Mercury and other heavy metals in the bottom sediments of Lake Loshamye (national park “Smolensk Lakeland”)

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Abstract. In 2008–2010, monitoring work in the national park «Smolensk Lakeland» showed an excess of mercury in the water of Lake Loshamye located in the protected area of the natural reserve. In 2014–2019, together with the staff of the national park, we studied the ecological and geochemical features of the catchment area and the water area of Lake Loshamye. We studied the patterns of distribution of several heavy metals: Hg, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Pb, Sr. We did not find an anthropogenic influence on the catchment area; this article presents the results of the study of the bottom sediments of the lake. As a result of the work, we determined that all heavy metals have a natural distribution in this lake, except mercury. High values of mercury in bottom sediments (up to 1000 ppb) are not typical for such natural object. The median of the sample is 152 ppb, and it is four times higher than expected mercury content considering its content in the soils of the catchment area and 2–5 times higher than the values obtained for similar objects by other researchers. The analysis of the patterns of mercury distribution in bottom sediments indicates a one-time, local anthropogenic pollution of the lake.

1. Introduction
The national park «Smolensk Lakeland» is the biosphere reserve. It was founded in the Smolensk region more than twenty years ago. As befits the national park, its territory has functional zones with different protection and management regimes (reserve, specially guarded, recreational, economic purpose, extensive nature management). Functional zoning system in the national park allows for solving many problems. Thus, the strict regime for the territory of the protected zone makes it possible to solve the problems of preserving natural systems and conduct scientific research. Minimization of anthropogenic impact in this zone allows us to identify background values of the state of the natural environment components during monitoring studies.

One of the sites with the potential background load in the conservation zone is the territory of Lake Loshamye. Despite the absence of human activity in this territory, the results of past monitoring by the
National Park showed that mercury concentrations in the lake’s surface water exceeded the limit values in 2008 and 2009. [1] Observations showed that the concentrations of toxicants such as Pb, Cd, Cu are extremely low and correspond to natural conditions. However, the dynamics of mercury in 2008–2010 showed a peak picture: a sharp, several-hundred increase in indicators over a multi-year level, then a decrease to a background level over 2 years.

The geochemical survey of the surface of the lake’s catchment area did not reveal anomalies; moreover, the median values of mercury concentrations coincided with the Clark value, and the sample as a whole was monotonous, with extremely low mercury contents. Therefore, we studied the final depot of migration of any lake system – bottom sediments to establish the presence of an anthropogenic source and determine the qualitative and quantitative characteristics of the impact.

2. Materials and methods
Since 2014, in the framework of the ecological and geological assessment of the state of the territory, the staff of the national park together with the Institute of Earth Sciences of St. Petersburg State University carried out several works. Among other things, we carried out the sampling of bottom sediments with a Van Veen grab with different sampling densities (a regular grid throughout the water area with a step of 100 m – 37 samples, samples of coastal deposits from a depth of 1.5–2.0 m – 14 samples, and 24 points along the thickened grid with a step of 50 m).

We divided some samples into three fractions to separate the psephyte and psammite dimensions from silt and pelitic sieves and establish the dependence of the chemical on the particle size distribution of samples (for 3 fractions> 1, 0.1–1 and <0.1 mm). We prepared and analyzed bottom sediments using X-Spec and AP-104 X-ray fluorescence analyzers for the content of Ca, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Pb and Sr (mg/kg), as well as for the content mercury we used the RA-915 M mercury analyzer. We carried all analytical work out at the Department of Environmental Geology and Geochemistry at the Institute of Earth Sciences of St. Petersburg State University.

3. Results and Discussion
The main feature of this object is that the lake is part of the conservation area of the natural reserve and does not experience direct anthropogenic impact, but earlier, before the creation of the national park, this lake could potentially be polluted. To assess the geochemical situation and determine the natural and anthropogenic components, we analyzed data on the content of not only mercury but also other heavy metals significant and most characteristic of the anthropogenic trace (Cr, Co, Cu, Zn, As, Cd, Pb, Sr) in the bottom sediments.

For the primary processing of the obtained analytical data, we used a set of mathematical processing methods to homogenize and determine the boundaries of the anomaly and the confidence interval of the anomaly of contents (3-δ rule). Further mathematical data processing used correlation and factor analysis.

The characterization of the distribution of elements and substances in the bottom sediments allows us to conclude, according to the relative sizes of boxes with whiskers and the length of the upper whisker (Figure 1), that there is a weak technogenic effect and contrasting polyelement anomalies, and the absence of a relatively long lower whisker indicates that the studied territories have the predominance of the entry of substances and elements into the environment over leaching (Cu, As, Cd, Pb, etc.). Another part of the elements has the distribution close to normal that may indirectly indicate the absence of their technogenic (and/or natural) introduction into the catchment area-water area of Lake Loshamy.

We conducted a factor analysis to establish a functional dependence of the content of HM, Hg and metalloids and to identify possible sources. During the selection of significant factors using the scree criterion, we found that in the analysis we can limit ourselves to three factors that capture more than 66 % of the total variance ($F_1 = 34\%$; $F_2 = 18\%$; $F_3 = 14\\%$) (Figure 2). Factor 3 describes the features of the distribution of large and medium fractions of bottom sediments depending on the depth and distance from the coast. Factor 2 combines the distribution of siderophile and manganophile elements...
in bottom sediments probably associated with the creation of favourable conditions for the deposition of iron ore of lake origin consisting of iron hydroxides with various impurities (Mn, Cr, Co, etc.). Numerous literary sources and archaeological data have documented the presence of the lake and marsh ores in the area. Factor 1 relates the distribution of the association of traditional heavy metals of the urban environment (Zn, Pb, and Cu) and calcium, which may be due to the change in the mobility of these elements with the increase in pH occurring due to the increase in the amount of Ca in soils.

![Figure 1. Distribution diagrams of pollutant content in bottom sediments of Lake Loshamye](image1)

**Figure 1.** Distribution diagrams of pollutant content in bottom sediments of Lake Loshamye

![Figure 2. Factor loads and the diagram of their distribution along the F1-F3 axes (Hg (1, 2, 3, total) – mercury content in the fraction more than 1 mm (1), from 0.1 to 1 mm (2), less than 0.1 mm (3), gross content in the sample)](image2)

**Figure 2.** Factor loads and the diagram of their distribution along the F1-F3 axes (Hg (1, 2, 3, total) – mercury content in the fraction more than 1 mm (1), from 0.1 to 1 mm (2), less than 0.1 mm (3), gross content in the sample)

Such distribution in the catchment area – water(coastal and bottom sediments) system is, as a rule, a general regularity for all studied HMs and is associated with a high deposition ability of bottom sediments due to the finely dispersed structure and the presence of a large amount of organic matter, and possible ways of pollutants to enter the system.

The methodology for determining the territories of pollution uses the comparison of the contents of various compounds in natural environments with a certain average value. In the area with low anthropogenic pressure, the best estimate indicator is the comparison with the median value. Since it
weakly depends on individual peak values of the indicator, it helps to separate the zones into clean and exposed ones. Besides, in areas with low workloads, we can use comparisons with regional backgrounds, Clark, etc.

The concentration of mercury in bottom sediments can vary significantly and depend on many natural factors, and often the influence of human activity complicates the picture. What are these limits?

For example, analyzing the marine sediments of the Amur estuary, researchers [2] determined that this indicator varies from 4 to 81 ppb. However, in the region of Blagoveshchensk and Nikolaevsk-on-Amur, the contents are already from 180 to 750 ppb [2], and in the Zolotoy Rog Bay (Vladivostok), where the city’s untreated sewage has been supplied for many decades, the mercury content is about 1,500 ppb [3]. Megacities often have increased mercury in bottom sediments; for example, in some water bodies in the city of St. Petersburg, mercury concentrations can vary from 100 to 8000 ppb [4].

Water bodies with a low anthropogenic impact can also have a fairly wide range of values. So, for the Sea of Okhotsk, the mercury content is subject to several laws and varies in different regions from 12 to 150 ppb increasing with depth, while the background is 29 ppb [5]. Moreover, the increase in concentration most often depends on the composition of the precipitate (a direct correlation with the content of organic matter, or, for example, sulfides). However, the same reservoir has areas where the mercury content increases sharply to values of the order of 500–700 ppb. The authors attribute this phenomenon to natural endogenous mercury sources: low-temperature hydrothermal, or gas sources localized along faults, intersecting, or limiting the spreading structure [6].

For natural freshwater reservoirs, different studies give similar estimates of background values: 30–50 ppb [7], not exceeding 70 ppb [8]. Also, studies from different years assess the relationship between the mercury content in the soils of the catchment area and bottom sediments. Most often, the mercury content in bottom sediments is higher but insignificant (1.5–2 times).

Thus, the natural values of the mercury content in bottom sediments can vary significantly. However, for areas without natural geochemical anomalies, these values are in the range of 10–150 ppb, with median values of 20-30 ppb, both in fresh and in marine waters [2, 5–8].

Figure 3 shows the histogram of the distribution of mercury in bottom sediments of Lake Loshamye (a), characterizing the entire sample (75 values) and differentiated characteristics of mercury contents in different sediment fractions (51 samples of each fraction).

![Figure 3. The histogram of the distribution of mercury content (a) and statistical differences in mercury content in different sediment fractions (b).](image-url)
The scatter in the values of mercury in the bottom sediments of the lake is significant. The maximum value is 1000 ppb. In comparison with the data of other researchers, we can call it a large value for the natural object without geochemical anomalies. The analysis of differentiated samples showed that the maximum Hg contents are confined to the fine fractions (less than 0.1 mm) of the samples (Figure 3, b). However, there is no overwhelming significance in the concentration of mercury of this component of the sample. Concentrations mainly differ between sample fractions by a factor of 1.5–3, only 10 % of the samples show a predominance of mercury content precisely in the silt-pelite fraction, and these were samples of minimum and maximum values of the range. Factor analysis shows that the dynamics of the Hg content in the fine fraction (> 0.1 mm) with the highest concentration values (Figure 2) cannot be combined with any of the factors that may be due to the presence of more than one, at least two sources of this heavy metal in the lake.

The histogram of the distribution of mercury contents of the entire sample (Figure 3) gives the clear picture of the bimodal distribution with modes in the range of 30–45 and 150–165 ppb, that confirms the multiple-source hypothesis obtained after factor analysis. We note that the lower mode (30–45 ppb) corresponds to the mercury content which different researchers take as the background for natural reservoirs without geochemical anomalies. This source, or rather the factor that influenced the formation of bottom sediment composition and was characterized by this part of the sample, is of natural origin.

The mercury content in the bottom sediments of the reservoir is usually either equal to, or 1.5–2 times higher than in the soils of its catchment area [8]. Bottom sediments most often act as the final depot of migration of some elements. Previous studies in this area showed that the background value of the mercury content in the soils of the catchment area is 43 ppb [1], so this indicator in bottom sediments could be in the range of 40–70 ppb. This indirectly confirms the correctness of assigning this part of the sample to the natural factor [9, 10].

The upper mode is 150–165 ppb together with the upper nonlinear part of the range and several outliers most likely resulted from the action of the second source. Since there are no natural geochemical anomalies in this region, given the high value of the mode of this interval, we can state that this source is anthropogenic.

Figure 4 shows the map of the area distribution of mercury in the bottom sediments of the lake. The classification of the colour scale considers several patterns characteristic of the process of mercury migration. So, the first two categories, 30 and 70 ppb reflect the value of the background of mercury in bottom sediments according to published data. The 150 ppb border reflects the median of the values for the entire sample.

Cartographic material, as well as statistical characteristics, shows that the level of mercury in bottom sediments is quite high. By interpolating our data to the area of the lake (by kriging interpolation method), we can confidently say that the minimum levels of mercury are typical for coastal zones and the southeastern shallow part of the lake separated from the central part of the lake by a shallow bank. Precipitation in the central part has the high mercury content (150 ppb or more) which is even higher than the background value of the entire sample. We should note that, in this part of the lake, the distribution of mercury is quite complex. We can distinguish two centres of increased mercury content: the first in the centre (1000 and 526 ppb) and the second in the western part of the lake (298 and 281 ppb), the zone of lower values in the southern part and rather chaotic distribution of the areas of high and low mercury in overall for the lake.

Based on the facts listed above, we can derive the following patterns of mercury migration in the water body: first, the mercury content in bottom sediments is four times or higher than this indicator in soils (the medians of two samples are 152 and 42 ppb, respectively). Therefore, the soil we cannot consider either the natural source for the accumulation of mercury in the lake or the transit hub for pollution.
Increased values of mercury in the lake can result from processes occurring in the lake and are not related to the catchment area. Considering the peak concentrations of mercury in water recorded in monitoring works in 2008, we can state that there was direct pollution of the water area. Secondly, several foci with increased mercury content and the lack of a relationship between this indicator and depth indicate that pollution occurred at several points in the main water area of the lake (central and western parts). Finally, the complex picture of the distribution of mercury over the lake, in which areas with peak values are adjacent to areas with relatively low content, indicates volley pollution, moreover, directly at the surface of bottom sediments. The mercury entered the lake system had not the possibility to evenly distribute over the entire surface of the bottom sediments. The preserved lower peak in the bimodal distribution of the sample confirms the single pollution assumption. In conditions of constantly entering pollution, this peak would come to nought.

4. Conclusion
Based on the results of the ecological and geochemical study of bottom sediments of Lake Loshamye, we did not establish excesses in the MPC for any elements. However, the distribution pattern and the range of generally high values of mercury contents may indicate the presence of an anthropogenic source.

The analysis of the distribution of element contents in bottom sediments made it possible to divide them into 2 groups: 1 – Hg, As, Cr, Cd, Pb, Mn — the structure of which allows one to judge the presence of the source of constant inflow into the system; 2 – Cu, Zn, Co, Sr, Ca, Fe – probably characterizes the natural features of local aquatic elementary geochemical landscapes. The results of the factor analysis of Hg contents and distribution patterns show the presence of at least two factors acting on the migration of mercury in the lake system. The first factor is associated with the formation of low mercury contents and corresponds to the natural conditions of the reservoir. The second factor is anthropogenic and links with the formation of bottom sediments with high mercury content in bottom sediments uncharacteristic for such natural objects. The bimodal distribution of the data array...
of the mercury content and the complex nature of the area distribution indicates one-time, rapid contamination of bottom sediments at several points simultaneously. Moreover, it can be either an object dropped from a boat and quickly sunk, or some anthropogenic source buried in bottom sediments that occasionally and extremely rarely appears on the surface.

Thus, the features of the distribution of most elements in bottom sediments allow us to conclude that there is the low and/or past technological impact on the territory of the Lake Loshamyne regarding the formation of low-contrast anomalies of Cu, As, Mn, Pb and Cr. The exception is Hg, its geochemical anomalies have the large gradient that confirms the fact of local direct pollution of lake waters in 2008.

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