Short communication

Spatio-temporal distribution of gross mercury contents in the bottom sediments of small lakes of the taiga zone



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ABSTRACT. The results of the study of the gross mercury content in the bottom sediments of small lakes in the taiga zone (humid sedimentogenesis) are summarized. It is shown that mercury concentrations in organomineral sediments correspond mainly to its contents in rocks of the upper continental crust (background values). In bottom sediments, mercury is adsorbed by organic matter, biogenic silica and layered silicates. The regularities of the vertical distribution of gross mercury in stratified sections of bottom sediments of lakes of the taiga zone, geographically located in different regions of Siberia and on the southeastern edge of the Baltic Shield, have been established.

Keywords: bottom sediment of small lake, Hg, geochemistry, areas of Siberia (north-south, west-east) and the southeastern edge of the Baltic Shield

1. Introduction

According to the international document on the problem of mercury pollution of the environment, adopted in 2013 by the UN, mercury is a priority environmental toxicant. Possessing unique ecological geochemical properties (toxicity, mobility, and and bioaccumulation aquatic continental in biocenoses), mercury can migrate over long distances and is recognized as one of the most dangerous global environmental pollutants (Douglas et al., 2012; Gamberg et al., 2015). Study of vertical distribution of mercury in stratified natural plates (bottom sediments of lakes) allows you to estimate the main sources (natural and anthropogenic) and the time of receipt of mercury in them. In the environment, the natural source of mercury is determined by the specifics of the geological environment, and the anthropogenic source is determined by human economic activity (Dauwalter et al., 2015; Yusupov et al., 2018). It is known that humic acids, slightly soluble in lake waters, contribute to the deposition of mercury (Douglas et al., 2012). The chemical composition of organomineral deposits can vary from lake to lake, even in those with a common catchment, water sources and a similar composition of rocks surrounding lake basins. According to the Si/Ca ratio in the chemical composition of bottom silts, classes of organo-mineral sediments are distinguished: silicon (Si > Ca); calcium (Ca > Si), mixed $(Si \sim Ca)$. The analysis

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of metallogeny data concerning the lakes catchment territories did not reveal lithochemical anomalies of Hg. The aim of the study is to generalize data on the gross mercury concentration in the bottom sediments of small lakes of the taiga zone, geographically located in different areas of Siberia (north-south, west-east) and the southeastern edge of the Baltic Shield, to assess the dependence of absolute contents on the latitude location and the material composition of the sediment.

2. Materials and methods

73 lakes were studied (Table). The studied lakes are located along 63°n. lat. at 33°-37°e. long. (southeastern margin of the Baltic Shield, Repub. Karelia), 72°- 78° e. long. (north of Western Siberia, YANAO) and 120°-130° e. long. (north of Eastern Siberia, Repub. Sakha), between 52° - 56° n. lat., from 76° to 85° e. long. (south of Western Siberia) and from 106° to 115° e. long. (south of Eastern Siberia, the southern and eastern shores of the l. Baikal and the Trans-Baikal Territory).

Lake waters differ in the degree of mineralization (from 0.01 to 1.32 g/dm³), pH (from 6.3 to 9.9), the content of oxygen dissolved in water (3 – 13 mg / dm³), the concentration of organic substances (0.28 – 8.32 mg/dm³), bicarbonates, calcium and sodium. Earlier, the authors found that the composition of

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organomineral deposits is determined by the species composition and the degree of productivity of the biota (Strakhovenko et al., 2021).

The formation of bottom sediments with a significant amount of organic matter in the Holocene is typical for small lakes of the taiga landscape and climatic zones of Siberia and the southeastern margin of the Baltic Shield (the territory of the Republic of Karelia). Variations in the ratio of organic and mineral parts (ash content) of organomineral deposits are significant both in spatial and temporal distribution: from 6% to 85% ash content, while the proportion of humic acids in the group composition of organic matter also varies greatly from 2.4% to 70% and the largest percentage is expected to be found in lakes with a swampy catchment. The sources of autochthonous organic matter in the studied lakes are primary producers (phytoplankton and macrophytes), as well as consults and reducents (zooand bacterioplankton, zoobenthos). Autochthonous organic substances undergo significant changes as a result of microbiota processing, which significantly affects the final composition of the mineral part of the bottom sediment (Ovdina et al., 2020; Strakhovenko et al., 2021).

Analytical studies were carried out in the Analytical Centre for Multi-Elemental and Isotope Research of the SB RAS (IGM, Novosibirsk). The major and trace element, Hg compositions were studied using the atomic absorption method. A detailed study of the structural features, the morphology at the level of individual mineral grains of the bottom sediment was carried out using scanning electron microscope (SEM). The specific modification of the equipment used an Si(Li) energetic detector, enabling quantitative chemical analysis to be carried out on micro volumes. The bottom sediments were dated through assessing the activity of ¹³⁷Cs and ²¹⁰Pb. The analysis for ²¹⁰Pb was made by gamma-spectrometry on a planar detector "ultrapure-Pb,W" semiconductor with protection from natural radiation.

3. Results and discussion

According to the data obtained (Table), the average level of Hg in the bottom sediments of the

small lakes of the studied territories is lower than the average values for the upper part of the continental crust, with the exception of higher concentrations in organomineral sediments of Si composition in the north and south of Western Siberia. Perhaps the higher concentrations of mercury detected in the lakes of the northern taiga of the Yamalo-Nenets Autonomous District and the southern taiga of the Tomsk region are due to the predominance of swamps in the landscape of the catchment areas of these lakes. It is known that humic acids contribute to the deposition of mercury in bottom sediments, of which there are many in the group composition of organic matter of organomineral sediments of lakes located in landscapes with a predominance of swamps. A possible reason for the increase in Hg concentrations, especially in the upper layers, may be the influence of primary processing and distillation of oil, since it is known that these processes can make a significant contribution to mercury pollution of air and water bodies (Gamberg et al., 2015). To clarify the general nature of the distribution of mercury in the time interval in all lakes, an analysis of its layered contents was carried out. A layer-by-layer study of the bottom sediment cores from lakes provides information about the spatial and temporal features of the material supply into the sediment. The distribution of ¹³⁷Cs and ²¹⁰Pb concentrations in all sediment cores of lakes from different part of the Siberia and southeastern margin of the Baltic Shield were conducted. Estimates of the rates of undisturbed sedimentation within the last 100 years, calculated using the ²¹⁰Pb constant flow (CF) model, approximately correspond to the dates obtained by simple extrapolation from ¹³⁷Cs. The sedimentation rate is estimated to be in the lakes of: 0.12 -0.22 cm/year in the northern parts of the West Siberia and southeastern margin of the Baltic Shield; 0.12 -0.22 cm/year in the northern and sorthern parts of the East Siberia; in the sorthern parts of the West Siberia 0.12 - 0.22 cm/year (Si class) and 0.06 - 0.11 cm/ year (Ca class). The assessment of sedimentation rates in lakes of different territories shows that the rate of sedimentation from lake to lake within a particular area varies within the same limits as for different regions. The sedimentation rate is significantly lower only for lakes with carbonate bottom sediments.

| Table. Mercury content in bottom sediments (mg/kg) in various regions according to the authors and literary sources. |
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| | Number samples | Average val. \pm art. off. | Min. and max. values |
|--|-------------------|------------------------------|-------------------------|
| southeastern margin of the Baltic Shield (Republic of Karelia) | 185 | 0,042±0,019 | 0,006-0,160 |
| eastern margin of the Baltic Shield (Murmansk region)*W | 289 | $0,055 \pm 0,037$ | 0,019-0,092 |
| northern taiga West. Siberia (YANAO) | 135 | 0,087±0,016 | 0,01-0,66 |
| middle taiga West. Siberia (Tyumen region) ** | 369 | $0,045 \pm 0,006$ | 0,012-0,45 |
| southern taiga West. Siberia (Si bottom sediment) | 640 | $0,092 \pm 0,019$ | 0,007-0,172 |
| southern taiga West. Siberia (Ca bottom sediment) | 198 | $0,013 \pm 0,008$ | 0,001-0,058 |
| northern taiga East. Siberia (Sakha Republic) | 354 | $0,035 \pm 0,019$ | 0,001-0,065 |
| middle taiga East. Siberia (Republic Buryatia) | 57 | $0,043 \pm 0,015$ | 0,011-0,205 |
| southern taiga East. Siberia (Republic Buryatia and Transbaikalia) | 75 | $0,046 \pm 0,025$ | 0,018-0,140 |
| Average values for the upper part of the continental crust*** | | 0,06 | |

Note: *(Dauwalter, 2015), ** (Morozova et al., 2015), ***(Taylor and McLennan, 1988).

To identify patterns of spatial and temporal distribution of mercury content within the northern taiga, sections of lakes located along 63° n. lat. at $33^{\circ}-37^{\circ}$ e. long. (southeastern margin of the Baltic Shield), 72°-78° e. long. (north of Western Siberia) and 120° were compared -130° e. long. (north of Eastern) (Fig 1a). The sections are averaged by the depth of core sampling for each region separately to a depth of 65 cm, since in many lakes of the northern taiga of Siberia, due to permafrost (ice sediment), it was not possible to select deeper. Taking into account the rate of sedimentation, this allows us to estimate the dynamics of changes in the geochemical composition of bottom sediments in a time interval of 200 years.

According to the nature of the distribution of Hg in sections along the depth of the bottom sediment (time of formation), two types are distinguished: 1 - the concentration of Hg does not change along the section, except for the uppermost part (0-10 cm) which are heavily watered and enriched with microbial organisms; 2 type of distribution - the mercury content increases to the tops of the sections, sometimes significantly from a depth of 30-40 cm. The second type of Hg distribution in the bottom sediments of lakes sharply prevails over the first in the lakes of the Republic of Karelia. Significantly higher Hg contents in the upper part of the bottom sediment profiles relative to the underlying horizons can be explained by natural causes, namely, the fact that it is Hg that has the maximum ability to covalently bind to proteins. The maximum amounts of organic matter in the sections of bottom sediments are confined to the silt formed at the interface of the media "water-bottom sediment" (Fig. 1b) (Kainz and Lucotte, 2006; Lein, 2013).

The peculiarity of the distribution of Hg in averaged vertical sections by depth (Holocene period – up to 1000 cm) of lake bottom sediments from various regions of Siberia and the southeastern margin of the Baltic Shield should recognize the presence of a global pattern of increasing mercury content from depths of 60-70 cm towards the upper layers of bottom sediments and a sharp increase in concentrations from depth 25-15 cm to the upper horizons in the studied lakes (Fig. 1c). Depths of 60-70 cm) correspond to the appearance of industrial production, including Hg compounds in the 19th and 20th centuries. A statistically significant increase in the Hg content at depths of 25-15 cm in the bottom sediments of all dated lakes occurred in the middle of the last century, and this is due to the intensive development of industry as a whole after World War 2 and with a significant increase in the upper layers of sediments of organic carbon content. Organomineral deposits, being a biocosal system, have a directed movement of nutrients, a number of elements to the interface of media controlled by both living organisms and physico-chemical conditions.

Conclusions

Thus, in the bottom sediments of the studied lakes, the Hg content is lower than the value of their content for rocks of the upper continental crust (0.06 mg/kg), with the exception of higher concentrations of Hg in the organomineral sediments of lakes, in the catchment of which wetlands predominate. A general trend in the spatio-temporal distribution of Hg in the sediments of the studied lakes has been revealed: a gradual increase in Hg content in the bottom sediments of lakes from depths of 60-70 cm towards the upper layers of sediments and a sharp increase in concentrations from a depth of 25-15 cm to the upper horizons. This is explained by natural causes, namely, an increase in the amount of organic matter in the upper horizons of bottom sediments, relative to the underlying horizons, as well as an increase in global anthropogenic atmospheric mercury intake over the past 80 years.

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Conflict of interest

The authors declare no conflict of interests.



Fig.1. Vertical distribution of the contents of Hg (μ g/kg) and ash (%) in bottom sediment cores from taiga lakes of various research areas: (a) the contents of Hg (μ g/kg), (b) ash (%) for lakes located along 63° n. latitude; (c) the contents of Hg (μ g/kg) for taiga lakes of various research areas

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