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Short communication

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Biogeochemical indication of technogenic mercury pollution of the ecosystem components in the Bratsk Reservoir (East Siberia) and the Bolshoye Yarovoye salt lake (Altai Territory)

Leonova G.A.[1]*, Andrulaitis L.D.[2], Badmaeva Zh.O.[1]

[1] V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Ac. Koptyug Ave., 3, Novosibirsk, 630090, Russia
[2] A.P. Vinogradov Institute of Geochemistry SB RAS, Favorsky Str., 1a, Irkutsk, 664033, Russia

ABSTRACT. Based on the results of long-term biogeochemical studies (1992-2003), the Bratsk Reservoir was classified as anthropogenically transformed water body. In its upper part, there was mercury pollution of the ecosystem components (water, bottom sediments and biological objects), which was associated with the discharges of mercury-containing wastewater from the Usolyekhimprom chemical plant producing chlorine and caustic soda (Usolye-Sibirskoye town). The results of the monitoring the ecological condition of the Bolshoye Yarovoye salt lake (1998-2004) revealed the local mercury pollution of the ecosystem components (water, bottom sediments and biological objects) by mercurycontaining onshore solid waste dumps of the Altaihimprom plant (Yarovoye town) producing chemical reagents, including mercury oxide.

Keywords: mercury pollution, biogeochemical indication, technogenic sources, mercury-containing waste, indicator biological objects

1. Introduction

The unique physicochemical properties of mercury, the ability to migrate easily, transform and be transported in the atmosphere over long distances, force to consider this toxic element a global pollutant. A correct assessment of the anthropogenic component of mercury entering the atmosphere requires the study of natural mercury compounds associated with modern volcanism and hydrothermal systems (Rychagov et al., 2014; Nuzhdaev, 2022) as well as with mercury deposits such as Aktash (Arkhipov and Puzanov, 2007).

The problem of mercury pollution of the biosphere is most acute in areas where powerful technogenic mercury sources are active: mining and metallurgical complexes processing mercury and mercury-containing ores (Robertus et al., 2015) as well as enterprises where a significant amount of mercury is used in technological cycles (Leonova et al., 2002; 2006; 2007; Koval' et al., 2003). In terms of the scale of technogenic mercury entering the environment, the Irkutsk Region is comparable with the world's known examples of mercury pollution (Koval' et al., 2003). Here, along with the background slightly polluted natural objects (Lake Baikal and the Irkutsk Reservoir), the heavily polluted Bratsk Reservoir is situated, the basin of which allocates the main technogenic mercury sources, chemical plants for the production of chlorine and caustic soda (Usolyekhimprom and Sayankhimprom).

Mercury pollution in the water area of the Bolshoye Yarovoye salt lake near the influence zone of the Altaikhimprom plant is of a local nature. However, it is alarming that in the immediate vicinity of the plant, in the town of Yarovoye, there is a regional physiotherapy balneo-mud treatment facility, unique in Russia, based on therapeutic mud forming in the lake after the death of the halophilic crustacean, *Artemia salina* L. (Grebennikov et al., 1977).

2. Materials and methods

Mass species of zooplankton (*Daphnia galeata* G.O. Sars and *Mesocyclops leuckarti* (Claus), aquatic plants (*Potamogeton pectinatus* L.), commercial fish species (*Perca fluviatilis* L.perch and *Rutilus rutilus* L. roach), bottom sediments (BS), and water served as a material for biogeochemical monitoring of mercury

*Corresponding author.
E-mail address: leonova@igm.nsc.ru (G.A. Leonova)

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pollution of the Bratsk Reservoir environment. Mercury in BS, plant and fish samples was determined through the ‘cold vapor’ technique with the detection of reduced mercury vapor by atomic absorption spectroscopy on a Yuliya-2 mercury analyzer (detection limit 0.002 μg/g). The water samples were analysed by atomic fluorescence spectroscopy with a preliminary concentration of mercury on a PSTM-3T silicon-organic sorbent (detection limit 0.0005 μg/L, analyst L.D. Andrulaitis).

Halophilic mesozooplankton (*Artemia salina* L.), filamentous algae (*Cladophora fracta* (Vahl.) Kutz.), BS, solid waste from storage pits, and brine (highly mineralized solution) served as a material for biogeochemical monitoring of mercury pollution of the ecosystem of the Bolshoye Yarovoye salt lake. Mercury in the analysed samples was determined through the ‘cold vapor’ technique with amalgamation on a gold sorbent and the detection of reduced mercury vapor by atomic absorption spectroscopy on a PerkinElmer atomic absorption spectrometer (analyst Zh.O. Badmaeva).

3. Results and discussion

We determined the general pattern of the spatial mercury distribution in aquatic organisms from the Bratsk Reservoir (Leonova et al., 2007): the mercury concentrations in zooplankton, aquatic plants and the muscle tissue of fish reached the maximum values in the upper part of the reservoir and decreased towards the lower part near dam (Fig. 1A, 1B and 1C).

In zooplankton, the highest concentrations were identified in the Balagansk extension, 0.65 μg/g dry weight (stations 17-19), and the concentrations were at the background level in the near-dam part, 0.013 μg/g dry weight. The Hg concentration in aquatic plants of the upper part (near the Svirsk town) averaged 0.4 μg/g dry weight and was a background in the near-dam part, 0.002 μg/g dry weight. The highest Hg concentrations in the muscle tissue of fish were typical of the Usolye-Sibirskoye town-Svirsk town area where 75% of the fish showed a significant excess of MPC for mercury (0.5 μg/g dry weight): two- to tenfold for perch (0.95 to 6.0 μg/g dry weight) and two- to threefold for roach (1.0 to 1.5 μg/g dry weight).

The bulk of technogenic mercury was detected in BS of the Angarsk part of the reservoir, in the Svirsk town-Priboiny settlement area (stations 13-23). Near the Svirsk town (station 20), there were the maximum mercury concentrations, 4.6 mg/kg dry mass. To a lesser extent, mercury pollution was recorded in the area from the Priboiny settlement downstream the Bratsk city (station 11-12 and 1-4); the mean Hg concentration was 2.5 mg/kg. The Oka part of the reservoir (stations 5-10) affected by the Sayankhimprom plant had much lower mercury pollution. Here, we observed only one anomaly that is station 9 located in the transient region (1.5 mg/kg dry weight). The boundaries of mercury pollution were unstable over time and gradually changed downstream, as evidenced by a comparison with the results of the studies of the upper sedimentary layer, which were carried out in different years (Koval’ et al., 2003). The mercury concentration in water was 0.00002 mg/L based on the method for determining Hg with a preliminary concentration on a PSTM-3T silicon-organic sorbent.

Biogeochemical testing of mercury pollution was carried out at five stations in the water area of the Bolshoye Yarovoye salt lake. Mercury was found in the lake brine in the form of chloride complexes, $HgCl_4^{2-} \approx$ 92-96%, $HgCl_3^{-} \approx$ 2.7-5.9% and $HgCl_2^{0} \approx$ 0.25-2.5%, that determined its increased bioavailability for aquatic organisms (Leonova et al., 2007). In mesozooplankton (*A. salina*), mercury was present in organic forms based on direct determinations by thermal analysis followed by atomic absorption spectroscopy (Gustaitis et al., 2006).

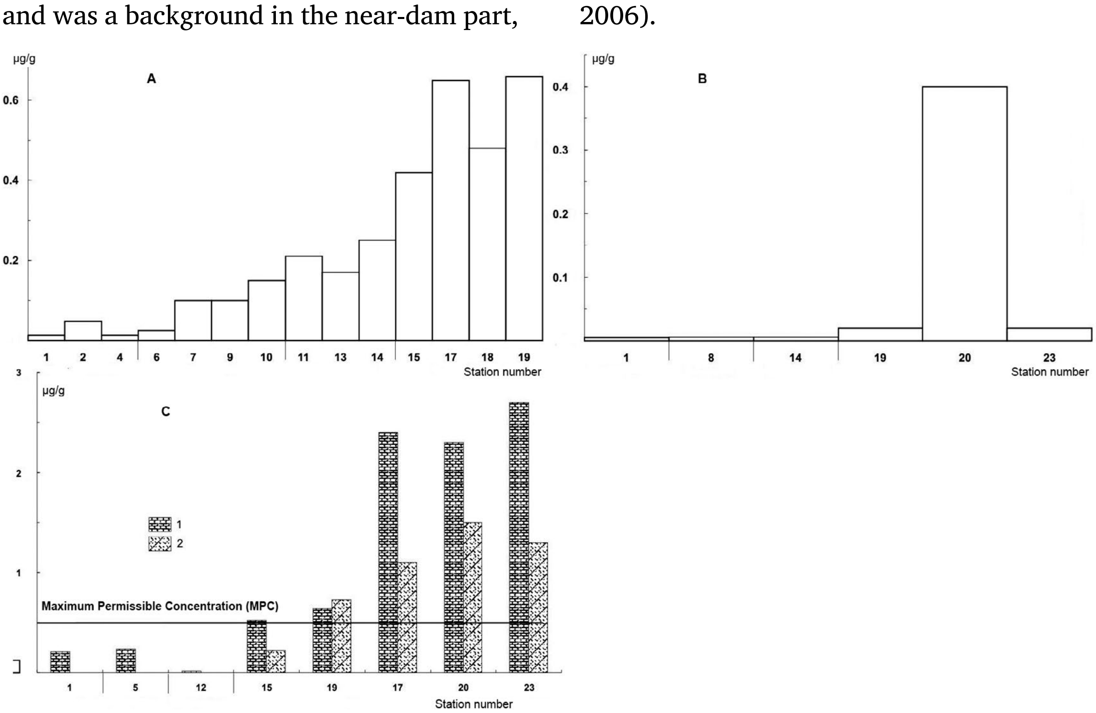

Fig.1. Mercury concentrations in the aquatic organisms of the Bratsk Reservoir: A) in plankton, B) in aquatic plants and C) in the muscle tissue of fish. 1 – perch and 2 – roach. The abscissa shows sampling stations.

Quantification of the pollution degree of the lake ecosystem was carried out based on the complex of informative geochemical criteria. Concentration coefficients (C_c) indicated a sevenfold excess of Hg concentration in BS and a fivefold excess for mesozooplankton (*A. salina*) near the onshore solid waste dump of the plant compared to the background (Leonova et al., 2007).

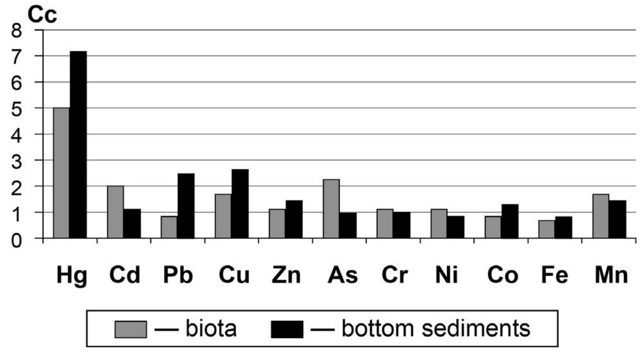

Fig.2. Elemental concentration coefficients (C_c) in the biota (*Artemia salina*) and bottom sediments of Lake Bolshoye Yarovoye in the influence zone of the Altaikhimprom plant.

4. Conclusions

1. Mercury concentrations in the muscle tissue of fish from the upper part of the Bratsk Reservoir, which were three- to five times higher relative to the background, were obtained at the Analytical Centre of A.P. Vinogradov Institute of Geochemistry SB RAS and confirmed by an independent examination at the University of Brussels (Leonova and Bobrov, 2012, p. 218). This served as a basis for the shutdown of the mercury electrolysis shop at the Usolyekhimprom plant to restructure the technological cycle, excluding mercury.
2. Based on the calculated value of the t-test for selections of mercury concentrations in 12 samples of the *A. salina* mesozooplankton (six samples from the background area and six samples from the influence zone of the plant), we concluded that, with a 95% confidence probability for five degrees of freedom, the difference between the mercury concentration in mesozooplankton from the influence zone of the chemical plant and from the background areas was significant, which again confirms the technogenic nature of mercury in the ecosystem of Lake Bolshoye Yarovoye and its source that is the onshore waste dumps of the Altaikhimrom plant.

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Conflict of interest

The authors declare no conflict of interest.

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