Long-term dynamics of mercury pollution of the Bratsk reservoir bottom sediments, Baikal region, Russia

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Abstract. This paper discusses the results of the monitoring of anthropogenic mercury contamination of the upper part of Bratsk reservoir. The paper shows that in the long-term, (1998-2018) there is an ongoing decrease of Hg concentration in the surface layer of bottom sediments. At the same time the study demonstrates that 20 years after the cessation of mercury electrolysis at the Usoliehimprom chemical plant, Hg concentration in the bottom sediments exceeds background levels by 5 to 54 times. Significant part of the Hg in the bottom sediments is stored in organic form, which is potentially dangerous since it may cause secondary contamination of aquatic environment and hydrobionts. The high amplitude of water-level fluctuations in the reservoir is one of the main factors influencing the distribution of mercury in the surface layer of bottom sediments and preventing the sealing of contaminated bottom sediments by terrigenous material

1. Introduction

The property of mercury to form methylated forms that can penetrate through cell membranes and bind to proteins predetermines its extreme toxicity, its ability to accumulate in living organisms and to be transmitted through food chains [1, 2]. The anthropogenic factor plays a significant role in the geochemical cycle of mercury - the industrial development has increased the amount of mercury in the atmosphere and in the upper layers of the world ocean by 2-3 times [3]. Among industrial enterprises, chlor-alkali plants are one of the main sources of anthropogenic mercury in the environment [4-6]. Mercury pollution is particularly dangerous for aquatic ecosystems which are most vulnerable to toxic substances.

Mercury contamination of the Bratsk reservoir (BR) is one of the most significant environmental problems in the Baikal region [7]. The total inflow of mercury into the reservoir from the main source of pollution, the Usoliekhimprom chlor-alkali plant (CAP), exceeds 76 tons. The main share of Hg is accumulated by bottom sediments of the upper part of the BR. The total volume of mercury emissions into the environment during the period of the plant operation is estimated at 1327 tons [8]. Since the ecological danger coming from the plant could lead to an environmental catastrophe any time, work of the mercury electrolysis unit of the plant has been stopped in 1998. In the same year, complex ecological and geochemical monitoring has been initiated in order to assess the degree to which mercury pollution affects the ecosystem of BR.

2. Materials and methods

Monitoring of mercury distribution in bottom sediments was carried out in the upper part of the BR, which is most susceptible to technogenic mercury pollution. To assess the dynamics of mercury concentrations, we analyzed the surface layer of bottom sediments selected during the reduction of mercury emissions from 1998 to 2018. Sampling was carried out at 15 monitoring stations that were evenly located in the upper part of the reservoir, beginning from the zone of stable sedimentation (3 km above the town of Svirsk) (figure 1). Sampling was carried out from the vessel using the GOIN-1 gravity tube. The obtained cores were divided into segments of 2 cm and placed in plastic containers. The average precipitation depth in the upper part of BR is 28 cm, and the maximum precipitation depth is 92 cm in the area of the main sedimentation barrier. Under laboratory conditions, bottom sediments were lyophilized and then sent for chemical analysis. As background value we used the average concentration of mercury in the bottom sediments of the Irkutsk reservoir, located upstream of the Angara River, which does not experience significant anthropogenic impact.

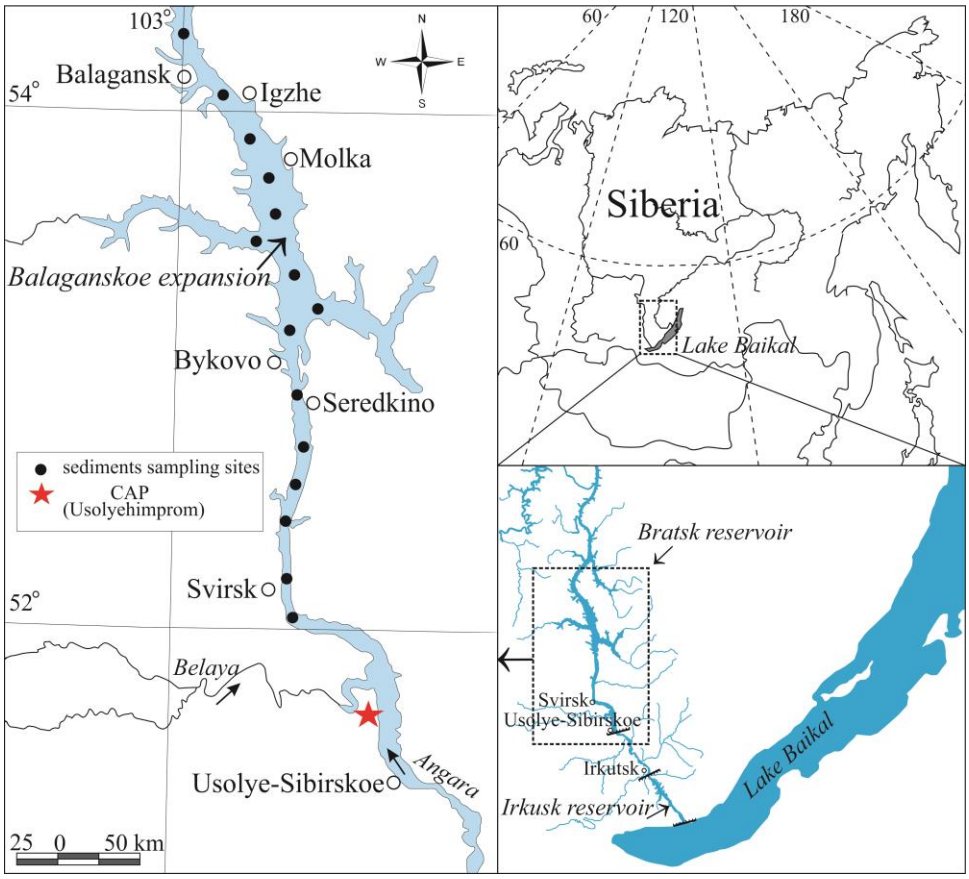

Figure 1. Map of location of sampling stations for bottom sediments of the Bratsk reservoir.

For analysis we used the scientific equipment of the Isotope and Geochemical Research Center of IGH SB RAS (Irkutsk). Determination of Hg concentrations was carried out on the atomic absorption analyzer RA-915+ with prefix RP-91 using the "cold steam" method. The forms of Hg (water-soluble, acid-soluble, organic, strongly bound, solid residue) in the cores of bottom sediments are determined using the method [9]. Mapping is performed using QGIS software. “Surfer” software was used for construction of the distribution fields; interpolation of Hg concentrations was performed employing the Kriging method.

3. Results and discussion

All in all, for the 20-year period, the monitoring results have shown decreasing mercury pollution levels in the superficial layer of bottom sediments in the upper part of BR. The average concentration of mercury has decreased from 2.03 to 0.79 mg/kg (figure 2). The most noticeable decrease occurred in the period from 2003 to 2009. However, the release of mercury from the bottom sediments in an aquatic ecosystem is a very time-consuming process. Despite the general positive trend towards purification of the sediments at the widening and in the section of the reservoir below the barrier zone of sedimentation, high concentrations of mercury exceeding 1.5 mg/kg are still observed in the surface sediments of the section near Bykovo settlement (figure 2). In 2018, mercury concentrations in bottom sediments at various sampling stations were 5 to 54 times higher than the background value. The reason for such inertia of the self-purification process is a complex of extra- and intra-reservoir factors, of which the most important are considered below.

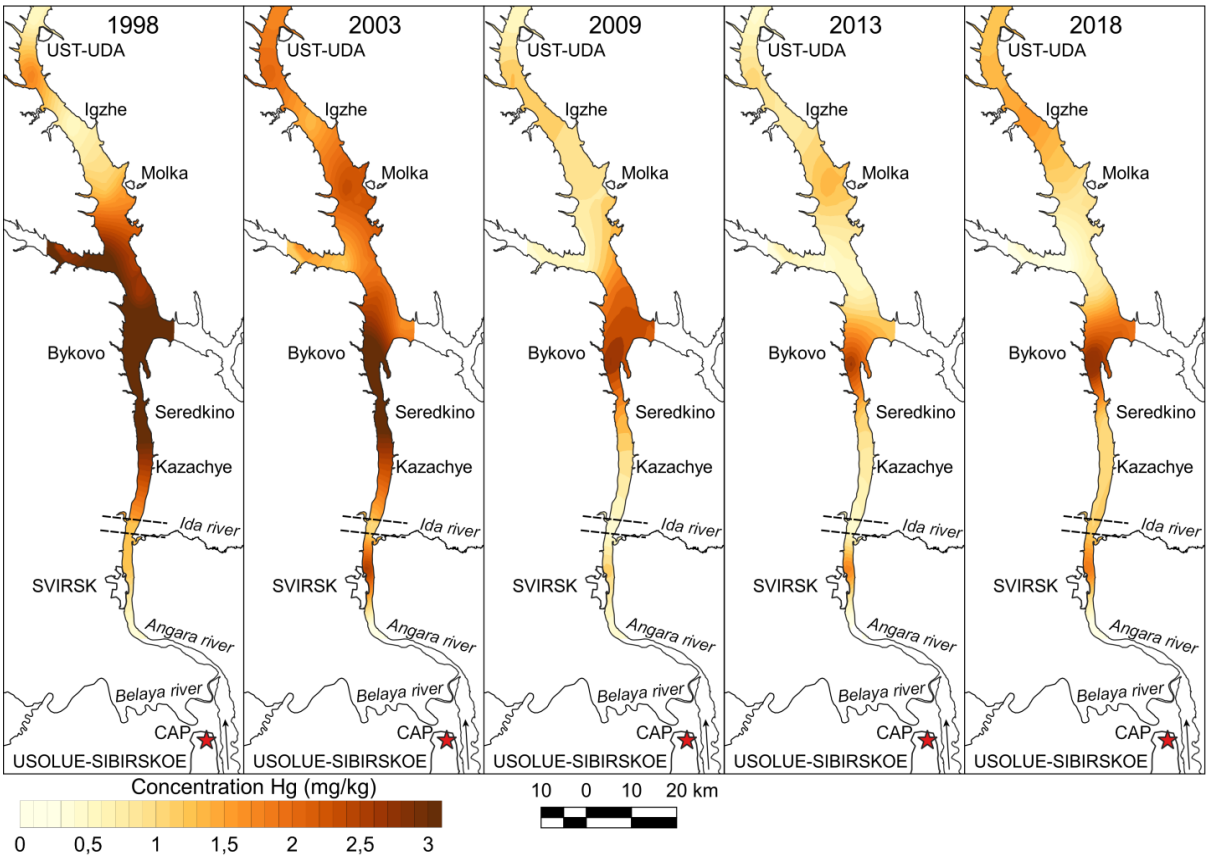

Figure 2. Interannual dynamics of mercury pollution of surface sediments in the upper part of the Bratsk Reservoir. Dotted lines indicate the zone of the main sedimentation barrier, asterisk indicates the location of the CAP.

Despite the complete shutdown of the CAP plant, high concentrations of mercury in alluvial sediments (1.7-2.9 mg/kg) are still confined to discharge points of organized CAP releases. These are significantly higher than the background values (0.03 mg/kg). This points to the continued inflow of this toxic element into the reservoir with the surface runoff, through the drainage ditch of the mercury-containing sludge storage facility and with the waste water of the ash disposal ditch. According to tentative assessments, with the surface runoff from the contaminated area of CAP occupying the area of 12 km2, ~115 kg Hg flows annually in the Angara river [10].

The high sedimentation rate at the main BR sedimentation barrier contributes to the discharge and consolidation of the main mass of technogenic mercury in the bottom sediments. Analysis of the

vertical distribution of Hg in the bottom sediments of this region has shown that the surface layers are less enriched with mercury than the middle layers of the core, where Hg concentrations reach 13.6 mg/kg. Significant concentrations of Hg in sediment layers correspond to years of intensive work of the CAP. As the production volumes decrease, they are overlaid by sediments with lower toxicant content. Large tributaries of the Angara river (the Irkut, Belaya and Kitoy Rivers) have a significant impact on the Hg concentrations in the reservoir bottom sediments, bringing in large quantities of uncontaminated terrigenous suspended solids during floods. However, most of this suspended matter is deposited in the barrier zone and only small amounts are transported downstream. The barrier, which during the period of high technogenic load served as a deterrent to the downstream spread of mercury in suspended form, currently prevents the transit of uncontaminated tributary sediments, thereby prolonging the period of overlaying of contaminated sediments with new layers.

One of the main factors influencing the mercury pollution dynamics of bottom sediments during the period of reduction of technogenic emissions is the water-level regime of the reservoir, the annual fluctuations of which can reach 7 meters. In years of low water availability, large parts of coastal shallow water areas are drained and sediment tranfer processes are less pronounced. During the period of water level rise, washing of bottom sediments takes place, leading to the release of sedimental layers with high mercury concentrations and the transfer and re-deposition of the polluted fine-grained fraction downstream. For example, during the dry period 2013-2017, mercury concentrations in the bottom sediments of the upper part of the BR decreased and stabilized. In contrast, in 2018, when the water level in the BR was rising significantly, mercury concentrations in the surface layer of bottom sediments increased and spread over the reservoir water area more quickly (figure 2). When the depth decreases and water temperature increases in the BR during dry periods, mass development of higher aquatic plants and plankton occurs. Consequently, the amount of autochthonous easily degradable organic matter in the reservoir increases. Significant amount of available organic carbon entering the bottom sediments and changes in redox conditions during the periods of water level rise foster the process of mercury methylation in the surface layers of the sediments [11-14].

Experimental research of the forms of mercury has shown that a significant share of Hg is quite firmly fixed in the bottom sediments of BR. Hg content in the most mobile water-soluble and acid-soluble fractions is very low - for all cores of bottom sediments it accounted for 0.0...% of the total sum of the extracted fractions. The strongly bound form of Hg increases in proportion to its gross concentration ($r = 0.94$, $p<0.001$). Probably, mercury in this fraction is located within the matrix of silicate minerals due to isomorphism of substitution. The fixed form of Hg also includes solid residue. The high content of mercury in the organic fraction, which includes Hg humates and methylmercury, indicates an important role of humus substances in migration of mercury. Organic complexes are potential reserves of mobile Hg in bottom sediments. Changes in the physical and chemical parameters of the environment in the sediment strata, sufficient amount of organic matter, and the activation of anaerobic Hg-methylation communities of microorganisms lead to the destruction of bound complexes, to the formation of methylated forms of mercury, and, consequently, to an increase in its bioavailability [11-12].

This is also confirmed by high levels of mercury accumulation in the fish of the upper part of the Bratsk Reservoir, where the fraction of methylated mercury in the muscle tissue is on average 94.2% [15]. The study of the forms of mercury in different layers of bottom sediments of the barrier zone has revealed an interesting pattern - it has been established that the higher the concentration of gross Hg in the bottom sediments, the smaller its share in the organic fraction (figure 3a). At the same time, the concentrations of gross Hg and Corg in the bottom sediments of the studied area have a pronounced positive correlation at a high level of significance (figure 3b). This imbalance can probably be explained by the fact that during the intensive operation of the plant's mercury electrolysis unit, mercury entered the water body with industrial waste in the form already firmly connected with the matrix of minerals and then migrated to the zone of the main sedimentation barrier. This is indirectly confirmed by the results of the study on the forms of mercury in natural and contaminated soils of Svirsk and Usolie-Sibirskoye [16], which show that the predominance of Hg in a particular fraction is

largely due to the original form of Hg, in which it came from a technogenic source. Other factors affecting the reduction of the organic fraction's proportion in layers with high grossmercury content may be the excess of organic matter, its partial destruction and subsequent diagenesis.

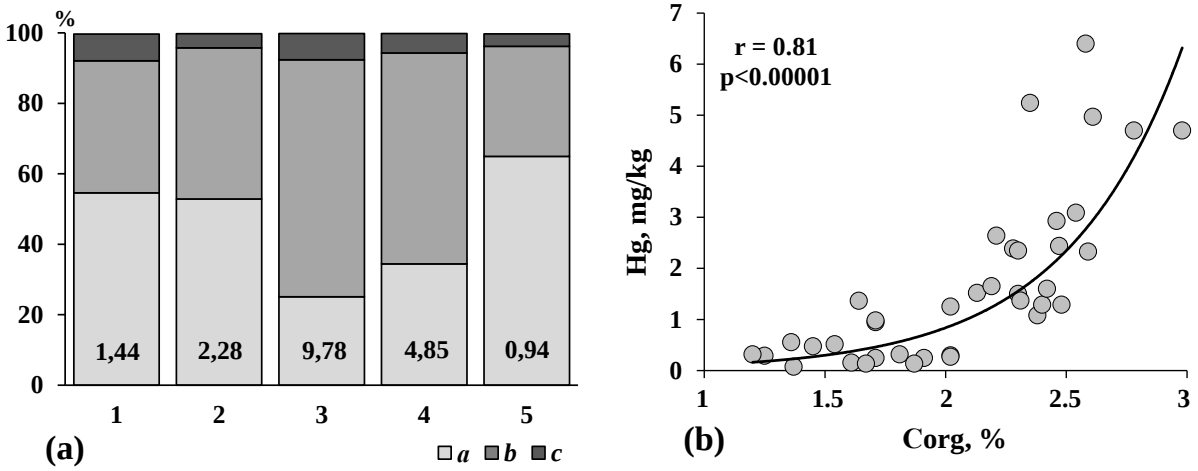

Figure 3. (a) – Distribution of Hg in different fractions of the bottom sediments of the Bratsk Reservoir (% of the total fractions). Bottom sediments of the main sedimentation barrier zone (1 – 0-10 cm, 2 – 16-17 cm, 3 – 24-25 cm, 4 – 35-37 cm) and the Seredkino settlement area (5 – 0-10 cm). The figures in the columns indicate the gross concentration of Hg (mg/kg); the fractions are: *a* – organic, *b* – tightly bound, *c* – solid residue. **(b)** – Dependence of Hg concentrations on organic carbon content in the bottom sediments of the barrier zones.

4. Conclusions

This study shows that a large aquatic ecosystem with a high degree of self-purification requires decades to normalize the environmental situation after years of intensive mercury inflow. The main factors preventing the purification of the water body are the enormous stocks of mercury in the bottom sediments, significant interannual and seasonal fluctuations in water level leading to its secondary inflow into the aquatic environment, an increase in the share of mobile forms and surface runoff from polluted areas.

Acknowledgments

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