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Mercury compounds in the environmental objects of the Baikalsk Pulp and Paper Mill influence zone

Morshina T.N., Lukyanova N.N., Mamchenko T.B., Kopylova L.P., Virchenko E.P.

[1] Research and Production Association "Typhoon", Pobedy Str., 4 Obninsk, Kaluga Region, 249038, Russia

ABSTRACT. The content of mercury compounds in the industrial wastes of the Baikalsk Pulp and Paper Mill, in soils on the territories of sludge storage sites, in the bottom sediments of Lake Baikal as well as small rivers flowing into the lake has been studied. There observed an increased content of total mercury and methylmercury in the sludge lignin waste.

Keywords: mercury, methylmercury, industrial waste, bottom sediments, soils

1. Introduction

Mercury is one of the most dangerous environmental pollutants. In the natural environment, mercury is present mainly in the form of inorganic compounds. Inorganic forms of mercury under the influence of environmental factors can be converted into mercury-containing organic compounds. Of all the organomercury compounds, monomethylmercury is the most abundant in the environment. The transformation of inorganic mercury into methylmercury occurs in various environments, including lakes, rivers, wetlands, bottom sediments, soils, open ocean, industrial and domestic waste and depends on the content of bioavailable bivalent mercury, sulfur compounds, organic matter, iron, number and activity of sulfate- and iron-reducing bacteria, methanogenic microorganisms, etc. (Ullrich et al., 2001). All mercury compounds are toxic, but methylmercury is the most hazardous form of mercury from an ecotoxicological point of view (Environmental Health Criteria..., 1989) because it is readily absorbed by organisms, accumulates at high trophic levels and is potent neurotoxic chemical.

The aim of this study was to investigate the mercury concentrations in the industrial waste of the Baikalsk Pulp and Paper Mill (BPPM), the soil and bottom sediments of Lake Baikal and the small rivers located in the zone of influence of the plant.

2. Materials and methods

The objects of the study were industrial waste, bottom sediments and soils in the area of BPPM location. Pulp and paper industry enterprises accumulate a large amount of industrial waste that is buried in special storage ponds. Waste from extensive wood processing is distinguished by its complex chemical composition and includes substances of varying degrees of toxicity and hazard. Two landfills with a total area of more than 150 hectares are used to store waste accumulated during the BPPM operation. The storage ponds located in a seismic and mudflow risk zone contain over 6.2 million tons of production waste. The Solzan sludge storage site (storage ponds No. 1 to 10) with an area of about 119 hectares is located on the slope of the Hamar-Daban foothills in the interfluve of the Malaya Osinovka and Solzan rivers 5 km southeast of the BPPM industrial site. The Babkha site (storage ponds No. 12 to 14) is located 8 km northwest of the BPPM industrial site between the Babkha and Utulik rivers. Intermediate storage pond No. 11 is located at the BPPM industrial site. The bulk of the waste is colloidal sludge lignin precipitates formed during biological and physicochemical wastewater treatment, ash from sludge lignin combustion, ash and slag from coal combustion, and ash from bark boilers (Kolotov et al., 2021). In the course of the study, 13 waste samples were taken from the storage ponds. Figure 1 shows the layout of the storage ponds at the waste storage sites. The layout of storage ponds at the waste landfills is shown in Figure 1.

To assess the impact of BPPM on the pollution of Lake Baikal, in the water area of the lake adjacent to the industrial site, 11 samples of bottom sediments were taken at distances from 50 to 1200 m from the coast, in the depth range of 15 to 400 m. The bottom sediments were sampled from the surface layer of the bottom sediments using the Van Veen grab sampler.

To assess the pollution of surface watercourses, samples of bottom sediments were taken from five small rivers that traverse the investigated area and flow

*Corresponding author.
E-mail address: morshina@typhoon.obninsk.ru (T.N. Morshina)

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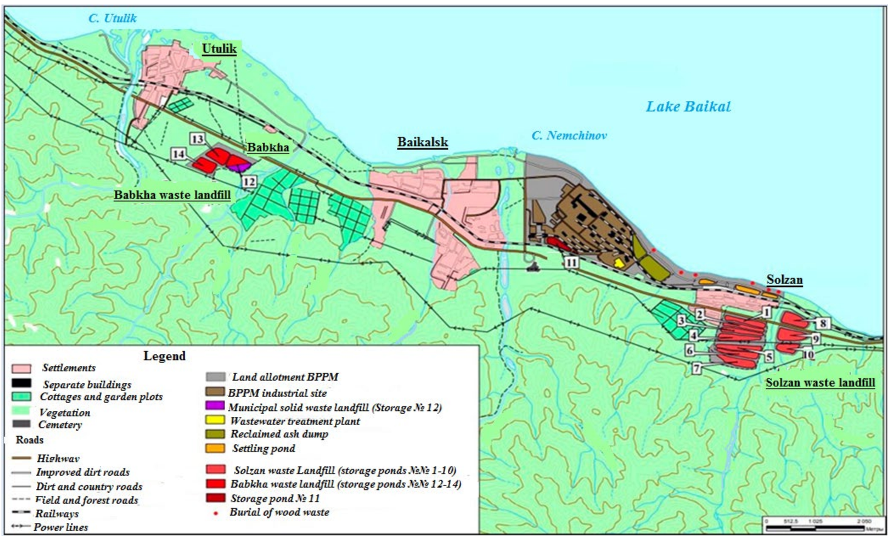

Fig.1. Layout of the storage ponds at the waste storage sites

into Lake Baikal. On the Babkha, Kharlakhta, Solzan, and Bolshaya Osinovka rivers, the samples were taken in areas not subject to the direct anthropogenic impact (above the waste storage sites or above the town of Baikalsk) and at the estuaries of the rivers before flowing into Lake Baikal. On the Malaya Osinovka River, the samples were taken near the storage pond No. 9 and at the estuary.

The soil was sampled in Baikalsk, at the Solzan and Babkha sites of sludge storage ponds and in the immediate vicinity of BPPM. In the investigated area, 20 soil samples were taken from a depth of 0 to 20 cm using the "envelope" method, including 4 samples from background sites, 13 samples from the waste storage sites and near the BPPM industrial site and 3 samples from the area of Baikalsk.

The total mercury and methylmercury (in terms of mercury) concentrations in soil samples, bottom sediments and waste were determined from air-dried samples by atomic absorption in cold vapor on a VGA 77 mercury accessory to a Varian AA 140 atomic absorption spectrophotometer. Total mercury was extracted with a mixture of nitrogen, sulfuric and perchloric acids when heated; organic mercury was extracted with potassium bromide solution in sulfuric acid in the presence of copper sulfate, followed by the extraction in toluene, re-extraction in sodium thiosulfate and decomposition with a mixture of acids. The detection limit for the determination of total mercury was 5 μg/kg, and that of methylmercury – 0.15 μg/kg (RD 52.18.827-2016 and RD 52.18.843-2016). For internal quality control of analytical work in determining total mercury and methylmercury, an ERM-CC580 certified sample of bottom sediments (estuarine sediments, Belgium) was used. The data that we obtained (n = 4) were in good agreement with certified values. The determined concentration of total mercury was 128 ± 6 mg/kg (certified: 132 ± 3 mg/kg); the concentration of methylmercury was 66 ± 10 mg/kg (certified: 75 ± 4 mg/kg). The correctness of the mercury determination was also confirmed involving the IAEA international calibration (IAEA-MESL-ILC-TE-SEDIMENT-2018). The certified value of the mercury concentration in the control samples was 29.9 μg/kg, and the measured value was 28.2 μg/kg.

3. Results and discussion

Analysis of industrial waste samples revealed that in the storage ponds No. 4, 5, 6, 7, 11, 13, and 14 filled with ashes from sludge lignin, bark boilers and coals, as well as with green liquor sludge, the concentration of total mercury ranged from 11 to 33 μg/kg; methylmercury was not detected in this waste. In the storage ponds No. 1, 2, 3, 8, 9, and 10 filled mainly with lignin sludge, the waste containds elevated levels of mercury (180 to 4100 μg/kg). The concentration of methylmercury in the sludge lignin waste varied from 1.0 to 13.5 μg/kg. The presence of organic matter and reducing environmental conditions facilitated its formation. The methylmercury fraction in sludge lignin ranged from 0.05 to 2 % of the total concentration. The methylation process slows down with an increase in the total mercury concentration in the sludge lignin (Fig. 2).

The concentrations of total mercury and methylmercury were much lower in the bottom sediments of the investigated water area of the lake. The total mercury concentration varied from 9.5 to 32.5 μg/kg, with the mean value of 21.7 ± 7.7 5 μg/kg. The methylmercury concentration ranged from

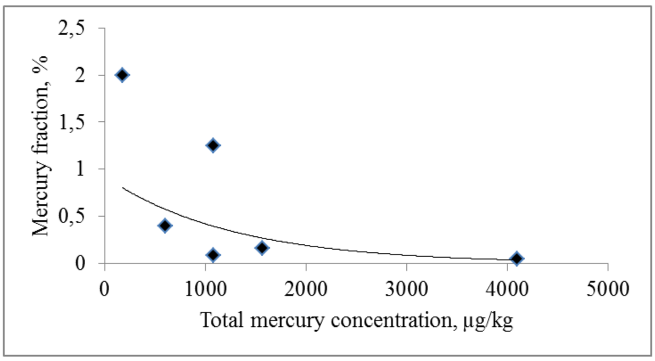

Fig.2. Dependence of the production of methylmercury on the total mercury concentration in sludge lignin

<0.15 to 0.33 μg/kg. Methylmercury levels below the detection limit were observed in 36 % of the examined samples. The mean value of methylmercury in the bottom sediments was 0.19±0.10 μg/kg. The contribution of methylated forms to the total mercury concentration did not exceed 1.5 %. On average, the bottom sediments contained 0.88±0.39 % of mercury in methylated form.

The concentrations of mercury and methylmercury in the bottom sediments of the BPPM influence zone were comparable to the concentrations in other areas of the lake. According to long-term observations, in 2015 to 2019, the mean mercury concentration near the Selenga shallow water and in the north of the lake, along the route of the Baikal-Amur Mainline, was 33±16 μg/kg, and the mean methylmercury concentration was 0.32±0.20 μg/kg (Morshina et al., 2021). The mercury levels in the bottom sediments of Lake Baikal corresponded to the concentrations in the sediments of Siberian continental lakes (3 to 69 μg/kg) (Strakhovenko et al., 2010).

The total mercury concentrations in the bottom sediments of small rivers varied from 5.5 to 11.1 μg/kg, and the methylmercury concentrations were below the detection limit in all samples.

The background mercury concentration in the soil of the investigated area was 29.8±13.3 μg/kg. At the Babkha waste storage site, no mercury pollution was identified in the soil (mean value 31 μg/kg). In the soil of the Solzan sludge storage site, the mercury concentration two to four times exceeded the background levels (71 to 117 μg/kg). The maximum soil pollution (365 μg/kg) was observed at the BPPM industrial site near the storage pond No. 11; the mercury concentration at this site was by an order of magnitude higher than the background. The elevated mercury levels (57 to 75 μg/kg) were also observed on the coast of Lake Baikal below the industrial site and the Solzan sludge storage site.

Conclusions

The sludge lignin stored at the Solzan site contained elevated levels of mercury (180 to 4100 μg/kg) and methylmercury (1.0 to 13.5 μg/kg).

There was no influence of the Solzan waste storage site on the pollution of the bottom sediments in Lake Baikal and the small rivers that traverse the investigated area and flow into Lake Baikal. The concentrations of total mercury and methylmercury in the bottom sediments of Lake Baikal and the small rivers in the BPPM influence zone were within the concentration range of unpolluted water bodies.

The mercury pollution of the soil, which two to ten times exceeded the background levels, was observed at the BPPM industrial site and the Solzan site. On the Baikal coast below the industrial site and Solzan site, the mercury concentrations were almost two times higher than the background.

Conflict of interest

The authors declare no conflict of interest.

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