Short communication

Dynamics of mercury concentrations in wastewater from the Usolye-Sibirskoye industrial zone in periods with different technogenic loads



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ABSTRACT. Usoliekhimprom is one of the most hazardous technogenic facilities in the Irkutsk Region, which triggers the importance of environmental monitoring. To establish the current hazard of Usoliekhimprom during the period of its closure, we analyzed the interannual dynamics of mercury concentrations of in the plant wastewater. The results revealed that the concentrations of the toxicant in the wastewater during the closure period were lower than during the operational period. However, it was not possible to completely cease the influx of mercury with wastewater into the environment after the closure of the plant. The high mercury concentrations in wastewater were primarily due to localized sites of extensive pollution in the area of the mercury electrolysis shop and to the surface runoff from the entire industrial site of Usoliekhimprom.

Keywords: mercury, wastewater, environmentally hazardous facility, pollution, monitoring

1. Introduction

As a matter of fact, the bulk of mercury released from the industries that employ Hg in technological processes enters the air, water bodies and soils. In the Usoliekhimprom plant, one of the largest sources of anthropogenic mercury, the mercury technology is applied for the production of chlorine, caustic soda and vinyl chloride. When the mercury electrolysis shop was operating, about 1,327.4 tons (mt) of mercury were released into the environment (Rush and Khitskiy, 2003). Importantly, mercury produces an extremely dangerous toxic effect on living organisms, including humans. Taking this into account, numerous studies were dedicated to investigate the effects of plant operations on the abiotic and biotic components of the Angara River environment (Gordeeva et al., 2017). The Usoliekhimprom plant site with an area of about 600 hectares is located close to the Angara and Belaya Rivers (Fig. 1). Therefore, the discharge of mercury into aquatic ecosystems is of great concern. The investigation revealed a negative impact of mercury emissions from this plant on the aquatic organisms of the Angara River (Pastukhov et al., 2019a).

The closure of the mercury electrolysis shop (1998) and the subsequent complete closure of the Usoliekhimprom plant (2012) eventually resulted in the limitation of the technogenic emission of mercury into the environment. Nevertheless, it was factually

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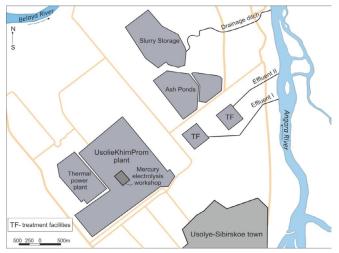


Fig.1. Schematic map of Usolye-Sibirskoye industrial zone.

not possible to completely remove the consequences of harmful operations. This was due to the accumulation of highly toxic waste through long-term activities over the entire Usoliekhimprom industrial site. The analyses of soil sampled at the industrial site revealed the mercury concentration that was 120 times higher than the maximum permissible concentrations in Russia (Pastukhov et al., 2019b). The problem of waste disposal

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has been a top priority for the government of the Irkutsk Region for some decades, with the goal of ensuring the environmental safety of the Angara River region. In 2020, the program to eliminate mercury pollution at the industrial site was launched via removing the mercury electrolysis workshop. However, this type of work poses a potential risk related to the possible release of mercury into the environment. Thus, the aim of this study was to measure mercury concentrations in the wastewater from the Usolye-Sibirskoye industrial zone because they represent the main sources of technogenic mercury and its transportation to the Angara River ecosystem.

2. Materials and methods

This study reports the results obtained on the effects of the Usoliekhimprom plant. Wastewater samples were collected from effluents I and II discharged from the plant and the drainage ditch used to remove excess water from the slurry storage facility during plant activity. The results of analyses of mercury concentrations in wastewater were compared between different periods of technogenic loads, from 2008 to 2020.

Chemical analyses were carried out at the Center for Collective Use "Isotope-Geochemical Research" of IGC SB RAS (Irkutsk, Russia). The concentration of mercury in water was determined by atomic absorption analysis with non-flame determination of reduced atomic mercury vapor using an RA-915⁺ equipment with the PP-91 attachment. The measurement range for the mass concentration of total mercury in water for direct determination varied between 0.05 and10 μ g/l.

3. Results and discussion

During industrial operations, the sewerage network was pre-treated at the complex treatment facilities and in the neutralization tanks. Despite this, the wastewater before discharging into the Angara River contained high concentrations of different organic and inorganic substances according to (State report, 2011; Alieva and Pastukhov, 2012). In 2000, mercury was defined as the most dangerous toxicant, with concentrations in drainage ditch water of 30-38 $\mu g/1$ (Rush and Khitskiy, 2003). In 2006 to 2008, mercury concentrations were also very high: up to 9.0 $\mu g/1$ in effluent I, up to 8.1 $\mu g/1$ in effluent II and up to 2.5 $\mu g/1$ in the drainage ditch (Alieva et al., 2011). In 2010, they were 2.39 $\mu g/1$ in effluent I –, 0.40 $\mu g/1$ in effluent II, and 1.99 $\mu g/1$ in the drainage ditch.

In 2012, the significant reduction in the flow of wastewater from effluent I and the drainage ditch, as well as the complete cessation of flow from effluent II, were distinctive features. When the plant was closed (2012), there was a significant decrease in mercury concentrations in all wastewater (Fig. 2). Since 2013, mercury concentrations in effluent I have increased again, ranging from 0.077 to 0.284 μ g/l. According to (Rush and Khitskiy, 2003), the variability of mercury

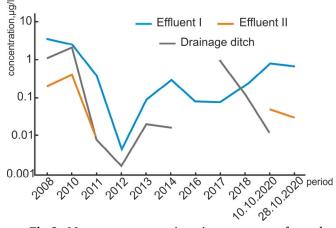


Fig.2. Mercury concentrations in wastewater from the Usolye-Sibirskoye industrial zone.

concentrations in plant effluents was not only associated with the production processes that activated mercury emissions from plant process facilities but also with the flushing of mercury compounds by surface water from the industrial site and its surrounding area. After 20 vears since the closure of the mercury electrolysis shop, the essential mercury pollution at the industrial site was due to localization of technogenic mercury underneath the mercury electrolysis shop, buildings, sludge, production wastes, etc. The catastrophic level of soil pollution can be cited from the available information in the media (internet), e.g. "117 tons of mercury have accumulated under the industrial site and 600 tons near the shop", "the volume of mercury-containing soil at Usoliekhimprom is about 12.500 tons". Moreover, "approximately 24 tons of mercury concentrated in the surface (up to 25 cm) layer of soil and subsoil at the plant site and surrounding areas" (Rush and Khitskiy, 2003). Therefore, during the period of plant closure, mercury concentrations in wastewater from effluent I were primarily associated with large localizations of mercury around the mercury electrolysis shop, as well as with the surface occurrence in the runoff from this highly polluted area.

After 2012, mercury concentrations in drainage ditch wastewater ranged from 0.017 to 0.944 μ g/l. Noteworthy is that, since 2016, the drainage ditch flow has been depending on the climatic characteristics in the study area (intensity of rainfall, snowmelt, etc.). The filling capacity of this watercourse, as well as the Hg concentration in the wastewater, were directly related to the volume and composition of the surface meltwater and rainwater flowing into it. The mercury concentrations in the surface water were mainly determined by the impact of the sludge storage facility. Hg concentrations as high as 8.3 mg/kg were recorded in the surrounding soil (Pastukhov et al., 2019b).

A special feature of 2020 was the resumption of wastewater flow from effluent II. We assume that the resumption of wastewater flow from effluent II was due to the dismantling works of the mercury electrolysis shop. During that period, the water curtain prevented the emission of technogenic mercury into the air. According to the available information in the media (internet), about 900 tons of water were used for the water curtain. Most likely, the used water entered the highly polluted collector system of the plant and was discharged into the Angara River through effluent II, being enriched in mercury. Like in 2010, the highest mercury concentration in the water of the collector system was determined in effluent I (0.791 μ g/l). The study of Hg forms in wastewater indicated that the element was predominantly transported (80%) in the solid form. The concentration of the pollutant was 0.051 μ g/l in effluent II, while in the drainage ditch it was 0.013 μ g/l.

In 2020, Hg concentrations in wastewater were lower than during of the plant operation. However, comparison of the results revealed that the concentration of mercury in the drainage ditch in 2020 was 153 times lower than in 2010; in effluent II – 8 times lower, and in effluent I – only 3 times lower. Therefore, the present study describes the dynamics of Hg concentrations in the wastewater of Usoliekhimprom during different periods of its activity. There were reports that even if the plant stopped its activities, wastewater still contains high concentrations of the toxicant. Even on a reduced scale, mercury enters the Angara River water.

Conclusions

The results of the study revealed that even after the complete closure of the Usoliekhimprom plant, wastewater from its site continues to discharge into the Angara River. Mercury concentrations in wastewater are still significant. Consequently, the Usoliekhimprom plant is an extremely hazardous facility in the Irkutsk Region from an environmental point of view and still impacts the abiotic and biotic components of the freshwater ecosystem of the Angara River. The study represents an important step to environmental safety and is expected to contribute to the environmental management policy of the Angara River region.

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Conflict of interest

Authors declare no conflict of interest.

References

Alieva V.I., Butakov E.V., Pastukhov M.V. et al. 2011. Characteristics of anthropogenic pollution and mercury transfer in Bratsk water reservoir. Geoekologiya. Inzheneraya Geologiya, Gidrogeologiya, Geokriologiya [Geoecology. Engineering Geology, Hydrogeology, Geocryology] 5: 431-438. (in Russian)

Alieva V.I., Pastukhov M.V. 2012. Hydrochemical characteristics of the Angara River in the area of influence of the Usolskiy Industrial Hub. Geografiya i Prirodnyye Resursy [Geography and Natural Resources] 1: 68-73. (in Russian)

Gordeeva O.N., Belogolova G.A., Pastukhov M.V. 2017 Mercury speciation and mobility in soils of industrial areas in the Baikal region, Southern Siberia, Russia. Environmental Earth Sciences 76: 558. DOI: <u>10.1007/s12665-017-6882-4</u>

Pastukhov M.V., Poletaeva V.I., Butakov E.V. 2019b. Distribution of mercury in the Usoliekhimprom sludge storage facility and its impact on the environment. In: International Scientific-Practical Conference dedicated to the memory of A.N. Antipov, Corresponding Member of the RAS, pp. 549-552. (in Russian)

Pastukhov M.V., Poletaeva V.I., Tirskikh E.N. 2019a. Long-term dynamics of mercury pollution of the Bratsk reservoir bottom sediments, Baikal region, Russia. IOP Conference Series: Earth and Environmental Science 321(1): 012041. DOI: <u>10.1088/1755-1315/321/1/012041</u>

Rush E.A., Khitsky Ya.V. 2003. Surface run-off as a main factor of mercury pollution of the Angara River. Proceedings of Higher Educational Establishment. Izvestiya Vysshikh Uchebnykh Zavedeniy. Geologiya i Razvedka [Geology and Exploration] 4: 80-84. (in Russian)

State Report on the State and Protection of the Environment of the Irkutsk Region for 2010. 2011. Irkutsk: OOO Forward. (in Russian)