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Geochemical characteristics of microelement distribution in surface sediments of Ust-Ilimsk Reservoir

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Geochemical characteristics of microelement distribution in surface sediments of Ust-Ilimsk Reservoir

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Abstract. This research examines the characteristics of spatial distribution of As, Pb, Hg, Cd, Zn, Ni, Co, Cu, Cr in bottom sediments of Ust-Ilimsk reservoir. Two zones of the reservoir with elevated accumulation levels of potentially toxic elements have been determined: Vihorevsky bay (inflow from anthropogenic sources) and the reservoir area near the dam (inflow from natural and anthropogenic sources). Mobility of studied trace elements and the probability of the secondary contamination has been assessed based on the determined speciation of trace elements in bottom sediments.

1. Introduction

Presently technogenic factors are inevitably overlapping with natural factors of reservoirs bottom sediment's chemical content formation which is determined by the influx the elements of antropogenic origin in the composition of suspended particles. Meanwhile heavy metals are especially dangerous the toxicity and migration properties of which predetermine negative consequences for living organisms. Thus, chemical composition of bottom sediments, which are the depositing environment, is considered one of the most objective indicators of the ecological status of water bodies [1, 2].

In present Angara River is the only surface runoff of the cleanest Baikal Lake vulnerable to extensive anthropogenic pressures. The transformation and deterioration of the water resources of the river is associated with the construction of Hydroelectric power stations cascade (Irkutsk, Bratsk, Ust-Ilimsk, Boguchany reservoirs) and the wastewater flow from municipal and urban districts. This paper focuses on Ust-Ilimsk reservoir (UIR) which is the third reservoir in the cascade of the Angarsk hydroelectric station, and its hydrochemical regime at different working periods is presented in detail at [3]. The published average data on the element concentrations of the whole UIR [4] bottom sediments do not reflect the processes and factors of the formation of their chemical composition necessary for the environmental assessment of the reservoir. In this regard the main goal of the research was the examination of spatial distribution and mobility of the elements in surface layer of UIR bottom sediments.

2. Materials and methods

UIR is the deep-water reservoir, consisting of the Angara and Ilim branches. The sampling points of the UIR bottom sediment (figure 1) are marked depending on the information obtained previously on its hydrochemical composition, reflecting the natural and technogenic input of elements into the reservoir ecosystem [3]. The bottom sediments were sampled from motorboat into plastic containers with the use of GOIN-1 tube. The thickness of the bottom sediments in riverbed is 4 cm in average, with a slight increase downstream.

   The Vikhorevsky bay is the zone with a high sedimentation rate at UIR. The highest sedimentation rates (over 100 cm) are observed in the area where the river of the same name confluence into this bay. At UIR the upper two centimeters layer of bottom sediments is represented, as a rule, by brown or red mud and at the estuary of Vikhorevsky bay only the oxidative conditions in the sediment are kept to a depth of 4 cm. Gray colored or gray veins sediments are observed down the section, this color indicates the reducing environmental conditions.
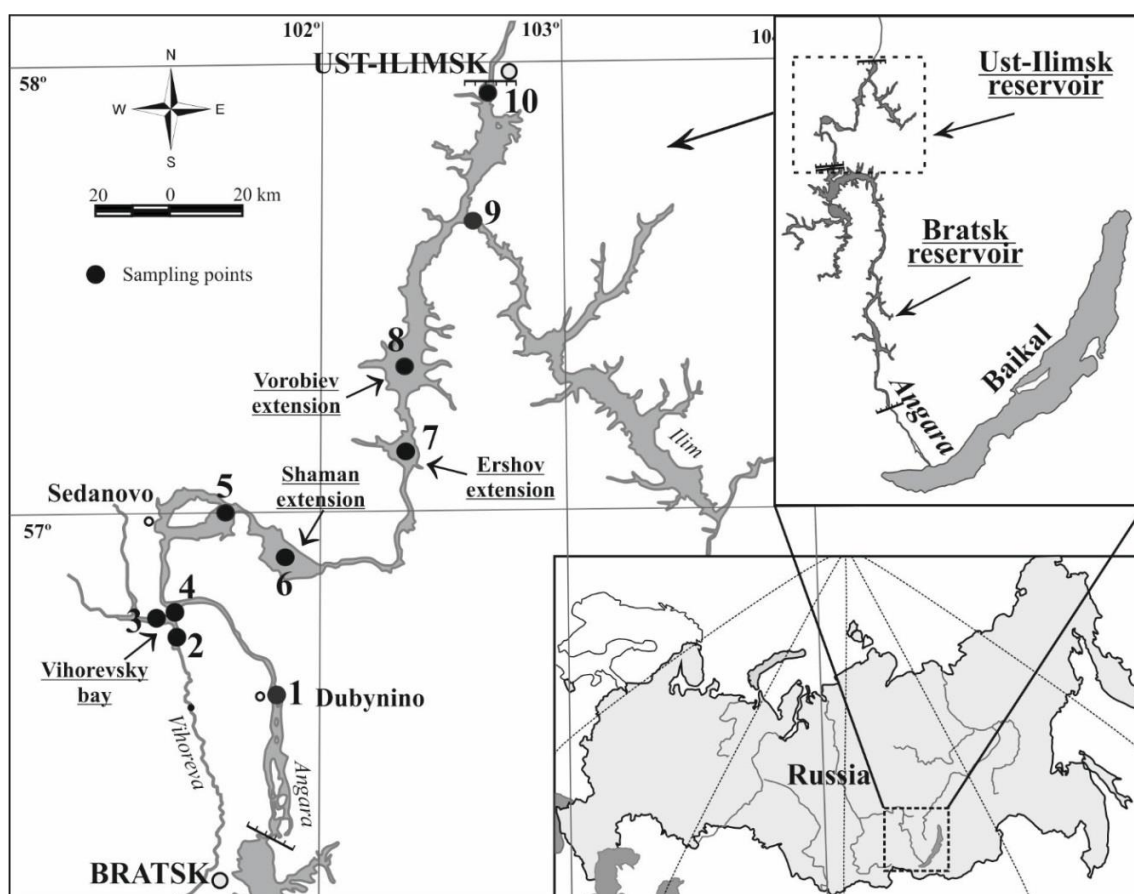

Figure 1. Map of location of sampling stations for bottom sediments of the Ust-Ilimsk reservoir.

   For the estimation of modern condition of water reservoir the upper layer (0-2 cm) of bottom sediment was studied. The chemical analyses were performed at the Center for Collective Use «Isotope-geochemical studies» at the Institute of Geochemistry (Irkutsk, Russia).The elements As, Pb, Cd, Zn, Ni, Co, Cu, Cr were defined in water by the ICP-MS method with mass-spectrometer ELEMENT-2 (Thermo Finnigan, Bremen, Germany). Mercury concentrations in water were measured by atomic-adsorption

analyzer RA-915+ with attachment RA-91 using «cold vapor» technique. The accuracy of analyses was controlled with the synthetic reference solution IQC-26 (NIST, the USA). The method [6] was used for the rest of the elements; according to this method, there were obtained the following fractions: water-soluble, easily exchanged, carbonate, organic fractions of the elements, the fraction of amorphous metal hydroxides and elements adsorbed on them and insoluble residue.

The widely used [7–9] concentration ratio of a chemical element (CR) was applied to characterize the geochemical anomalies. CR is characterizing the degree of element accumulation in bottom sediments regarding to the background content:

$$CR = \frac{c_i}{c_b} \tag{1}$$

where C_i – the content of i-s element, C_b – background content of the elements in bottom sediments. The median of element concentrations determined in the bottom sediments in whole UIR was taken as the conditional background concentration.

3. Results and discussion

The spatial distribution of gross concentrations of trace elements in the upper layer of the UIR bottom sediments is shown on figure 2. According to the average concentrations of trace elements it can be ranked in the following distribution range: Zn> Cr> Ni> Cu> Pb> Co> As> Cd> Hg, which is quite close to the distribution of trace elements in the bottom sediments of Bratsk reservoir, the second in the cascade of the Angarsk hydroelectric power station: Cr > Zn> Ni> Cu> Pb> Co [10]. The comparison of average and background concentrations of the elements of these adjacent water bodies on Angara River reflects the transformation of chemical composition of bottom sediments. Concentrations of Cu (30 mg/kg), Co (20 mg/kg) and Cr (77 mg/kg) in the bottom sediments of the Bratsk reservoir [10] are close to the similar observed at UIR. The concentrations of Zn (49 mg/kg) in bottom sediments at the upstream of Bratsk reservoir are much lower; the concentrations of Pb (22 mg/kg) and Ni (30 mg/kg), on the contrary, decreases in bottom sediments of UIR.

The results of the analysis of trace elements spatial distribution in the bottom sediments of the UIR (figure 2) observes that the lowest concentrations of most trace elements are confined to the middle part of the reservoir (section from Podelansky Island to Vorobievsky expansion). The performance such of a kind indicates that the chemical composition of bottom sediments of this part of the reservoir is mostly depending on the natural factors of its formation.
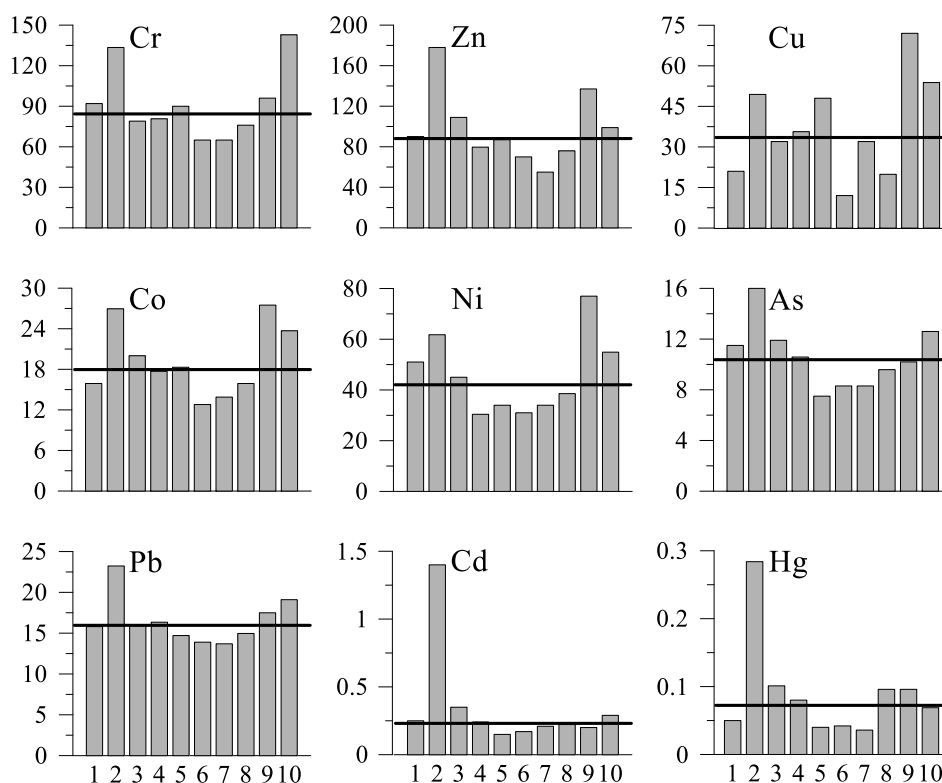
Figure 2. The concentration of trace elements (mg/kg) in upper layer of sediments of Ust-Ilimsk reservoir. Station numbers are consisted with figure 1. Line - conditionally background concentration.

In accordance to the accumulation of microelements in the bottom sediments, two zones are divided at UIR where the associations of microelement with CR are indicating pollution of bottom sediments (CR ≥ 1.5). The most contrast zone is the Vikhorevsky Bay where all the elements are increasing to various extents. On this section, the following association of elements is determined based on the increased values of CR: $Cd_{6.1}$–$Hg_{4.1}$–$Zn_{2.0}$–$Cr_{1/6}$–Pb,Cu,Co,$As_{1.5}$. High concentrations of potentially toxic trace elements in Vikhorevsky Bay are connected with industrial pollution of Vikhorevka River, receiving the wastewater of the Bratsk timber industry complex and domestic wastewater of Bratsk. The hydrodynamic parameters are contribute to the active sedimentation of suspended material, and, thereby, the removal from the aquatic environment and accumulation in the bottom sediments of elements of anthropogenic origin at the confluence of Vikhorevka River to the bay.

In bottom sediments of the estuary of Vikhorevsky Bay, concentrations of elements are close to the background values, but slightly increased compared to the less polluted middle part of the reservoir (figure 2). The decrease of the concentration of trace elements in the bottom sediments in this area of the reservoir is connected to that the majority of contaminated suspension does not reach the stream water part of the reservoir as a result of the integrated interaction of various physical, chemical, biogeochemical and other processes occurring in the barrier zone of the bay. Moreover, a great impact on chemical composition of the estuary part of the bay has the flow of less polluted terrigenous material along the main streambed of the reservoir.

The second less contrast zone is rather extensive area (from the confluence of the Ilimsk part to the dam of the Ust-Ilimsk hydroelectric power station). According to RC, the elements with elevated concentrations are distinguished in the vicinity of the confluence of the Ilim branch: $Cu_{2.1}$–$Ni_{.8}$–$Zn,Co_{1.5}$. In the area of the dam of the Ust-Ilimsk hydroelectric power station, the concentration of Cu stays high (CR = 1.6) and the concentration of Cr increases (CR = 1.7). Despite the fact that the RC of the rest elements in the selected area does not exceed 1.5, their concentrations are higher than the background value (Figure 2).

The increasing of concentrations in bottom sediments at the upstream of the Ust-Ilimsk dam may depend on several factors. The first is the flow of suspended matter with the waters of the Ilim branch. It should be noted that at the estuary of the Ilim branch, the technogenic pressure is the smallest in comparison with to the other sections of the reservoir. Thus, the chemical composition of bottom sediments, to a greater extent, reflects the natural processes of their formation associated with weathering of Ordovician and Carboniferous rocks, which, according to [4], are the most eroded UIR rocks and give more than half of the total abrasive matter input. The inflow of sedimentary material determines the areal distribution of Ni, Zn, Cu, and Co transported as part of the clay material and genetically related to the composition of the bedrock that forms the reservoir banks. The second factor influenced to the accumulation of the elements at the near-dam part is probably the accumulation of fine suspended matter, which contributes to the construction of the dam of the Ust-Ilimsk hydropower station, which increases the concentration capacity of bottom sediments of such a section. The third factor is airborne and surface drainage of elements from the industrial zone of Ust-Ilimsk and their further deposition in the dam part of the UIR. Ten large enterprises are located at Ust-Ilimsk with a total emission of pollutants from stationary sources of more than 26000 tons/year [11]. The most significant of them are: Ust-Ilimsk timber industry complex, Ust-Ilimsk hydroelectric power station, Ust-Ilimsk combined heat and power.

The correlation analysis data on concentrations of metals in bottom sediments (figure 3) are showed to common sources of the elements input to UIR ecosystem. The results of the analysis allocates two groups of elements: Ni, Co, Cu and Zn, associated with the natural factors of their formation, and Cd, Pb, Hg and As; its accumulation, increasingly, reflects human activity.
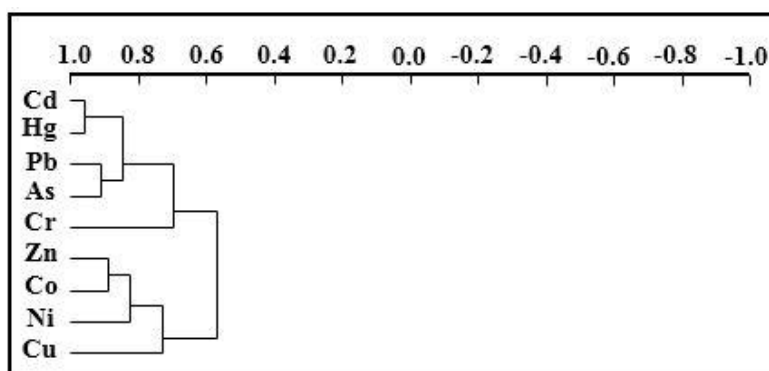

Figure 3. Dendrogramme of correlation analysis of trace element composition at UIR bottom sediments.

The assessment of probable secondary pollution of the aquatic environment and hydrobionts by potentially toxic trace elements accumulated in the bottom sediments is carried out basing on migration characteristics of the elements by studying their forms of location [12, 13]. The results of the statistical fractionation of bottom sediments of UIR are indicated that the concentrations of metals in determine fractions are significantly change. From the environment point, the most dangerous is the water-soluble

fraction, which determines the free ions in the pore water [6]. The concentration of most of the elements in this fraction does not exceed 1% in UIR bottom sediments (here and further, data are given in % of the gross concentration). The highest concentrations were determined for Cd ($\leq$ 6.9%), Co ($\leq$ 2.0%), Zn ($\leq$ 1.7%).

Light and relatively mobile elements are considered to be in the easy-exchange, organic and carbonate fractions [14]. The accumulation of elements in the light-exchange and carbonate fractions increases in comparison with the water-soluble fraction, amounting to 0.1 to 4% for Cu, Ni, Cr, As and Pb. The most significant increase in the concentrations of elements in these fractions is observed for Cd ($\leq$ 27.1%), Co ($\leq$ 18.2%), Zn ($\leq$ 16.1%). The greatest variations in the concentrations of the considered elements are determined in the organic fraction of the UIR bottom sediments (0.6-80.6%), where the percentage of the considered elements is also change (Hg> Cd> Cu> Ni> Co> Cr> Zn> As> Pb). The accumulation of Hg (10.5–80.6%) in this fraction is determined by its ability to easily form complexes with organic matter due to the high stability of its organic compounds constant [15]. In addition to Hg, an increase in Cu concentrations (7.0-57.3%) is observed in the organic fraction.

The total accumulation of Cd, Hg, Zn, Co and Cu in fractions mentioned above shows that in geochemical environment of UIR under the changes of pH, Eh, O_2 concentrations, microbiological activity, hydrodynamic parameters and other factors change, they can be released from bottom sediments into water and accumulate by living organisms. The concentration of these elements are arranged in descending order in the mobile and potentially mobile fractions shows that Cd is the most mobile element, and then in terms of mobility, follows Hg, Zn, Co and Cu.

Pb, Ni, Cr, and As are refers to the most fixed in UIR bottom sediments, the elements that are difficult to access for living organisms. The total content of these elements in the fractions of iron-manganese oxides, highly destructible silicates and the residual fraction is more than 80%.

4. Conclusions
The results of the research are allowed to make preliminary assessment of the distribution in the upper layer of bottom sediments of potentially hazardous trace elements for the UIR ecosystem. It was determined that the formation of the chemical composition of bottom sediments is influenced by both natural and technogenic factors. Two anomalous zones are marked (Vikhorevsky bay and upper part of the dam of Ust-Ilimsk hydropower station) based on relatively uniform distribution of most trace elements in the bottom sediments of the central UIR zone. The correlation cluster analysis obviously specify the associations of trace elements of technogenic and natural intake - Cd, Pb, Hg, As and Ni, Co, Cu, Zn, respectively. This research has shown the important role of the Vikhorevsky bay as a sedimentation geochemical barrier that blocks the transport of pollutants from Bratsk facilities to the mainstream of UIR. At the same time, while retaining the high technogenic pressure and large amplitude of the water level of the reservoir, the buffering capacity of the gulf can be weakened and, as a result, come to a significant expansion of technogenic pollution zone. Increased concentrations of Cd and Hg are severely hazardous; its accumulation in bottom sediments and toxicity are predetermining the negative impact on UIR ecosystem. Determination of the main forms of elements in bottom sediments showed that the most trace elements have a low degree of mobility and are in a tightly bound state. At the same time, relatively high mobility of Cd, Hg, Zn, Cu, and Co in sediments indicates the potential danger of secondary pollution of the aquatic environment and possible negative consequences for hydrobionts.

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