorption

To determine the heavy metals in the obtained samples in the laboratory, they are first dried to an air-dry condition; then, a sample of about 5.0 g is taken from the air-dry sample. To determine the mobile forms of metals, the samples are processed with the use of ammonium acetate buffer solution (pH 4.8), followed by the determination of metals in the resulting solution by means of atomic absorption analysis [60].

Heavy metals in the samples are determined by the flame atomic absorption spectrometric method using an AA-7000 atomic absorption spectrophotometer (Shimadzu, Kyoto, Japan) with a hollow cathode lamp for the corresponding metals to correct the nonspecific absorption coefficient, as well as a nozzle burner operating on an acetylene–air mixture [60].

The method, updated in the State Register of Kazakhstan, is based on the property of metal atoms whereby they are able to absorb light of certain wavelengths (Cu—324.7 nm; Zn—213.9 nm; Pb—283.3 nm; Cd—228.8 nm), which they then emit in an excited state.

2.5. Used Standard Samples

In the spectrometric determination of the metals, to build calibration graphs with correlation coefficients r = 0.99 [S 2, 3], state standard samples (SSS) are used:

- Composition of aqueous solution of copper ions (3K-1) SSS 7998-93 (C_{Cu} = 0.0125; 0.025; 0.05; 0.1 mg/L);
- Composition of aqueous solution of zinc ions (4K-1) SSS 7837-2000 (C_{Zn} = 0.0125; 0.025; 0.05; 0.1 mg/L);
- Composition of aqueous solution of lead ions (2K-1) SSS 7012-93 (C_{Pb} = 0.05; 0.1; 0.15; 0.2 mg/L);
- Composition of aqueous solution of cadmium ions (1K-1) SSS 6690-93 (C_{Cd} = 0.0125; 0.025; 0.05; 0.1 mg/L).

State standard samples and calibration graphs are required in order to reliably determine the heavy metals content in bottom sediment samples.

Both sampling and analysis of toxicological samples were carried out in accordance with the updated standards in the State System of Ecological Monitoring of Kazakhstan [60].

3. Results

3.1. Concentration of Heavy Metals in Bottom Sediment

Because of the importance of performing a modern assessment of the water body ecosystem, this paper presents the results of a toxicological analysis of the heavy metal concentrations measured in the bottom sediment of the Kapshagay Reservoir in comparison with other results and standards. The zinc concentration in the bottom sediment of the Kapshagay Reservoir water area reached up to 37.0 mg/kg, and lead up to 8.80 mg/kg, while copper and cadmium were found in lower concentrations, not even reaching 1.0 mg/kg (Table 1).

Table 1. Heavy metal concentrations in bottom sediment of the Kapshagay Reservoir.

Metals	mg/kg			
	Zn	Cu	Pb	Cd
amplitude	30.0–37.0	0.12–0.38	1.20–8.80	0.16–0.96
average	33.6	0.23	5.18	0.46

Comparing the Kapshagay Reservoir data of metal concentrations in the bottom sediment with the values provided in US studies by MacDonald D.D. et al., 2000 (Table 2) [61], an excess of up to 3 times was typical for cadmium, and up to 1.1 times for zinc, but the concentrations of copper and lead are considerably lower [62,63]. This result of the anthropogenic load of water body ecosystems is quite acceptable for the water bodies of Kazakhstan, because stricter regulations will guarantee that the water quality remains within normative conditions.

Table 2. Comparison of measured heavy metal concentrations in reservoir bottom sediment with standards from USA [61] (mg/kg).

Metals Content	Heavy Metals			
	Zn	Cu	Pb	Cd
Kapshagay Reservoir bottom sediment	33.6	0.23	5.18	0.46
USA standards	30	21	10	0.16

As mentioned above, pollution of bottom sediment in water bodies occurs with sedimentation processes, both as a result of the migration activity of metals and as a result of soil properties within the reservoir catchment area. When assessing the degree of reservoir water area pollution on the basis of the concentrations of chemical elements in the bottom sediment, in the absence of norms and the concept of "maximum permissible concentrations" (MPC), background indicators, such as the Clarke values of the considered metals in the lithosphere, can be used as a standard [64–67].

3.2. Assessment of the Bottom Sediment Pollution Level

Yu.Ye. Sayet et al. developed a total pollution index Zc to assess the pollution of bottom sediment [68]. The calculation of the total indicator for metals concentration in the bottom sediment was carried out according to the following Equations (1) and (2):

$$Kc = \frac{Ci}{Cb} \tag{1}$$

$$Zc = \sum Kc - (n-1) \tag{2}$$

where Kc is concentration factor; Ci is pollutant concentration; Cb is pollutant concentration at the background point; n is the number of elements to be determined.

Background concentrations of pollutants are calculated in consideration of the indicators of the considered metals in the lithosphere [64–69]. Table 3 shows that the concentrations of metals in the bottom sediment are an order of magnitude lower than their background values, with the exception of cadmium, which depends on the adsorption capacity of mobile forms of this metal in neutral and weakly alkaline environments [46,47,62], i.e., Greysems and meadow–boggy soils, which are characterized by high biological activity. The metal concentration is also dependent on the acidity of the environment, with increased solubility and incredased concentrations of metals in the bottom sediment occurring with decreasing pH [63,64]. Low concentrations of zinc, copper and lead indicate their low migration activity in the reservoir sediments and the low intensity of the leaching processes [70].

Table 3. Calculation of the pollution level of the bottom sediment.

Parameters	Zn	Cu	Pb	Cd
Background [65]	83.0	47.0	16.0	0.13
Concentration	33.6	0.23	5.18	0.46
Kc	0.40	0.005	0.32	3.54
Zc		1.26		

The assessment of the degree of contamination of the reservoir water area based on the concentration of chemical elements in the bottom sediment showing a low level of Zc = 1.26, which is characterized as "within the background limits", and in terms of sanitary and toxicological hazard considered to be acceptable (Tables 3 and 4).

3.3. Spatial Distribution and Migration Activity of Heavy Metals in Bottom Sediment

The spatial distribution and migration activity of heavy metals in the bottom sediment of the Kapshagay Reservoir water area are shown in Figures 3–6. To visualize this process, map models were prepared using the Surfer software product in the water–bottom sediment system, which plays a significant role in the assessment of the ecological conditions of the reservoir. In the created model maps, small tributary rivers for reservoir pollution were also considered.

Table 4. Indicative scale by pollution index Z_c for water pollution assessment [69] with the help of heavy metal concentrations in bottom sediment.

Pollution Level	Z_c	Sanitary and Toxicological Danger	Content of Toxic Elements in Water
Low	10	Acceptable	Mostly within background limits
Middle	10–30	Moderate	Many are higher relative to the background; some occasionally reach MPC
High	30–100	Dangerous	Many elements are above the background; some exceed MPC
Very high	100–300	Very dangerous	Many are many times higher than the background; some consistently exceed MPC
Extremely high	>300	Extremely dangerous	Mostly many times higher than the background; many consistently exceed the MPC

Figure 3 shows an increase in copper concentration from 0.36 to 0.38 mg/kg in the bottom sediment at the mouths of Kaskelen and Turgen rivers and up to 4.4 and 4.7 µg/L in the water in the upper reaches of the reservoir. The data in the Cu–water and Cu–bottom sediment systems have a strong positive relationship, R^2 = 0.85, which indicates a regression of sediment pollution from water pollution by this metal.

The deposition of copper in the bottom sediment can be traced at the mouths of the rivers, i.e., from the northern shore and near the dam part of the reservoir to the southern shore, whereby a decrease in pollution activity of this metal is observed. The concentration of this metal increases in the upper reaches of the reservoir to 4.7 µg/L, while in the direction of the dam part, it gradually decreases to 0.6 µg/L, apparently already being deposited in the bottom sediment, because sedimentation of the main mass of sediments brought by the Ili River occurs as the water mass moves to the central and near-dam parts of the reservoir.

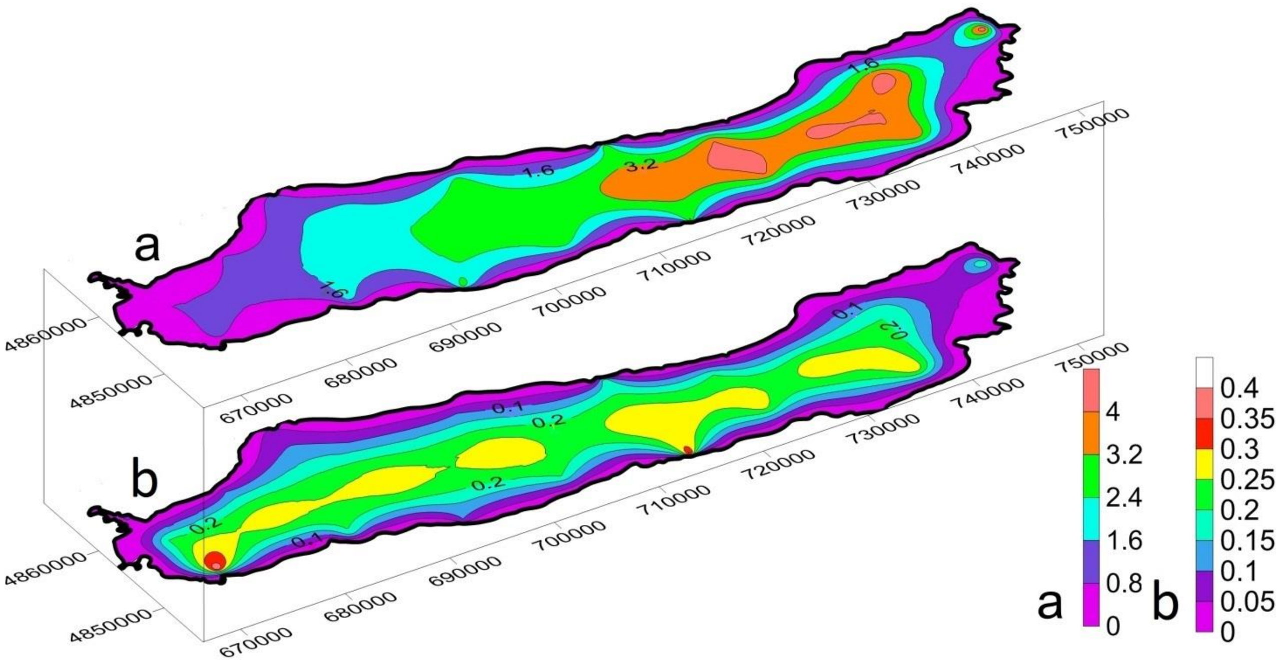

Figure 3. Spatial distribution of copper in water and bottom sediment of the Kapshagay Reservoir. (**a**) Water—µg/L, (**b**) bottom sediment—mg/kg. (authors Ismukhanova L.T., Madibekov A.S.).

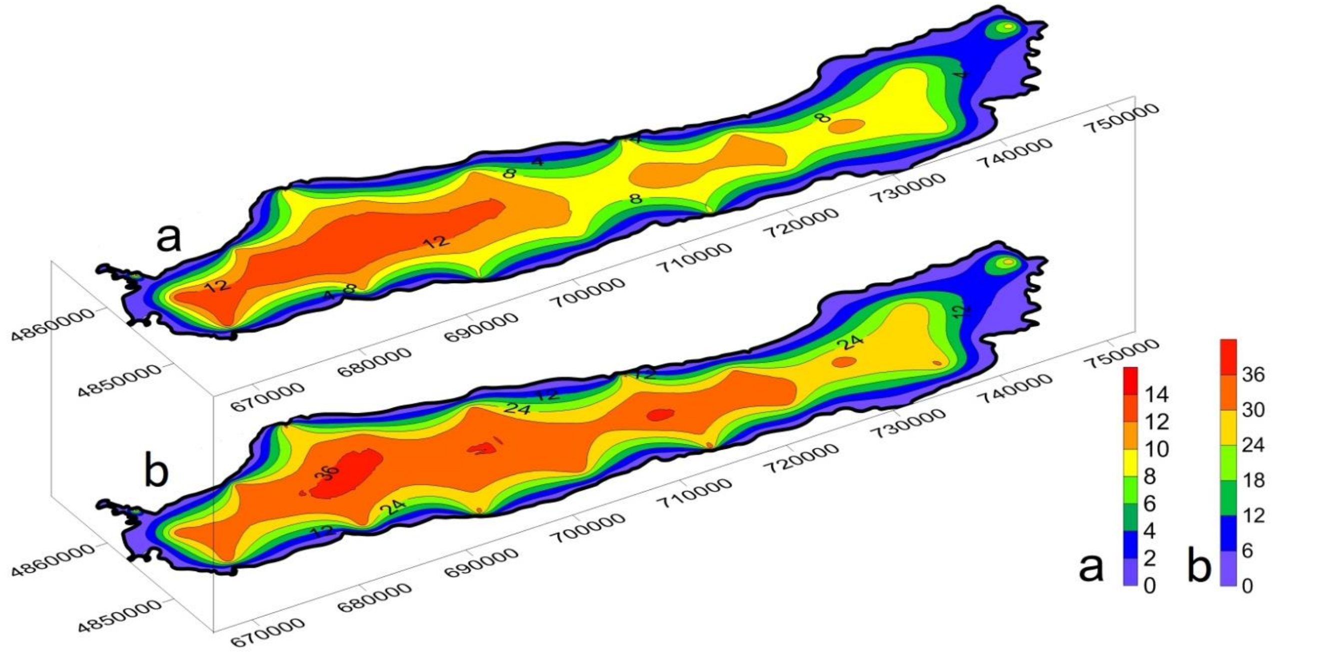

Figure 4. Spatial distribution of zinc in water and bottom sediment of the Kapshagay Reservoir. (**a**) Water—µg/L; (**b**) bottom sediment—mg/kg. (authors Ismukhanova L.T., Madibekov A.S.)

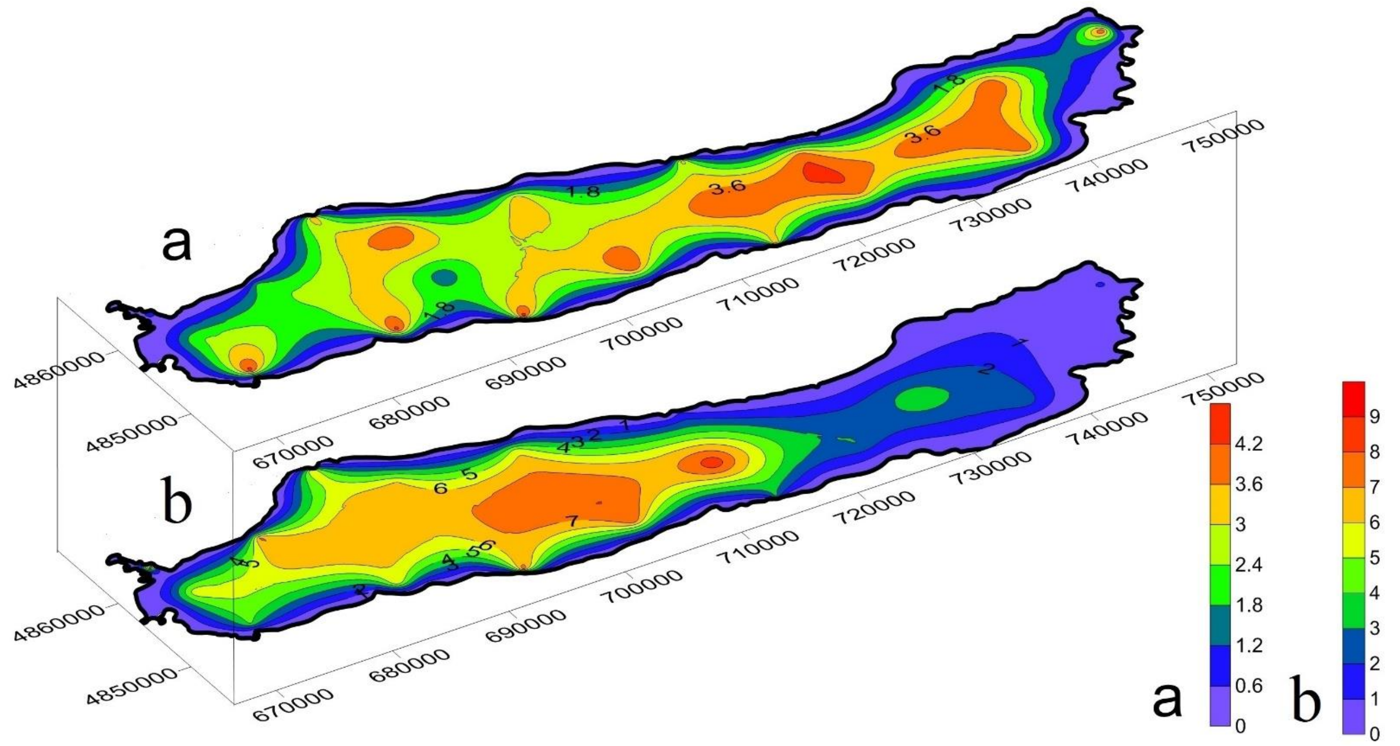

Figure 5. Spatial distribution of lead in water and bottom sediment of the Kapshagay Reservoir. (**a**) Water—µg/L; (**b**) bottom sediment—mg/kg. (authors Ismukhanova L.T., Madibekov A.S.).

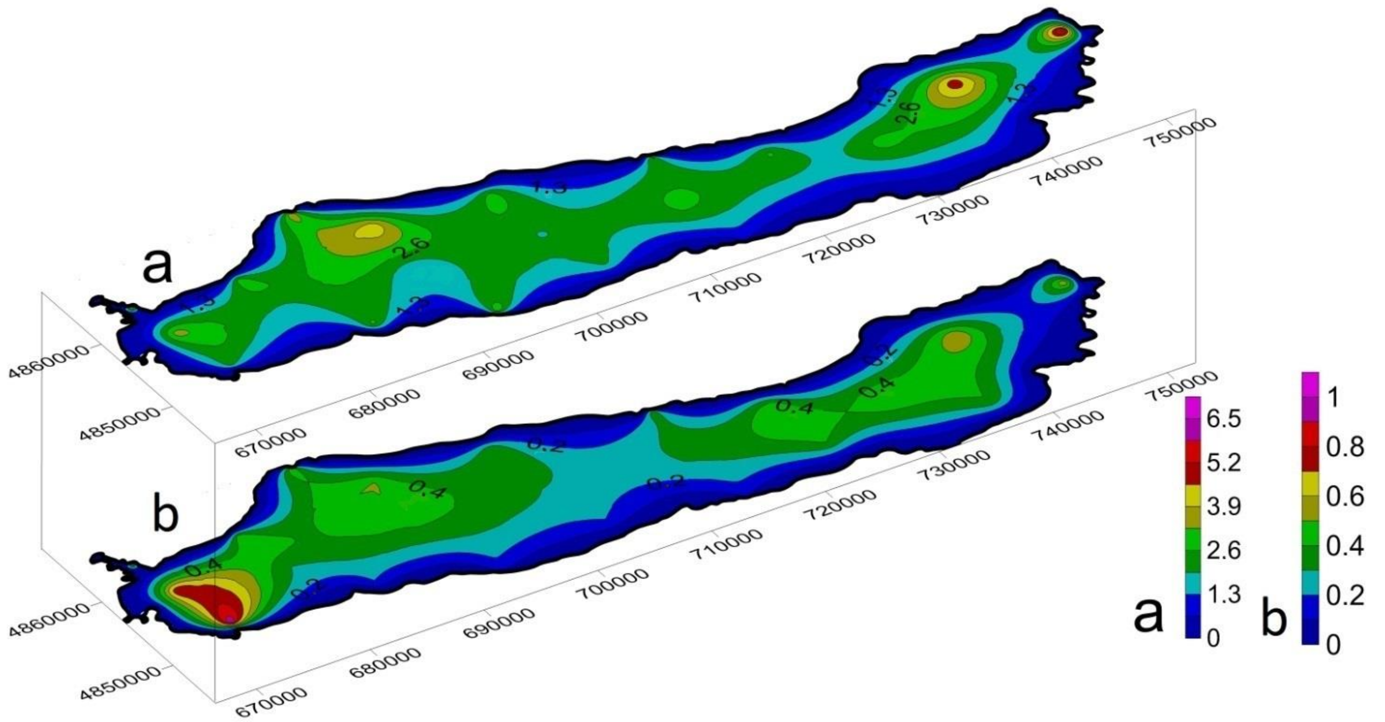

Figure 6. Spatial distribution of cadmium in water and bottom sediment of the Kapshagay Reservoir. (**a**) Water—µg/L; (**b**) bottom sediment—mg/kg. (authors Ismukhanova L.T., Madibekov A.S.)

Zinc concentration varies from 30 to 37 mg/kg in the bottom sediment throughout the whole reservoir water area, with deposition occurring in the area of the Turgen River confluence (Figure 4). Zinc deposition in the bottom sediment is also high, reaching up to 34–35 mg/kg, respectively, in the runoff areas of the Kaskelen and Shengeldy rivers. In the water of the reservoir, a high zinc concentration can be traced in the confluence zone of the Kaskelen River and in the dam part. In the Zn–water and Zn–bottom sediment systems, the regression has an inverse relationship $R^2 = -0.78$.

Lead concentration of up to 8.8 mg/kg in the bottom sediment of the reservoir were recorded in the central and dam zones, as well as on the coasts of the reservoir. It is assumed that the debris cone of the Yesik, Turgen and Shengeldy rivers affects the sedimentation processes for lead in the sediments (Figure 5). The accumulation of lead by the transboundary runoff of the Ili River occurs close to the central and dam zone of the reservoir water area. Increased lead concentrations in the reservoir water are observed in the areas of the rivers inflow, moving from the upper reaches to the dam zone, gradually being deposited in the bottom sediment. Such a lead distribution in water can also be observed at the mouths of the Kaskelen and Yesik rivers.

As can be seen from Figure 6, the cadmium-contaminated water mass of the Ili River runoff at concentrations of up to 6.4 µg/L moves from the upper reaches to the central part of the reservoir, being deposited in the dam zone at concentrations of up to 0.5 mg/kg in the bottom sediment, while in the confluence areas of Kaskelen River, the concentration reaches up to 1.0 mg/kg, and for the Turgen River up to 0.6 mg/kg. Such a distribution and deposition of cadmium indicates a significant level of anthropogenic load of the ecological conditions of the Kapshagay Reservoir. As is widely known [2,3,5,7], cadmium is especially toxic in high concentrations and in combination with other toxic metals, which in turn can negatively affect aquatic organisms, thereby being the initial link in the trophic chain. In the Cd–water and Cd–bottom sediment systems, the regression has a positive relationship $R^2 = 0.51$.

Consequently, the presented material provides a general picture of the heavy metal distribution in the surface layer and bottom sediment of the reservoir water area, clearly showing the centers of their distribution. The obtained results indicate that both transboundary inflow and small tributary rivers have a significant impact on the ecological conditions of the reservoir, and making it possible to assess the water pollution in these watercourses.

3.4. Sources of Anthropogenic Pollution

In the data on the transboundary inflow of pollutants along the Ili River, significant amounts of heavy metals are brought from the territory of China [54,71,72]. During the period from 2001 to 2014, the total inflow of heavy metals amounted to 1220 tons of copper and 1710 tons of zinc (Figure 7). Moreover, in the period 2001–2014, the actual inflow in some years exceeded the allowable values for copper by more than 7 times, and for zinc, by up to 10 times [54,71,73].

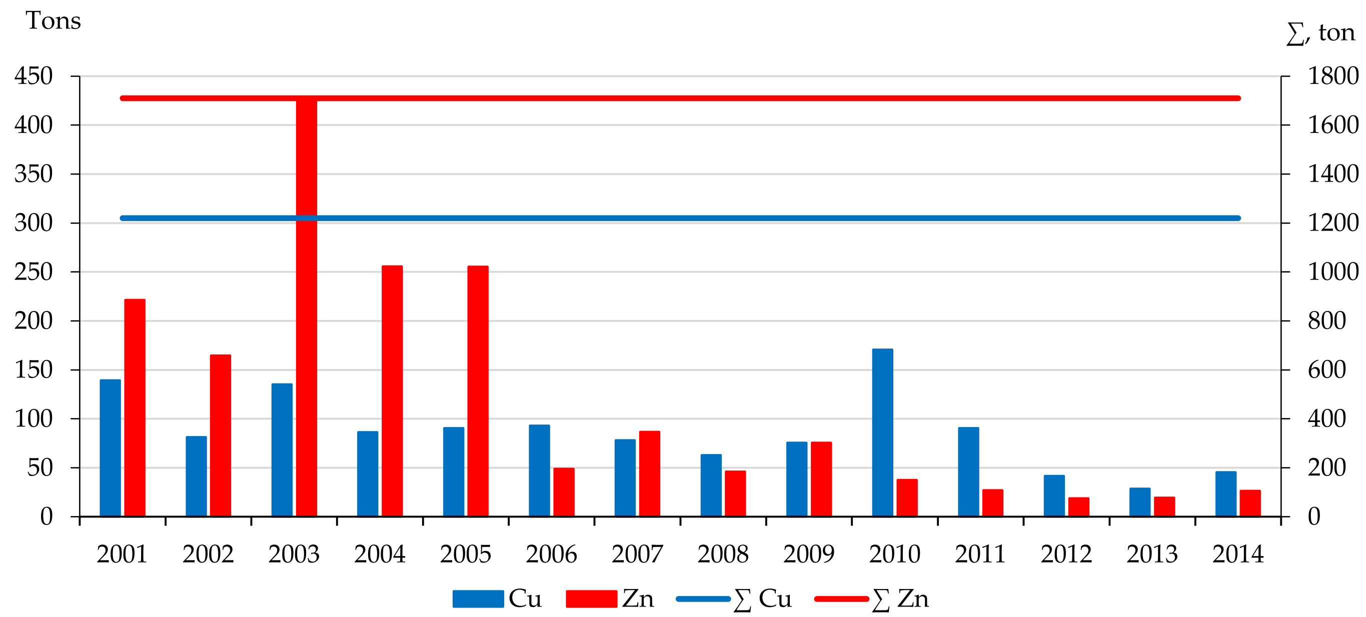

Figure 7. The inflow of heavy metals according to the data from cross-section Dobyn [54].

According to the results of the analysis of the Kazakhstan State Enterprise "Kazhydromet" materials, for the border cross-section of Dobyn for 2013, an increased level of inflow was recorded during the spring flood—Cu (9.11 t); Zn (5.93 t); Pb (1.94 t); Cd (0.07 t)—which remained in the summer season Cu (7.61 t); Zn (4.81 t); Pb (1.12 t); Cd (0.09 t) (Figure 8).

The increase in the level of heavy metal inflow in the spring–summer period is due to the increase in the water content of the river itself, which is caused by precipitation and melting of glaciers.

The transboundary inflow of pollutants varies considerably by season. Throughout the entire observation period, the maximum inflow of pollutants was recorded during the spring–summer period, and the minimum during winter. The dynamics of changes in the intra-annual regime of the Ili River in the border cross-section Dobyn was determined on the basis of the volume of incoming pollutants, as a function of their concentration in the river water.

Among Kazakh pollutant sources, the main reservoir pollutants come from the communal services of settlements (Almaty city and the small towns of Yesik, Talgar, Kaskelen), from agriculture (in particular, irrigated crop farming), and from enterprises belonging to various industries. There are 1928 industrial enterprises in the region, of which 175 are large- or medium-sized, 93.5% belong to the manufacturing industry, 0.5% to mining, and 6.0% represent the production and distribution of electricity, gas, and water. The leading places in industrial production are occupied by food production (35%), pulp and paper industry and publishing (9.4%), production of non-metallic mineral products (10.6%), and metallurgical industry and production of finished metal products (14.3%) [73,74]. Thus, there is an inflow of heavy metals entering the reservoir water area during the spring period, which is deposited in the bottom sediment.

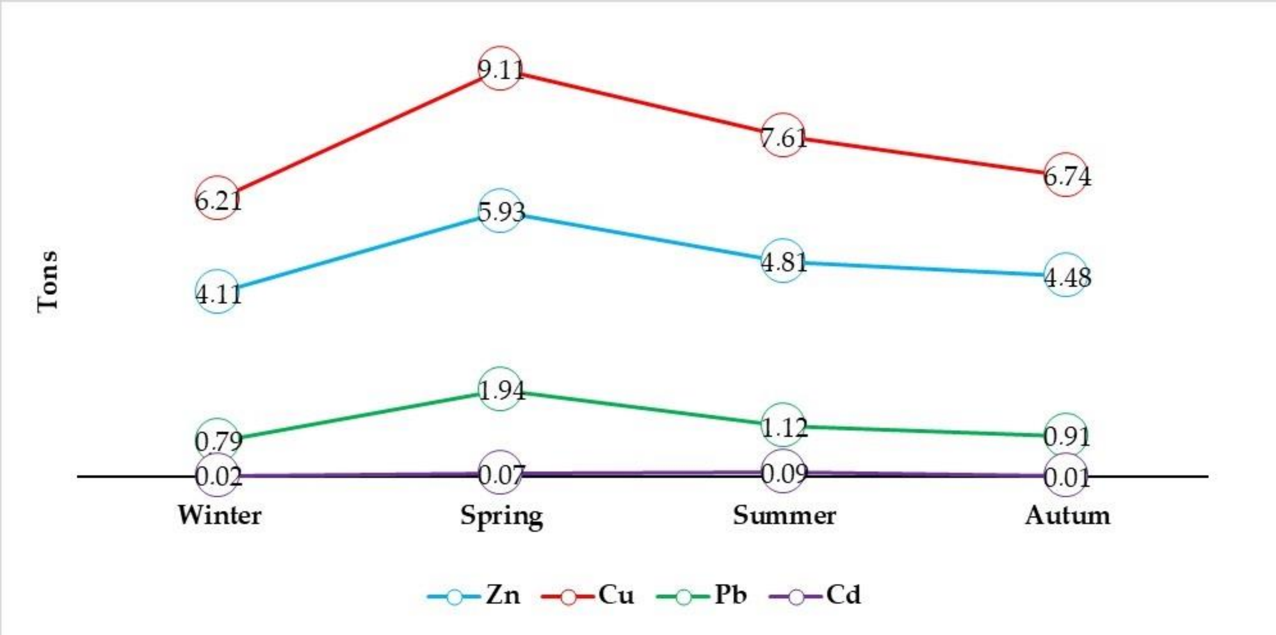

Figure 8. Seasonal inflow of heavy metals along the Ili River in the border cross-section Dobyn (2013) [54].

4. Discussion

An important natural factor in the spatial distribution of bottom sediment in water bodies is sedimentation processes, which depend on several factors. These processes are traced in the distribution of metals in the bottom sediment of the reservoir, which can form various complexes or salts of metals, as well as their occurrence in the lithosphere of the object under study. In acidic environment, microelements such as lead, cadmium, copper, zinc, manganese, nickel, cobalt, iron, and chromium are the most mobile; in an alkaline environments, the most mobile microelements include arsenic, selenium, uranium, molybdenum; while those mobile in a wide range include lithium, rubidium, cesium, fluorine, bromine, boron [21–24,75]. Besides the pH value, the mobility of metals also depends on the granulometric and mineralogical composition of the mineral substrate and the degree of its humus content. Light and slightly humus soils are usually depleted in heavy metals compared to silt and organic matter, since the minerals found in clay and humus have a greater absorption capacity [76,77]. In this regard, in the water–bottom sediment system, the copper content in the water from the upper reaches (4.7 µg/L) to the dam zone (1.6 µg/L) decreases, but in the bottom sediment, these values have a different character, because from the upper reaches (0.16 mg/kg) to the dam zone, the concentration of copper (0.36 mg/kg) increases, which is associated with a change in the granulometric composition of the bottom sediment from a sandy to a silty and clayey composition. In the process of migration and sedimentation, the mobility of copper in the aquatic environment is explained by the nature of the precipitation of its compounds and the content of this metal in the lithosphere (47.0 mg/kg) of the reservoir [64]. Lead and cadmium concentrations in the aquatic ecosystem of the Kapshagay Reservoir show the same behavior as pollution with copper, with high concentrations from the upper reaches to the dam zone in the aquatic environment and the bottom sediment.

A different trend is observed for pollution of the water ecosystem of the reservoir with zinc, whereby the polluted water mass (9.8 µg/L) increases towards the dam zone (13.7–13.8 µg/L) before being deposited in the estuarine zone, with the pronounced clayey and muddy bottom of the tributary rivers Turgen and Kaskelen reaching concentrations of up to 37.0 and 35.0 mg/kg, while at the dam zone they reach up to 33.0 mg/kg. High values of zinc in the bottom sediment may depend on its content in the lithosphere c.f., [64], which may reach up to 83.0 mg/kg.

We studied the mobile forms of metals in the aquatic ecosystem of the Kapshagay Reservoir. However, determining the proportion of metals in the aquatic environment itself and in bottom sediment, along with the proportion of secondary pollution is a difficult task, both in theoretical and practical terms, since all processes are subject to various factors, including weather conditions (wind, waves, rain). Nevertheless, other authors (Wojtkowska; Kalembasa and Pakuła) have also successfully determined Zn, Cu, Pb and Cd in the bottom sediment of Lake Czernyakovskoe, located within the borders of Warsaw (Poland), as reported in [78–80]. The results of this study showed that in the bottom sediment of Chernyakov Lake, fractions associated with both iron and manganese oxides (for lead and zinc) as well as with organic substances (for copper), carbonate fractions (for cadmium) predominate [81–84]. This confirms the need to monitor sediments not only in Chernyakov Lake, but also their applicability to other water bodies, both in terms of total concentrations and in terms of the determination of the forms of the metal compounds in the bottom sediment. Similar studies have also been carried out by a number of scientists considering the migration and forms of metals found in the bottom sediment [60,85–88].

Studies conducted to assess the pollution and environmental risk, analyze the spatial variability of metal concentrations, and identify potential sources and factors in six reservoirs in Poland (Je'zewo, Jutrosin, Rydzyna, 'Sroda, Wrze'snia), revealed that pollution with Cd; Cr; Cu; Ni; Pb mainly originates from geogenic sources, while Zn concentrations originate from point sources associated with agriculture [88]. According to the results of studies by Sojka and other authors (2003) [89], the metal concentrations are dependent on the granulometric composition of the bottom sediment (sand, silt and clay) [2,15,16] and, in turn, accumulate in the areas of river inflow and near the dam zone, thereby confirming our results, which indicated that from the Ili River runoff, polluted by heavy metals, moves from the upper reaches to the central part of the reservoir, depositing in the dam zone, as indicated by the sandy bottom, as well as in the silted areas of the Kaskelen and Turgen rivers inflow.

According to several authors [90,91], the decisive role in both the presence and the concentration level of metal in bottom sediment and suspended solids is played by the pH value, depending on oxidation-reduction conditions in the bottom sediment [62]. Changes in these conditions in the bottom sediment lead to changes in the valence of metals and the forms of occurrence for natural waters of any type, regardless of their chemical composition or hydrological regime [92]. The concentration of metals is dependent on the acidity of the environment, as a result of their increased solubility, with increased concentrations of metals occurring in the bottom sediment with decreasing pH, and when entering the aquatic environment, they hydrolyze and interact with other ions, while in the pH range of waters (6.5–8.5), they are able to sparingly form soluble hydroxides, phosphates and sulfides [63,64]. Therefore, the acidity of the environment affects the intra-aquatic processes of complex formation and transformation of various forms of metals [93].

Low concentrations of zinc, copper and lead indicate their low migration activity in the sediments of the Kapshagay Reservoir, as well as the intensity of the leaching processes. During the study period, the magnitude of the active reaction of reservoir water characterized the water as being slightly alkaline, with pH values ranging from 8.1 to 8.6. pH presented low values in the reservoir zones that were subject to the influence of the small tributary rivers and the Ili River runoff.

Another important factor is to determine the concentration of metals of primary and secondary origin in bottom sediment, which is associated with the processes of redistribution of pollutants in bottom sediment, worsening the conditions for the existence of benthos in the aquatic ecosystem and, accordingly, their balance [88].

It is generally known that, along with the accumulation of heavy metals in bottom sediment, various inorganic and organic substances (petroleum products, pesticides, etc.) are deposited as a result of physical, chemical and biological processes that can easily be subjected to decomposition processes. For example, up to 30% of oil products are absorbed by bottom sediment, and up to 86% of metals [94]. When the accumulation of metals reaches a high level, they become toxic [12,95].

Independently of the fact that the accumulation of metals in bottom sediment is higher than in water, it is necessary to consider that these interactions between water and sediments are still only poorly studied, and it is not known which part is more mobile and accessible to hydrobionts [62,96–98]. Depending on the aquatic food chain, some fish species accumulate heavy metals in soft and hard tissues [12,39,40,99], and some in the gills as they absorb metals from the water, while others show a higher metal concentration in the bowel compared to other organs following absorption of metals from bottom sediment [100,101]. Unlike organic substances, heavy metals can only be redistributed between the layers of water systems, and are found in various forms that enter benthic organisms and, through trophic chains, into fish, then humans, accumulating in bones and tissues, as follows: plants→hydrobionts→fish→humans [62,96,98,99]. For this reason, heavy metals are among the pollutants that are considered very dangerous, and which are receiving attention in different countries [101–103].

Thus, the study of the influence of physicochemical and biological factors necessary for the selection and justification of measures to prevent adverse impacts on the ecosystem of the Kapshagay Reservoir is closely related to the conditional systems between water–bottom sediment and aquatic organisms. The data obtained by us regarding the levels of heavy metal accumulation in the water and bottom sediment of the Kapshagay Reservoir exceed the standards for copper, zinc, and lead for fishery reservoirs, and given the long-term preservation of toxic substances in water and bottom sediment and their migration along the trophic chain, they show that it is impossible to exclude the accumulation of toxicants in fish in the future, which in turn plays an important role in providing the population with environmentally friendly fish products.

5. Conclusions and Future Perspectives

Bottom sediment actively accumulates heavy metals. As a result, it can be both a primary and a secondary pollution factor of the entire aquatic ecosystem, which is associated with the process of redistributing pollutants in bottom sediment, as a result of which the conditions for the existence of benthos in the aquatic ecosystem worsen. In the bottom sediment of the Kapshagay Reservoir, high values were determined for zinc (up to 37.0 mg/kg) and lead (up to 8.80 mg/kg). Copper and cadmium concentrations were found to be at lower values, not even reaching 1.0 mg/kg. The assessment of the degree of contamination of the water area of the reservoir showed a low level of Zc = 1.26, which can be characterized as "within the background limits", and with respect to the sanitary and toxicological danger, it can be classified as acceptable.

High concentrations of metals were found in the bottom sediment at the mouths of the Kaskelen and Turgen rivers, indicating the significant impact of anthropogenic load on the ecological conditions of Kapshagay Reservoir. The obtained results also indicate the nature of the water pollution of these watercourses, which allows the reservoir to be contaminated with agricultural and domestic wastewater.

Anthropogenic load, to which the entire ecosystem of the reservoir is exposed, has a very close relationship in the conditional systems between water–bottom sediment and aquatic organisms. The long-term preservation of toxic substances in both water and, especially, in the bottom sediment can be expected. Metal migration through the trophic chain, and the accumulation of toxicants in fish cannot be excluded in the future, which in turn plays an important role in the provision of the population with environmentally friendly fish products.

More studies on the migration processes of water–bottom sediment systems in water bodies would make it possible to assess the role of bottom sediment in the self-purification of aquatic ecosystems.

Climate change, causing both decreased runoff and low water level situations in reservoirs and spring floods in combination with a high level of sediment input, has to be considered in future research. What effects will these factors have regarding both input situations and the sorption and desorption of metals in bottom sediment?

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