Ecological and geological soil assessment of the Loshamye Lake catchment area (national park “Smolensk Lakeland”)

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Abstract. The authors conducted the ecological and geochemical study of Lake Loshamye and adjacent territories (national park “Smolensk Lakeland”) to identify the distribution patterns of heavy metals and their associations (Hg, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Pb, Sr, etc.) in soils of the lake’s catchment area. In 2008, the annual monitoring by the national park revealed abnormally high concentrations of mercury in the water of Lake Loshamye (20 MPC). In subsequent years, the mercury concentration decreased to the minimum natural level. A set of studies in the catchment area and in the lake itself established a probable technogenic source and determined the qualitative and quantitative characteristics of the impact. Scientists studied the soil of the catchment area of the lake to verify the version of the pollutant intake from outside. The article presents the results of the study, a set of mathematical methods of information processing. Authors conducted a correlation, factor and cluster analysis to identify patterns of distribution of heavy metals in soils. Peculiarities of the distribution of most elements in the soil today indicate the presence of a low technogenic impact on the soils of the Lake Loshamye basin regarding the formation of low-contrast anomalies Cu, As, Mn, Pb and Cr, Hg. Patterns of the distribution of heavy metals including mercury in soils and their concentration have natural character. The gross mercury content in soils is significantly lower than the MPC (2100 μg/kg), the median of the sample is 42 μg/kg, which practically corresponds to the world Clark of mercury in soils (40 μg/kg). The research results show that the soils of the lake’s catchment area do not bear traces of anthropogenic impact. This suggests that there are no sources of contamination with mercury and other heavy metals in the study area, and this area is not a transit hub for the movement of the pollutant from the outside, and in 2008 there was probably salvo-type pollution directly into the lake’s water.

1. Introduction
The national park “Smolensk Lakeland” is the environmental, educational and research institution, its territory and water area includes natural complexes and objects of a special, including environmental value. Following the functional zoning scheme, the territory of the park has several sections supposed to restrict nature use to varying degrees. Such a system of functional zoning allows identifying background areas to develop parameters for normalizing the anthropogenic load on the territory of the national park during monitoring studies. These studies are relevant since the anthropogenic load on the...
The territory of the park is increasing. This load mainly corresponds to the implementation of one of the main tasks of creating the national park – the provision of environmental education and tourism. However, other aspects of changing the quality of the natural environmental components need constant monitoring.

One of the sites with the potential background load (conservation area) is the catchment area of Lake Loshamye. Despite the lack of human activity in this territory, monitoring of past years showed the excess of maximum permissible concentrations of mercury content for water bodies for drinking and cultural water use in the surface water of the lake in 2008 and in 2009, which later disappeared.

To establish possible sources of pollutants entering the final migration depot, bottom sediments, we performed a geochemical survey of the surface of the lake's catchment area, the area of which we arbitrarily determined using isohypse (200 m above sea level).

The catchment basin is the most typical integral and relatively independent unit in the organization of the earth’s surface, integrating terrestrial and water components of ecosystems [1], which requires observation in the framework of environmental and geological monitoring using modern software products, means of monitoring and bioindication.

Along with the climate, one of the main natural factors determining the modern appearance of the lakes is the geological structure of the region. As noted by B.B. Polynov, the geological substrate of the territory determines the type of ecosystem according to the scheme: mother breed → soil → vegetation → animal world. Following this statement, we pose the problem of studying the substance and structure of sedimentary deposits of lake basins and soils of the catchment area [2, 3]. The material composition of the sediment fully reflects the leading natural and technogenic conditions and processes of the biogeochemical evolution of the lake system.

Thus, one key aspect of the ecological and geochemical study of the adjacent territories and the water area of Lake Loshamye is the identification of pollutants and their associations in the soils of the catchment area to establish the anthropogenic source and determine the qualitative and quantitative characteristics of the impact.

2. Materials and methods
In August 2014 and 2015 we conducted lithogeochemical surveys in the catchment area of Lake Loshamye to achieve the goal. In the framework of these works, we took soils from the surface (0.0–0.2 m) through a 200 × 200 m network. A total of 24 soil samples were taken. In the selection process, we recorded information on the type of soil, which were conditionally divided into mineral and biogenic (the content of humic substances is more than 5%). In 2016, we collected an additional 74 soil samples from the catchment area to analyze the mercury content.

Soil samples were analyzed for the content of Ca, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Pb and Sr (mg/kg) using an X-ray fluorescence analyzer, as well as for mercury using a mercury analyzer RA-915 M.

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 [4].

3. Results and Discussion
Lake Loshamye is freshwater and has a glacial origin. The main sources of nutrition are groundwater and precipitation. According to geological classification, the northwestern, northern, and northeastern shores of the lake can belong to the accumulative type. The southern coast includes approximately uniformly sections of the abrasive and accumulative-abrasive types.

The results of fieldwork in 2014–2016 found that podzolic and sod-podzolic sandy and sandy soils with varying degrees of podzolization prevail in the territory, as well as bog soils.

The analysis of soil composition data using the Statistica 10.0 program, the Basic Statistics and Tables module and displaying stable estimates of mathematical expectation and dispersion allowed us
to divide the elements according to the value of the variation range into two groups (Figure 1): elements with uneven and relatively uniform distribution. The small actual box size (50 % of the sample size) and relatively long whiskers (maximum value) allow us to talk about the possible presence of the constant influx of pollutant from the system (Hg, As, Cr, Cd, Pb and Mn), about its possible conservation at the geochemical barrier (physicochemical) or the insufficient resolution of the XRD analysis method for some elements of this group (Sr, As and Cd) [5]. The uniform distribution of the content of elements in the soil can be established by the proportionality of the box and whiskers, as well as the actual size of the latter. Such distribution may result from the inconsistent intake or absence of external sources into the pollutant system and/or its high mobility (Cu, Zn, Co, Ca, and Fe in Figure 1).

Figure 1. Soil contamination distribution diagrams

All samples in the catchment area meet the requirements of the environmental standard (MPC for soils), and the mercury content does not exceed 2100 μg/kg (Figure 1). In general, considering the standard deviation (36 μg/kg), we can talk about the fairly monotonous distribution of values, while we defined one highlighted point as an outlier against the general background, several points correspond to increased value.

According to the analysis of field data from 24 selected soil samples, we can conditionally classify 18 soils as mineral and 6 soils as biogenic. To establish the dependence of the distribution of pollutant content values in soils of different types, we performed the cluster analysis of the transposed lithogeochemical matrix (the rows present contents; the columns present sampling points) [1], based on which we can conclude that there is the clear differentiation of the obtained analytical data (Figure 2). Also, by comparing the values of the average contents of almost all elements (except Sr, Cd and As) in the samples of the selected soil groups (according to the Student t-criterion and the conditions of equal variances and normal distribution) we established significant differences in the content of pollutants in different types of soil (at p <0,05).

Soils with the humus content of more than 5 % are the capacious adsorption system for organophilic pollutants and, accordingly, their composition can reflect the temporal aspect of pollutant intake to the whole territory [6–8]. Thus, if mineral soils have the same distribution parameters of the elements as biogenic soils, then we can assume that these soils (the territory of their selection) are their source of input and/or the dispersion flux of the anomalous zone outside the study area.

To establish the geochemical relationship between the distribution of mercury and other estimated elements, we used the method of multivariate statistical analysis and, in particular, the factor analysis
method that seeks orthogonal factors representing the linear combination of the observed variables and explain all their variability [4]. We ranked the contents of all elements using quartile intervals to use the soil type parameter in factor analysis [5].

Figure 2. Dendrogram of cluster analysis results of the content of pollutants in various soil types (1 – mineral type; 2 – biogenic type)

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 72 % of the total variance (F1 – 45 %; F2 – 17 %; F3 – 10 %). Factor 2 (F2) binds the distribution of elements (Ca, Mn, Cu and Sr), the establishment of the technogenic source of which on the territory of the Smolensk region causes great difficulties, so it is possible to conclude the presence of natural roots of the existence of this association. Factor 3 (F3), controls the distribution of the group of elements in which lead is of subordinate importance because it is a slow migrant that is firmly attached to organic matter or aluminosilicates, its main technogenic source until 2004–2005 was road transport (leaded petrol). Therefore, we can assume that the origin of this group of elements resulted from previous general contamination (the entire research area), and we cannot reliably identify its technogenic source at present.

Figure 3. Factor loads and the diagram of their distribution along the F1-F3 axes (* – soil type; ** – absolute value of the coefficient)
The first factor (F1) relates soil features (Figure 3), the distribution of Fe (as a medium-forming element), Zn, As, Cd and Hg. Since we conditionally distinguished two types of soils: mineral and biogenic soils, which content of elements differs (there are more elements in organogenic type), we can conclude that there is the high degree of organophilicity in the whole association [9, 10], which also belong to the group of chalcophilous, according to the geochemical classification of elements proposed by V.M. Goldschmidt. In addition, Zn, As, Cd, and Hg are hazard class I pollutants traditionally present in the soils of urbanized territories, i.e. the presence of such an association is the consequence of non-specific anthropogenic effects.

We should note that the presence of Hg and As (easily migrating, often in free-form) elements in the association, which are usually found in the marginal parts of the anomalies [11], and the absence of significant excesses in the background and permissible concentrations may indirectly indicate that the source of exposure is outside the study area [12].

Continuing the study of the geochemical features of the territory next year, we collected an additional 74 samples of the upper soil horizon over a grid of 1 km to study the distribution of mercury in soils and to clarify the possibility of migration of this element from the catchment area.

As in studies of previous years, the gross content of mercury in soils is significantly lower than the MPC (2100 μg/kg), and on average corresponded to 48 μg/kg. Through statistical processing of the results, we found that the distribution of mercury corresponds to the lognormal law, which corresponds to the geochemical features of the natural distribution. Numerous sampling points makes it possible to isolate background values of mercury using on sample analysis. In such cases, it is logical to take the median of the sample as the background values, a value independent of local outliers. The value of 42 μg/kg as the background, in general, correlates well with Clark of mercury in soils (0.04 mg/kg). We note that such values are characteristic precisely for soils not exposed to humans. So, for example, in some regions of Russia, there are increased concentrations of mercury relating to Clark soils, and background values in urban areas are higher (70–80 μg/kg) than in protected areas that are minimally subject to anthropogenic impact.

An analysis of the values of the variation coefficients in soils near Lake Loshamye showed an uneven distribution of mercury. This may indicate that there are zones of the most intense predominance of the element. We calculated element concentration coefficients to identify the areas of the greatest mercury accumulation.

The concentration coefficient of mercury varies from 2 to 7.7. However, in most of the area around the lake, the mercury content is uniform and does not exceed the background by more than two times. On the site of the southern shore of Lake Loshamye, the mercury concentration is 4-6 times higher than the background value (6 samples). In the same site, as well as at individual points of the north of the study area, the Hg content exceeds the background by more than 7 times, although in general, the distribution of values is quite monotonous. Besides, the maximum value of the content was 292 μg/kg and certainly exceeds the background values in clean areas but 8 times below the MPC. The small number of such points and their fragmentation confirms that, on the whole, the catchment area of the lake cannot be either a source or a transit site for mercury pollution of the lake.

4. Conclusion
We carried out the ecological and geochemical study of the soils of the Lake Loshamye catchment area and, according to its results, did not establish the excess MPC of any elements. However, the nature of the distribution and the range of concentration values may indicate the external pollution sources that are not fully manifested in this territory.

The method of conditional separation of soils according to the content of organic matter has proved that the biogenic type of soil is the capacious adsorption system for organophilic pollutants and, accordingly, its composition can reflect the time aspect of their entry into the whole territory. Thus, if mineral soils have the same distribution parameters of the elements as biogenic soils, then we can assume that these soils (the territory of their selection) are their source of input and/or the dispersion
flux of the anomalous zone outside the study area. In the catchment area of Lake Loshamye, we could not establish this fact, i.e. the potential source is either local or located outside the surface catchment.

The values of the mercury content in the soils of the catchment area correspond to the natural distribution: the average values and the median of the sample correspond to Clark, the distribution corresponds to natural laws.

Thus, the features of the distribution of most elements in the soil allow us to conclude that there is the low and/or past technogenic impact on the territory of the Loshamye Lake Basin in terms of the formation of low-contrast anomalies Cu, As, Mn, Pb and Cr, Hg.

References
[1] Gleeson T, Befus K M, Jasechko S, Luijendijk E and Bayani Cardenas M 2016 Nat. Geosci. 9 161–7
[2] Beyer J, Trannum H C, Bakke T, Hodson P V and Collier T K 2016 Mar. Pollut. Bull. 110 28–51
[3] Anderson P J, Warrack S, Langen V, Challis J K, Hanson M L and Rennie M D 2017 Environ. Pollut. 225 223–31
[4] Dubrova S V, Podlipskiy I I, Kurilenko V V and Siabato W 2015 Environ. Pollut. 197 165–72
[5] Ivanyukovich G A, Zelenkovskiy P S and Dubrova S V 2016 Ecol. Ind. Russ. 20(1) 37–41
[6] Jiang Y, Lei M, Duan L and Longhurst P 2015 Biomass Bioenergy 83 328–39
[7] Blanco-Canqui H 2017 Soil Sci. Soc. Am. 84 687–711
[8] Bunemann E K, Bongiorno G, Bai Z, Creamer R E, De Deyn G, De Goede R, Fleskens L, Geissen V, Kuyper T W, Mäder P, Pulleman M, Sukkel W, van Groenigen J W and Brussaard L 2018 Soil Biol. Biochem. 120 105–25
[9] Tchounwou P B, Yedjou C G, Patlolla A K and Sutton D J 2012 Exper. Suppl. 101 133–64
[10] Van Oosten M J and Maggio A 2015 Environ. Exp. Bot. 111 135–46
[11] Oguri T, Suzuki G, Matsukami H, Uchida N, Tue M N, Tuyen L H, Viet P H, Takahashi S, Tanabe S and Tagikami H 2018 Sci. Total Environ. 621 1115–23
[12] Suwanteep K, Murayama T and Nishikizawa S 2016 EIA Rev. 58 12–24