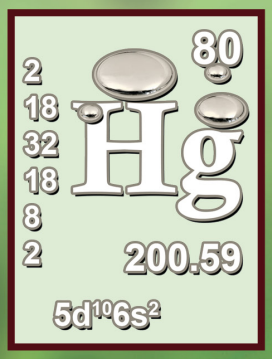
ISSN 2658-3518
Special Issue



LIMNOLOGY & FRESHWATER BIOLOGY

Mercury in Biosphere: Environmental and Geochemical Aspects

2022, № 3

> abiotic and biotic water components;
> ecosystem-level studies;
> systematics and aquatic ecology;
> paleolimnology and environmental histories;
> laboratory experiments and modeling

Editorial

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Mercury in Biosphere: Environmental and Geochemical Aspects

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Mercury is recognized as a global environmental pollutant due to its toxicity, mobility and ability to accumulate in the environment.

The Minamata Convention on Mercury that took effect on 16 August 2017 resulted from long-term scientific research and was based on Global Mercury Assessment as part of the United Nations Environment Program (UNEP), including the information about mercury as a chemical substance and its health effects, sources, long-range transport, and mercury-related prevention and control technologies.

The text of the Convention indicates that mercury is a chemical of global concern due to its long-range transport in the atmosphere, persistence in the environment after its occurrence as a result of anthropogenic activity and potential to bioaccumulate in ecosystems as well as due to significant negative consequences for human health and the environment caused by its impact.

Mercury-related issues are regularly discussed in detail within the framework of the largest international conference “Mercury as a Global Pollutant”. However, the representation of the experts from the Russian Federation and the Commonwealth of Independent States (CIS) countries at this conference is minor.

The problem of mercury pollution is also acute for our country. Although Russian Federation has not yet ratified the Minamata Convention, serious attention is traditionally paid to the study of the mercury negative impact on the environment and humans.

In the Russian Federation, the symposium “Mercury in Biosphere: Environmental and Geochemical Aspects” was organized twice: in Moscow (2010) and Novosibirsk (2015). This symposium is actually the only venue where issues relevant for the Russian Federation such as natural and anthropogenic migration of mercury and its impact on the environment and people are discussed.

The third Symposium aims to combine individual studies, forming a general pattern of the state of research in the field of chemistry, biogeochemistry, ecotoxicology, and analytics of mercury in the Russian Federation and the CIS countries. Leading experts are invited to the symposium, who will share their experience in studying mercury cycles in the environment, development and application of the best environmental practices. As a part of the Symposium, a school for young researchers “Interdisciplinary Approach to the Study of Mercury in Various Environmental Objects” will be held where conditions will be created for cooperation and exchange of experience between students from Russian and foreign universities as well as postgraduates and young scientists from scientific centres.

The agenda of the Symposium focuses on the representatives of academic and educational institutions, industrial organizations, and environmental authorities involved in research on this hazardous toxicant.

The materials of the Symposium will serve as a good basis for preparing recommendations to reduce the negative impact of mercury on the natural environment and public health as well as to develop the National Action Plan of the Russian Federation within the framework of the Minamata Convention on Mercury.

Received: July 14, 2022; ***Accepted:*** July 15, 2022;
Available online: July 31, 2022

Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Distribution of mercury in the system water-suspended matter-bottom sediments of Lake Onega (NW Russia)

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ABSTRACT. For the first time for Lake Onega, the lateral distribution of gross mercury in the water-suspended matter and bottom sediments system was revealed. Regularities in vertical distribution of gross mercury in two types of bottom sediments were established. The average content of mercury in water is 0.321 μg/L; in the material of sediment traps - 0.621 μg/g; in the upper and lower parts of bottom sediments - 0.067 μg/g and 0.034 μg/g, respectively.

Keywords: Lake Onego, bottom sediments, mercury, geochemistry

1. Introduction

Mercury is among the ten most hazardous chemicals due to its high mobility and bioaccumulative capacity (O'Connor et al., 2019). In aquatic ecosystems, Hg can be converted to methylmercury, a more toxic form that bioaccumulates in aquatic food chains. Lakes are one of the main objects of the freshwater ecosystem. Mercury enters freshwater systems from a variety of sources and undergoes complex transport pathways. Studying the migration routes of pollutants is the most important task of geochemistry.

This work was carried out in order to study in detail the distribution of mercury concentrations in the system water-suspended matter-bottom sediments.

2. Materials and methods

The object of the study is Lake Onega. The factual material was sampled at 2016-2021 by the R/V"Ekolog" throughout Lake Onega. Sampling was carried out for the Povenetsky, Zaonezhsky, Small Onego, Lizhemskaya, Unitskay, Kondopoga and Petrozavodsk Bays in Big Onego, Central Onego, Southern Onego (Fig. 1). During the expedition, water samples were sampled in conjunction with suspended matter, sedimentary material from sediment traps, and bottom sediments.

Mercury in water was determined by the "cold vapor" method using the amalgamation technique on a Perkin Elmer 3030 atomic absorption spectrometer with an MHS-20 mercury hydride attachment. In bottom sediments, the gross mercury content was determined on the RA-915M analyzer with the RP-91S attachment (Russia).

Analytical work was carried out at the Analytical Center for multi-elemental and isotope research SB RAS, Novosibirsk, Russia.

3. Results and discussion

3.1 Mercury in the water-suspended matter system

The total content of mercury in the water of Lake Onega is on average 0.321 μg/L. The minimum values were obtained for the Povenetsky Bay – 0.022 μg/L. The maximum values were obtained for water samples taken in Southern Onego (0.852 μg/L) and Big Onego (0.552 μg/L).

The concentration of mercury in suspended particles in the water of Lake Onega varies from 0.002 μg/L (Lizhemskaya Bay) to 0.073 μg/L (Zaonezhsky Bay), the average content is 0.021 μg/L. The content of mercury in dissolved + colloidal form varies in a wide range: from 0.01 μg/L in Kondopoga Bay and Povenets Bay to 0.85 μg/L in South Onego. Thus, the predominant form of mercury in water is solution + colloid. Only in the Kondopoga Bay and the Pavenets Bay, mercury in suspended form predominates, which is explained by the location of industrial facilities on the shores of the Kondopoga Bay and the Pavenets Bay, which can be a source of mercury-containing particles.

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Received: May 28, 2022; ***Accepted:*** June 15, 2022;
Available online: July 31, 2022

Fig.1. Scheme for sampling the components of the lake ecosystem of Lake Onega. With removed and color-coded mercury content in the upper part of bottom sediments. I Povenetsky Bay; III Small Onego; IV Unitskaya Bay; V Lizhma Bay; VI Kondopoga Bay; VII Petrozavodsk Bay; VIII Big Onego; IX Central Onego; X South Onego. The points color shows the mercury content in the ranges 0.05 -0.08-0.11-0.14 μg/g from white to black.

We found that the mercury content in the material of sediment traps varies in a wide range from 0.062 μg/g to 4.37 μg/g. It should be noted that high values are observed only in two areas of Lake Onega: in the area of the Lizhemskaya Bay (4.37 μg/g) and in the Povenetsky Bay (0.76 μg/g).

3.2 Mercury in bottom sediments

The geochemical and mineral composition of the bottom sediments of Lake Onega was described in detail in Strakhovenko et al. (2020) Based on the analysis of the composition and geochemical features of the upper particles (0-20 cm) of the bottom sediments of Lake Onega, the authors found that the Holocene sediments of Lake Onega can be divided into two types.

Both types of section are characterized by higher mercury concentrations in the upper parts of the sections (Fig. 2). Moreover, the concentrations of mercury in both types are close to each other in terms of values. And they differ only in the thickness of the zone with increased values of mercury concentration, which is just different for the two types of sections. From the analysis of mercury concentrations in the section of bottom sediments, it was found that in the upper part of the section (up to 20 cm), the concentration is higher than in the lower part of the section (on average 0.065 μg/g and 0.034 μg/g for the upper and lower parts of the section, respectively). At the same time, increased concentrations are observed precisely for layers of oxidized layers and layers enriched with Fe-Mn.

In the course of the work, the lateral distribution of mercury in bottom sediments was studied

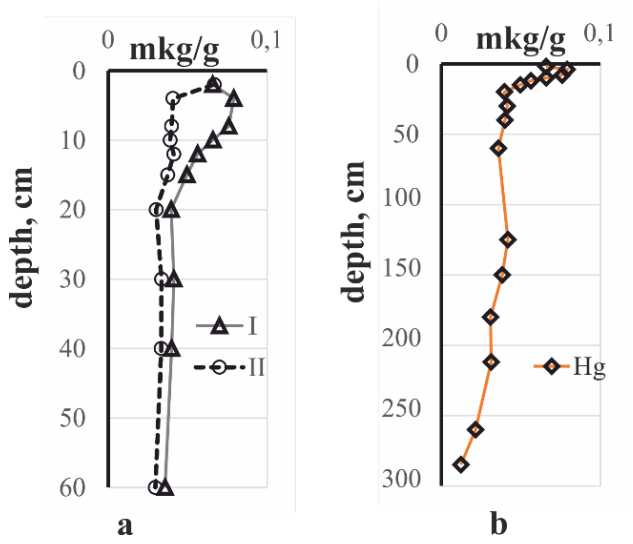

Fig.2. Distribution of mercury: a) in the I and II types of sections of bottom sediments of Lake Onega, b) in the average section of bottom sediments of Lake Onega

throughout Lake Onega. It has been established that the northeastern part of Lake Onega (the Povenetsky and Zaonezhsky Bays, Small Onego) is characterized by lower values than for the rest of Lake Onega. The maximum values of mercury content in the upper part of the bottom sediments are reached in the Kondopoga Bay (0.089 μg/g).

Throughout the entire water area, the mercury content in the lower part of the bottom sediment section is lower than the concentrations in the upper

part of the bottom sediment section and averages 0.034 μg/g. The lowest values are observed in the bottom sediments sampled in the Unitskaya Bay - 0.016 μg/g, the maximum values in the Bolshoy Onega swarm 0.058 μg/g.

As can be seen from the results obtained for Lake Onega, the concentration of mercury in the material of sediment traps is higher than the content of mercury in bottom sediments. This is most likely due to the greater amount of organic residues in the material of the sediment traps, since mercury has a high bioaccumulative capacity.

4. Conclusions

The research of mercury concentrations in various components of ecosystem of Lake Onega led to the following conclusions:

1) The total content of mercury in the water of Lake Onega is on average 0.321 μg/L. The predominant form of mercury in water is solution + colloid, with the exception of water samples from Kondopoga Bay and Pavenets Bay.

2) From the analysis of mercury concentrations in the section of bottom sediments, it was found that in the upper part of the section (up to 20 cm), the concentration is higher than in the lower part of the section (on average 0.065 μg/g and 0.034 μg/g for the upper and lower parts of the section, respectively).

3) It has been established that the northeastern part of Lake Onega (the Povenets and Zaonezhsky Bays, Small Onego) is characterized by lower values than for the rest of Lake Onega. The maximum values of mercury content in the upper part of the bottom sediments are reached in the Kondopoga Bay (0.089 μg/g).

4) We found that the mercury content in the material of sediment traps varies in a wide range from 0.062 μg/g to 4.37 μg/g and is higher than the content of mercury in the corresponding bottom sediment cores.

Acknowledgments

The work was supported financially by the Russian Foundation for Basic Research (Project No. 19-05-50014) and by the Russian Science Foundation under Research (Project No. 18-17-00176-п).

Conflict of interest

Conflicts of Interest: The authors declare no conflicts of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Mercury compounds in the environmental objects of the Baikalsk Pulp and Paper Mill influence zone

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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

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Received: June 7, 2022; ***Accepted:*** June 23, 2022;
Available online: July 31, 2022

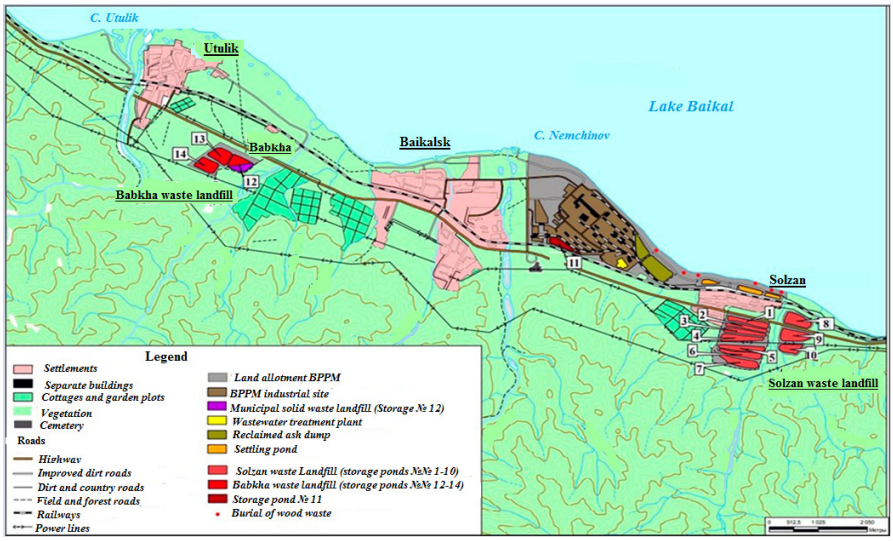

Fig.1. Layout of the storage ponds at the waste storage sites

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

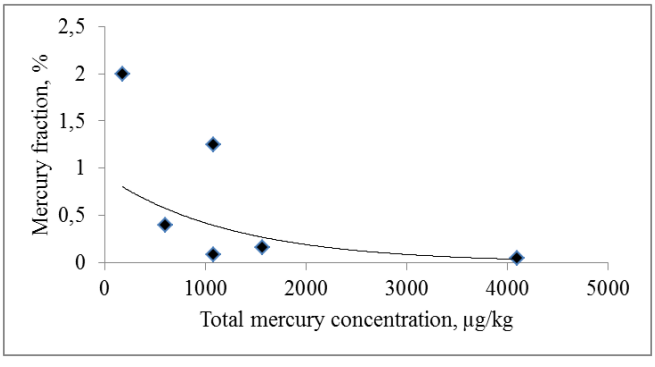

Fig.2. Dependence of the production of methylmercury on the total mercury concentration in sludge lignin

<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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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Hg minerals formed in the dispersion halos of mining waste (Western Siberia)

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ABSTRACT. The article presents the specialties of Hg minerals formed in natural organic matter from the dispersion halos of tailings and in suspended particulate matters of snowmelt and river waters in the dispersion halos of mining waste. The results were obtained due to studying of mining wastes from Novo-Ursk and Aktash deposits of the Kuznetsk-Altai mercury belt. The formation of secondary Hg minerals of similar shape and size (sulfides and selenides; ternary and quaternary chalcohalides, presumably) were found in both objects. Minerals appear as complex thin intergrowths and that currently do difficult certain identification of them compositions.

Keywords: mercury belt, hypergenesis zone, mining waste, mercury, secondary minerals

1. Introduction

Knowledge about the occurrence forms (speciation or species) of potentially toxic elements (including Hg) in the environmental components is the key of understanding the special aspects of their migration and accumulation, as well as bioavailability under surface conditions, supposed the relevance of such studies. Information about the mineral species of elements is the basis confirming theoretical concepts about element's behaviour in the environment. Authigenic (secondary) minerals, i.e. those formed *in situ* due to precipitation at the water-rock interface (Novikov, 2020) provide data on the biochemical processes and geochemical conditions in the environmental components and are also used for paleoreconstructions (Glenn and Filippelli, 2007). Furthermore, authigenic minerals control the migration and toxicity of elements under hypergene conditions (e.g. in soils) (Smieja-Król et al., 2022). Usually the secondary minerals are found as the thin complex aggregated phases in the heterogeneous environments (soils, suspended particulate matters or bottom sediments). Research of these minerals is laborious and can be technically complicated due to the characteristics of the substance and phases themselves. Nevertheless, this research is increasing in scope and relevance (Smieja-Król et al., 2022). In Western Siberia, there is a natural source of Hg in the form of mercury zones are combined in the Kuznetsk-Altai mercury belt that is part of the Altai-Sayan mercury province (Obolensky et al., 1995). The study's aim is to identify the specialties of secondary Hg minerals in environmental components from the halo of tailings and mining wastes within the mercury belt.

2. Materials and methods

2.1 Study object

Studies were carried out on the example of two objects of the Kuznetsk-Altai mercury belt (Salair and Kurai mercury zones) (Obolensky et al., 1995). The first object is located within the Ursk plutonic and volcanic structure of the Salair Ridge (Kemerovo Region, Ursk settlement) in the area of the Novo-Ursk massive sulfide ore deposit. For the study, we used natural organic matter (NOM) from the tailings dispersion halo (Lazareva et al., 2019), which had been in contact ~ 100 years with Hg-containing drainage waters and mining wastes (Myagkaya et al., 2022a). This led to the formation of some secondary minerals, including Hg-containing ones (Myagkaya et al., 2020).

The second object is located within the Anuya-Chuya forearc trough and the junction of the Kadrin and Kurai branches of the Kurai deep fault in the Kurai mercury zone in the halo of the epithermal Aktash mercury deposit (Altai Mountains, Aktash settlement). The deposit mined by Aktash Mining and Metallurgical Enterprise (AMME) is situated on the bank of the Yarly-Amry River that flows into the Chibitka River (Gustaitis and Myagkaya, 2022; Myagkaya et al., 2022b). For the 2019 study, the following samples were taken: (i) snow suspended matter near AMME and along the Yarly-Amry valley; (ii) suspended matter from temporary

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Received: June 10, 2022; ***Accepted:*** June 21, 2022;
Available online: July 31, 2022

watercourses that are formed near mines when snow melts and (iii) suspended matter from the Yarly-Amry River near the AMME dispersion halo (1.4 km distance from AMME).

2.2 Methods

The composition and micromorphology of the tested substances from both objects were examined using a *MIRA 3 LMU* scanning electron microscope (Tescan Orsay Holding) with Aztec Energy/INCA Energy 450+ XMax 80 and INCA Wave 500 (Oxford Instruments Nanoanalysis Ltd) microanalysis systems that allow studying nanosized particles.

3. Results and discussion

There were several varieties of mercury minerals (Fig. 1A, B) in the NOM from the dispersion halo of the tailings dump in the Novo-Ursk deposit. The bulk of them was characterised by the formation of complex aggregates consisting of separate fine-grained individuals (from 100 nm to 1 μm). Their composition includes the Fe, Zn, Cu, Ag, As, S, Se, I, Br, and Cl admixtures in different proportions. As previously shown (Myagkaya et al., 2020), Zn sulfides (sphalerite group) form thin intergrowths with Hg sulfides (presumably metacinnabarite) with different amounts of Ag, Zn, Cu, Se, I, Cl, and Br. There were also Hg selenides (timannite), Ag iodides (iodargyrite) and Au^0.

Mercury and Hg-containing minerals in the ores of Siberian deposits are represented by native metals and intermetallics, arsenides and antimonides, halide compounds, sulfides, selenides, seleno- and sulfosalts, oxides, sulfates, and arsenates. The halide, oxyhalide, oxide and sulfate compounds of Hg are rare among the secondary minerals of the oxidation zones of the mercury deposits. The composition of sulfohalides is not constant and depends on the number and type of halide atoms in their crystal structure (Magarill et al., 2007; 2008). The sulfohalide varieties are closely coexistent with each other, with cinnabarite and metacinnabarite (Podgornykh and Vishnevsky, 2020).

We specified the composition of complex Hg sulfides in NOM, which contained Ag, Se, I, Cl, and Br admixtures, using triple diagrams (Hg – S+Se – Hal and Hg – Se – S systems, where Hal = the sum of I, Cl and Br) according to the data of possible Hg minerals in the oxidation zone (Fig. 2) (Magarill et al., 2007; 2008). Among the chalcohalides, there are ternary halides with the general formula $Hg_3(S,Se)_2Hal_2$ where *Hal = I, Br* and *C* that form a group of polymorphic compounds (grechishchevite, lavrentievite, arzakite, kenshuaite, and radkeite) and quaternary ones with the general formula *AgHgS(Hal)*, which also form the group of polymorphic compounds (perroudite, capgaronnite and iltisite) (mindat.org; webmineral.com; Magarill et al., 2007). Based on the Hg – S+Se – Hal and Hg – Se – S systems (Fig. 2), in the NOM samples show that the formation of Ag-Hg sulfohalides is possible

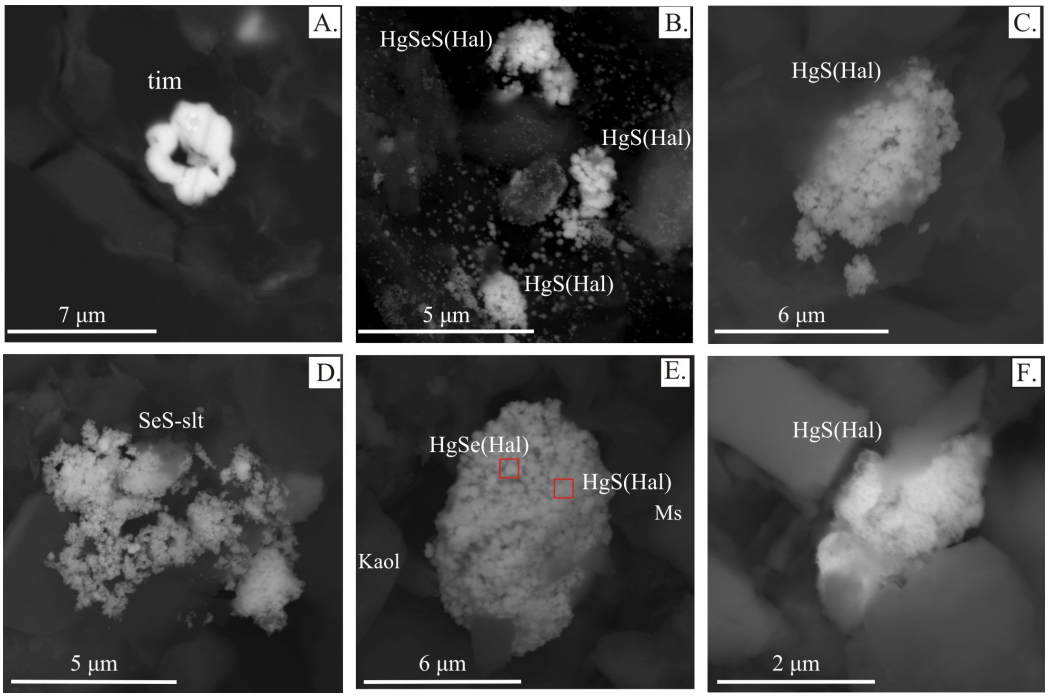

Fig.1. SEM images (BSE) of secondary Hg minerals in NOM from the dispersion halo of the Ursk tailings dump (A and B), in the snow suspended matter near AMME (C and D), in the suspended matter of temporary fluxes formed during snowmelt near the AMME mines (E), and in the suspended matter of the Yarly-Amry River sampled at a 1.4 km distance from AMME (F): A – cross section of the timmanite tube (tim); B – accumulation of globular and nodular Hg sulfide particles with Cu, Ag, I, and Cl (HgS(Hal)) in contact with Se-containing phases (HgSeS(Hal)); C – nodular aggregation of Hg sulfides containing Se, I and Cl admixtures; D – flocculated segregations of I-containing Hg seleno- and sulfosalts in muscovite; E – aggregations of Hg sulfide and selenide particles with Ni, Cu and Br admixtures; F – fine-grained aggregations of Hg sulfides with Ni, Cu and I admixtures.

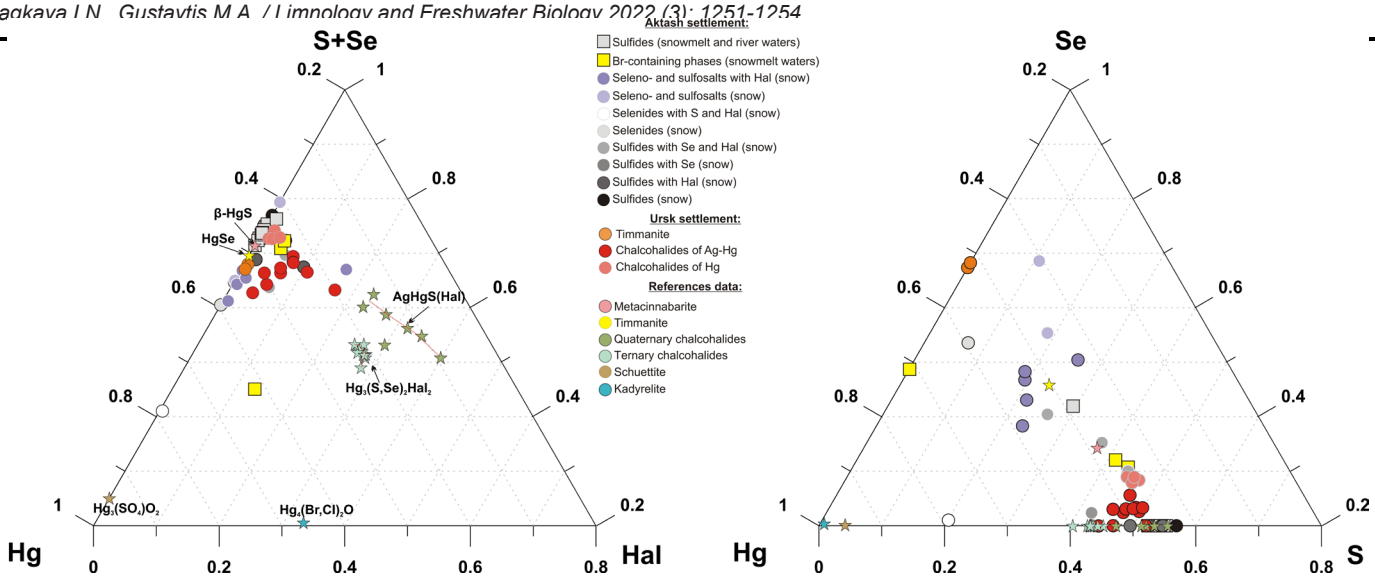

Fig.2. Triple diagram (Hg – S + Se – Hal and Hg – Se – S systems, where Hal = the sum of I, Br and Cl) of the composition of Hg minerals (atomic ratios) in the studied samples of the Salair (Ursk settlement) and Kurai (Aktash settlement) mercury zones according to reference data (stars mark the electronic mineralogical sources mindat.org and webmineral.com): Kadyrelite ($Hg_4(Br,Cl)_2O$); Schuettite ($Hg_3(SO_4)O_2$); Ternary chalcohalides with the general formula of $Hg_3(S,Se)_2Hal_2$ where Hal = I, Br and Cl; Quaternary chalcohalides with the general formula of AgHgS(Hal); Timmanite (HgSe), and Metacinnabarite (β-HgS).

and their composition are similar to perroudite ($Hg_5Ag_4S_5(I,Br)_2Cl_2$) common in oxidation zones (Hunt et al., 2016). There are also mercury phases without Ag and with a small Se content, which can be assigned to seleno- and sulfosalts (Fig. 2). However, it is rather difficult to make an accurate identification taking into account the size of the phases. Timmanite (HgSe) and metacinnabarite (β-HgS), having a miscibility gap between each other (Vasil'ev, 2011), are also identified among secondary mercury phases.

In the suspended matter of snowmelt and river waters near AMME, among secondary Hg minerals, there were Hg-containing phases (Fig. 1C-F) similar in shape and size to the minerals observed in NOM of the dispersion halo of the Novo-Ursk deposit (Fig. 1B). Comparison of the compositions of authigenic minerals in the area of the Kurai mercury zone (without Ag) with the compositions of the known phases (Fig. 2) suggests the presence of several varieties that form thin intergrowths: sulfides, selenides and compounds close to seleno- and sulfosalts in composition (ternary chalcohalides). Notably, secondary Hg minerals as considered are seasonal, i.e. appearing and disappearing periodically depending on the change in climatic and atmospheric conditions (Obolensky et al., 1995).

4. Conclusions

In summary, the presence of the Hg authigenic minerals (sulfides and selenides; ternary and quaternary chalcohalides) as complex thin intergrowths with a wide range of composition variations were found in both study objects. Among the seleno- and sulfosalts, those containing I and Cl predominate as well as Br to a lesser extent. Further research will be aimed at identifying the processes that promote the formation of these minerals and, in turn, control the Hg migration under surface conditions.

Acknowledgements

The authors are grateful to their colleagues: I.S. Kirichenko, PhD E.V. Lazareva (Geology and Mineralogy), V.I. Malov, and B.Yu. Saryg-ool.

This study was partly carried out within the framework of the IGM SB RAS State Project at the Analytical Centre for multi-elemental and isotope research of IGM SB RAS. The study of the composition of Hg phases for the substance from the dispersion halo of AMME was supported by the Russian Science Foundation (No. 18-77-10056).

Conflict of interest

The authors declare no conflict of interests.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Distribution, sources and forms of mercury occurrence in the street dust of Mezhdurechensk (Kemerovo Region)

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ABSTRACT. The aim of this study was to investigate mercury concentration and forms of its occurrence in the dust component of the atmospheric air (street dust) to assess the geo-ecological condition of the area where coal is mined, processed and transported. The mean mercury concentration of 29 street dust samples collected along a uniform network throughout the city was 36.4 ± 4.7 ng/g, with a minimum (4.6 ng/g) and a maximum (104.6 ng/g) value, respectively. This value was much lower than the mean concentration in soil samples taken previously at the same sites (58.4 ng/g) but higher than the mean concentration in snow solids (29.8 ng/g), which was likely due to precipitation that washed out mercury from the street dust and to the wind blowing.

The method of successive chemical extraction revealed a weakly bonded water-soluble form, inorganic poorly sorbed mercury compounds, an organic form of mercury, and mercury associated with minerals. The proportion of each fraction accounted for on average 10.94%, 10.32%, 44.76%, and 33.97%, respectively. Water-soluble and acid-soluble mercury forms were less common. The bulk of mercury had metal-organic and sulfide forms.

The study of mercury distribution based on particle size indicated that the mercury concentration increased as the diameter of the grains of dust material decreased. The fine fraction with a diameter of 20 to 50 μm contained the bulk of mercury, which stayed in suspension form for a long time before settling on the surface.

Keywords: mercury in depositing environments, forms of mercury occurrence, street dust, particle size distribution of street dust

1. Introduction

The city of Mezhdurechensk is part of the Kemerovo Region, the area of which allocates the Kuznetsk Coal Basin, the largest in the country and the world. Interest in the study of street dust arises from the functioning of the large Russian coal mining enterprises near this city (3 to 12 km). There are losses of the components of raw materials and their redistribution in environmental objects, which are hazardous for biological systems, including humans. Even with a possible slight decrease in coal production in Kuzbass, a rapid improvement of the ecological condition in the region should not be expected because it takes a long time and requires appropriate measures to reduce the level of compounds and substances accumulated in depositing environments. Mercury concentrations in depositing environments (soil and dust) of urban agglomerations are of special interest in the areas with technogenic pollution. Compounds of this toxic element can migrate and be found in different phase states as well as accumulate in plant and living organisms and be redistributed metamorphically and biogenically. The distribution of mercury in areas of intensive coal mining and coal processing requires an individual study. A rough estimate of mercury emission indicates that, with mean mercury concentrations in coals, at the clarke level, of 0.08 mg/kg, mercury distribution coefficient in the atmosphere of 81 % and the volume of coal burnt annually at the thermal power plant of 947041 tons of equivalent fuel (Report…, 2017), 61.4 kg of mercury enter the atmosphere. At the same time, mercury concentrations in the Kuzbass coals can reach even higher values.

This study aims to investigate the mercury concentration in the street dust from Mezhdurechensk (Southern Kuzbass) where a large number of mines and quarries in the immediate vicinity of the city form a certain level of pollution. The constant inhalation of dust-loaded air is a risk factor for public health.

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Received: June 21, 2022; ***Accepted:*** June 22, 2022;
Available online: July 31, 2022

2. Materials and methods

For a comprehensive study of the chosen area, samples (29 samples) were taken within the city limits of Mezhdurechensk according to the sampling procedure: along a uniform areal network (Scale: 1:25 000) and at sites accessible for sampling where the maximum accumulation of dust emissions transported from coal objects during drilling and blasting, as well as from thermal power facilities, towards the city is possible. In choosing the sampling sites, we tried to avoid the influence of vehicles. The samples were taken by sweeping with clean plastic brushes with hard bristles in the asphalted areas, following the methods described in (Vlasov et al., 2015; Lau and Stenstrom, 2005). A statistically significant number of samples was taken. Samples weighing at least 500 g were placed in tight plastic bags. Thereafter, the samples were dried under laboratory conditions at room temperature, sifted through sieves with a mesh size of 1 mm to separate the samples from street and domestic waste and divided into granulometric fractions by sieving using a standard set of sieves to obtain fractions of 1000-100, 100-50 and 50-20 μm according to (Ljung et al., 2008).

Additional experiments were carried out to obtain a fine fraction of 20-4.5 μm by elutriation according to the procedure presented in (Ljung et al., 2008; Kasimov et al., 2016). A sample with a fraction less than 20 μm was dispersed in distilled water, followed by filtration of the resulting solution with a fine suspension through membrane filters with a pore size of 4.5 μm to obtain a fine fraction (20-4.5 μm).

Mercury concentration in the street dust was determined by atomic adsorption on an RA 915+ mercury analyzer with a PYRO-915+ attachment (PNDF 14.1:2:4.243-07, 2007). This technique is based on the reduction of bound mercury in the sample by pyrolysis, followed by the air transfer of the formed atomic mercury from the atomizer to the analytical cuvette. A standard soil sample (SDPS-3) with a mercury concentration of 290 ± 58 ng /g was used as a standard.

The sample aliquots that were preliminarily crushed and dried at room temperature were (45.0-60.0) ± 0.1 mg. The limits of relative measurement error ranged from 20 to 28% depending on the mercury mass fraction in the samples with a confidence level of 0.95 and three parallel measurements.

To determine the forms of mercury occurrence in the soil, the method of sequential or autonomous soil extractions was used (Bloom et al., 2003). The most mobile (water-soluble) forms were extracted with double distilled water; ion exchange forms associated with clay minerals, oxides and hydroxides of Al, Fe and Mn, as well as acid-soluble forms (with different migration ability), were extracted with a mixture of 0.1 acetic and 0.01 M hydrochloric acids. The solubility in 0.1 M NaOH solution characterised the amount of mercury associated with organic matter. Strongly bound forms were extracted with concentrated 12M nitric acid. Each extraction included intensive stirring for 10-12 hours and centrifugal sedimentation of the insoluble part, followed by decantation.

3. Results and discussion

The mean mercury concentration in street dust of urban area was 36.4 ± 4.7 ng/g, 26.3 ± 5.3 ng/g in the Western district and 41.8 ± 6.3 in the Eastern district. Intervals of minimum and maximum values for the entire city and the Eastern district were 4.6 to 104.2 ng/g and 7.7 to 4.7 ng/g for the Western district (Table 1). The next summer, with fewer number of samples along the sparse network, the mean value of mercury was 26 ± 5 ng/g; the minimum value – 6 ng/g, and the maximum value – 70 ng/g. We obtained significant positive correlations between mercury concentrations at different time intervals (correlation coefficient was 0.92). With the unchanged volumes of coal mining and processing, provided that climatic conditions have not changed in one year, this is a good evidence of the possibility and reliability of using street dust as an indicator of environmental quality in the summer. Maximum mercury concentrations in coal dust are formed under the influence of coal mining objects that are moved towards the city during drilling and blasting.

Table 1. Hg concentration and concentration coefficient (CC) in street dust of Mezhdurechensk

Indicators	City	Eastern district	Western district	Clarke, ng/g (Kasimov and Vlasov, 2015)
Number of samples	29	19	10	
C Hg, ng/g	36.4 ± 4.7	41.8 ± 6.3	26.3 ± 5.3	
C min, ng/g	4.6 ± 4.7	4.6 ± 6.3	7.7 ± 5.3	
C max, ng/g	104.2 ± 4.7	104.2 ± 6.3	64.7 ± 5.3	
$CC_{(Yaroshevskiy)}$	3.64	4.18	2.63	10
$CC_{(Vinogradov)}$	0.43	0.50	0.32	83
$CC_{(Beus)}$	1.10	1.26	0.79	33
$CC_{(Grigoriev)}$	0.56	0.64	0.40	65
CC_{MPC}	Do not exceed maximum permissible concentration			2100

Note: C Hg is the mean Hg concentration in dust; C min is the minimum Hg concentration in dust; C max is the maximum Hg concentration; CC (Yaroshevskiy, etc.) is the concentration coefficient relative to clarke according to Yaroshevskiy A.A., clarke according to Vinogradov A.P., clarke according to Beus A.A., and clarke according to Grigoriev A.P.

Table 2 compares mercury concentrations in street dust, soil and snow solids. The mean mercury concentration in street dust was slightly lower than in soil samples that had previously been taken at the same sites (58.4 ng/g) but higher than that in snow solids (29.8 ng/g). This was likely due to the atmospheric precipitation that washed out mercury from the street dust and to the wind blowing.

We determined the following ratio of mercury occurrence forms: mobile (water-soluble) was 10.94% (9.8% to 28.6% mercury), ion exchange form associated with clay minerals, oxides and hydroxides of Al, Fe and Mn – 10.32% (8.8% to 26.0% mercury) and mercury associated with organic matter – 44.76% of its total concentration, with a minimum value of 34.6% and a maximum value of 62.5%. The proportion of strongly bound mercury that was soluble only in concentrated nitric acid and is likely of 'coal' origin was 33.97%, with a minimum value of 13.3% and a maximum value of 70.13%. A wide range of values indicates the uneven nature of the mercury distribution in the samples depending on their sampling site and total concentration. The greater the bulk mercury concentration in the sample, the greater the contribution of the water-soluble form.

The study of the mercury distribution based on the particle size of street dust revealed that the mercury concentration increased as the diameter of the grains of dust material decreased. The fine fraction contained the bulk of mercury.

4. Conclusions

The obtained data, as well as data on the composition of dust and aerosol fallouts in the area of Mezhdurechensk and adjacent areas in the winter, indicated that they differed in much higher (two- or threefold) mercury concentrations than those in the background area. At the same time, the proportion of coal particles accounted for 20% to over 80% of the volume of solid fallouts. With a mean mercury concentration in Kuzbass coal of 0.08 mg/kg, the contribution of coal dust to the total amount of mercury in dust and aerosol can range from 45% to 90%. In fact, coals in the south of the Kuznetsk Coal Basin are much richer in mercury than the average estimates for Kuzbass, and their real proportion in the balance of the element in the soil may exceed 90%. For example, according to (Arbuzov et al., 2015; Osipova et al., 2019), coals of the Mezhdurechensky coal mine contain 0.75 mg/kg of mercury. Similar values were also obtained for other coal mining enterprises in the south of Kuzbass. Therefore, coal dust, along with coal combustion products, determines mercury accumulation levels in street dust and adjacent areas. The study of the mercury distribution based on particle size of street dust revealed that the mercury concentration increased as the diameter of the grains of dust material decreased. The fine fraction with a diameter of 20 to 50 μm contained the bulk of mercury. Fine dust formation is especially hazardous because it remains in suspension form of for a long time before settling on the surface, and mercury is concentrated in this dust. Particle-size analysis combined with the method of selective chemical extraction indicated the presence of mercury with different degrees of bonding and, hence, different migration abilities, which allowed us to more objectively assess the risk of pollution and identify sources of mercury emissions.

Acknowledgements

This study was supported by RFBR and carried out within the framework of the project No 20-05-00675 A.

Conflict of interest

The authors declare no conflict of interests.

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Table 2. Comparison of Hg concentrations (ng/g) in street dust, soil and snow solids

	Soil			Street dust			Snow		
	City	Eastern district	Western district	City	Eastern district	Western district	City	Eastern district	Western district
C Hg, ng/g	58.4	63.9	55.5	36.4	41.8	26.3	29.8	30.8	27.8
C max, ng/g	173.6	173.6	116.9	104.2	104.2	64.7	49.0	49.0	35.0
C min, ng/g	10.2	11.8	10.2	4.6	4.6	7.7	15.0	15.0	20.0

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Geochronology of mercury distribution in the bottom sediments of Inkerman Bay (Sevastopol Bay)

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ABSTRACT. Geochronological reconstruction revealed the mercury pollution in the water area of Inkerman Bay between 2002 to 2021. Mercury concentrations in the profile of bottom sediments in this water area ranged from 99.0 to 264.1 μg·kg^{-1}. The studies indicated that the largest mercury influx occurred in 2016 and 2017. The sorption saturation limit of the water area was not exceeded and amounted to 9.6% relative to the maximum value. The mercury deposition flux into the bottom sediments, which was calculated based on the geochronology of mercury distribution, was 0.6 kg·year^{-1}.

Keywords: mercury, bottom sediments, Inkerman Bay, Sevastopol Bay, Black Sea

1. Introduction

Inkerman Bay was artificially created in 1955 to 1961 and is currently the apex of Sevastopol Bay at the confluence of the Chyornaya River (Boltachyov et al., 2010). Inkerman Bay was formed as an estuary with special hydrodynamic conditions and an ecotone. As the sea current removes the silt brought by the river, the bottom sediments in this water area mainly consist of soft ooze (Kostova and Ivanov, 2009). Various hydrodynamic, physicochemical and biological phenomena occur at the river-sea hydrological barrier: slowdown of the flow of river waters, their dilution and saturation with sea salts, sedimentation of large fractions of suspended matter, coagulation of fine clay particles, physicochemical interaction of substances, which is not reduced to simple dilution (flocculation of organic matter and metals, sorption-desorption), and rapid development of production processes (Lisitsyn et al., 1983). The water of the Chyornaya River that inflows to the apex of the Sevastopol Bay near Inkerman carries an additional amount of nutrients and pollutants. The river-sea boundary plays the role of an important geochemical barrier, at which the bulk of suspended matter and diluted material is deposited, and chemical elements transform (Gordeev, 1983). In particular, most of the produced monomethylmercury is ultimately removed by deposition (Mason, 1993).

Inkerman Bay is well protected from the waves of the Black Sea, due to which it serves as a depot for various pollutants. Biogeochemical activity of the river-sea barrier zone is largely associated with the accumulation of living and non-living organic matter, mineral components and related trace elements there. At the same time, natural and anthropogenic metals can serve as specific indicators of anthropogenic pollution as well as convenient markers of natural biogeochemical processes. The layer-by-layer study of the core of bottom sediments can provide the chronology of the mercury influx as well as an assessment of the ability of the waters to self-clean.

The study of the mercury distribution in water is due to the high spatiotemporal variability of mercury concentration, depending on the seasonal changes in the river runoff and the development of phytoplankton communities. Therefore, to study the long-term dynamics of mercury accumulation processes in bottom sediments, geochronological methods are the most convenient to use.

The aim of this study was to geochronologically reconstruct mercury deposition in the bottom sediments of Inkerman Bay as well as to calculate mercury fluxes into the bottom sediments. In this regard, the following tasks were solved: determining the vertical distribution of mercury concentrations in the bottom sediments and calculating the fluxes of mercury deposition into the bottom sediments as criteria for estimating water quality in relation to mercury in Sevastopol Bay.

2. Materials and methods

Bottom sediments were sampled in May 2021 from Inkerman Bay. The cores of the bottom sediments were dissected into horizontal 1 cm thick layers under laboratory conditions using a piston extruder. The

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Received: June 17, 2022; ***Accepted:*** June 21, 2022;
Available online: July 31, 2022

preparation of the bottom sediment samples for the Hg determination was carried out according to GOST 26927-86. Hg concentration was determined by cold vapor atomic absorption spectroscopy on a Hiranuma-1 analyzer. The accuracy of the analysis results was controlled using state standard reference samples of the composition of the sod-podzolic sandy loam soil (SDPS-1). To determine the age of the layers of the bottom sediments, the average sedimentation rate of 7094 $g \cdot m^{-2} \cdot year^{-1}$ was used, which was calculated by S.B. Gulin with ^{137}Cs based on gamma ray spectrometry analysis. The average sedimentation rate was 9.3 $mm \cdot year^{-1}$ (Egorov et al., 2018).

3. Results and discussion

The distribution of mercury concentrations in the column of the bottom sediments was heterogeneous. The highest concentration was detected in the 4-5 cm layer and amounted to 264.1 $\mu g \cdot kg^{-1}$ (hereinafter on a dry basis). According to the geochronology, the layer corresponded to 2016 and 2017 (Fig. 1).

Subsequently, the mercury concentration, in general, decreased monotonously from 199.3 $\mu g \cdot kg^{-1}$ in the 5-6 cm layer (2015-2016) to 164.0 $\mu g \cdot kg^{-1}$ in the 13-14 cm layer (2007-2008) and down to the minimum value of 99.0 $\mu g \cdot kg^{-1}$ at a depth of 17-18 cm (2002-2003) (Fig. 1).

According to the literature, the natural concentration of total mercury in marine shelf bottom sediments is 100 $\mu g \cdot kg^{-1}$ (Prokofiev and Stepanchenko, 1981). The NeueNiederlandischeListe standard is 300 $\mu g \cdot kg^{-1}$, which was not exceeded in this study (Neue Niederlandische Liste, 3/95). Also, mercury concentration can be estimated from the sorption saturation limit calculated for Sevastopol Bay and accounting for 2740 $\mu g \cdot kg^{-1}$ (Kostova et al., 2001), which is a more adequate estimate for high mercury concentrations. With the maximum mercury concentration of 264.1 $\mu g \cdot kg^{-1}$ the sorption saturation limit was 9.6%. Compared to other water areas of Sevastopol Bay, this value was not critical as well as in the bottom sediments from the Gollandiya, Ravelin and Inkerman stations where, with the maximum mercury concentrations in the profile of the bottom sediments, the sorption saturation limits were 48.0, 34.6 and 8.9%, respectively. At the same time, in the water area of Pavlovsky Cape, the sorption saturation value, with the mercury concentration of 3179.1 $ng \cdot g^{-1}$ in 2002, exceeded the previously detected limit (Stetsiuk, 2021). Therefore, the degree of reaching sorption saturation limit can serve as an indicator of water pollution, as confirmed by the previous research conducted near Pavlovsky Cape that was designated as a critical zone (Kostova and Ivanov, 2009). Lower mercury concentrations in the bottom sediments of Inkerman Bay can be associated with a faster period of horizontal water exchange than in the central part of Sevastopol Bay (Egorov et al., 2018), leading to more significant effect of hydrological factor on self-cleaning of water in Inkerman Bay from mercury.

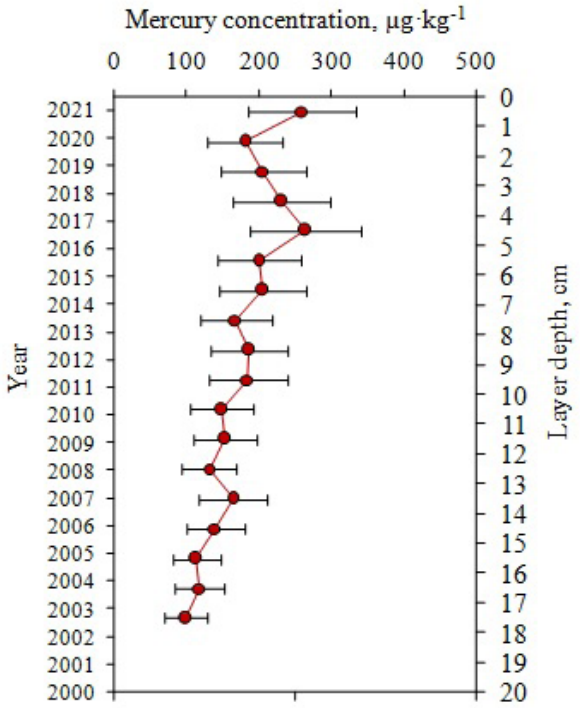

Fig.1. Profile of the mercury distribution in the bottom sediments of Inkerman Bay.

Water quality estimation in the water area can be based on mercury deposition fluxes into the bottom sediments (Egorov et al., 2018). Specific flux of pollutant deposition can be calculated by the following formula:

$$F_s = MAR \cdot C_{bs}, \quad (1)$$

where MAR (Mass Accumulation Rate) is the absolute mass of bottom sediments ($kg \cdot m^{-2} year^{-1}$), and C_{bs} is the pollutant concentration in the upper layer of the bottom sediments ($\mu g \cdot kg^{-1}$).

Hence, $F_{sHg} = 1836.6$ ($\mu g \cdot m^{-2} year^{-1}$).

Thereafter, the mercury flux in the entire Inkerman Bay was calculated by the following formula:

$$F_{Hg} = F_{sHg} \cdot S, \quad (2)$$

where S (m^2) is the water area = 322130 m^2 (Egorov et al., 2018).

Thus, the mercury deposition flux into the bottom sediments of Inkerman Bay was 0.6 $kg \cdot year^{-1}$, which was calculated for the upper layer corresponding to 2021. Variation of fluxes in 2002 to 2021 was 0.2 to 0.6 $kg \cdot year^{-1}$ (Fig. 2). This may indicate that during this period the water area of Inkerman Bay was self-cleaning from mercury with different intensities. The total mercury flux between 2002 and 2021 was 7.2 $kg \cdot year^{-1}$.

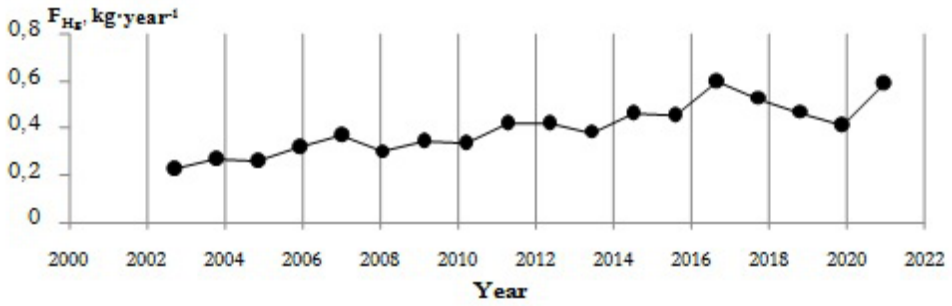

Fig.2. Mercury deposition fluxes (F_{Hg}) in the water area of Inkerman Bay

5. Conclusions

In summary, radiometric dating methods for the bottom sediments of Inkerman Bay allowed us to reconstruct in stages the chronology of mercury influx between 2002 and 2021. At the maximum mercury concentration of 264.1 μg·kg^{-1}, the sorption saturation limit in the studied water area was not reached, amounting to 9.6% with the deposition flux = 0.6 kg·year^{-1}.

Acknowledgements

The author thanks I.N. Moseichenko, lead engineer of the Department of Radiation and Chemical Biology at Institute of Biology of the Southern Seas of RAS, for sampling the cores of the bottom sediments.

This study was carried out within the framework of the State Project “Molismological and biogeochemical foundations of the homeostasis of marine ecosystems” (No. 121031500515-8).

Conflict of interest

The authors declare no conflict of interests.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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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 and geochemical properties (toxicity, mobility, bioaccumulation in aquatic and continental 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~Ca). The analysis 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. (south-eastern 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/dm^3), pH (from 6.3 to 9.9), the content of oxygen dissolved in water (3 – 13 mg / dm^3), the concentration of organic substances (0.28 – 8.32 mg/dm^3), bicarbonates, calcium and sodium. Earlier, the authors found that the composition of

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Received: June 3, 2022; ***Accepted:*** June 22, 2022;
Available online: July 31, 2022

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 (zoo- and 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 ^{137}Cs and ^{210}Pb. The analysis for ^{210}Pb was made by gamma-spectrometry on a planar semiconductor detector with "ultrapure-Pb,W" 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 ^{137}Cs and ^{210}Pb 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 ^{210}Pb constant flow (CF) model, approximately correspond to the dates obtained by simple extrapolation from ^{137}Cs. 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.

	Number samples	Average val. ± 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±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±0,006	0,012-0,45
southern taiga West. Siberia (Si bottom sediment)	640	0,092±0,019	0,007-0,172
southern taiga West. Siberia (Ca bottom sediment)	198	0,013±0,008	0,001-0,058
northern taiga East. Siberia (Sakha Republic)	354	0,035±0,019	0,001-0,065
middle taiga East. Siberia (Republic Buryatia)	57	0,043±0,015	0,011-0,205
southern taiga East. Siberia (Republic Buryatia and Transbaikalia)	75	0,046±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°-37° 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.

The study has been supported by RFBR) grant №19-05-50014 (geochemistry and mineralogical composition of bottom sediments of the Baltic Shield) and on state assignment of IGM SB RAS by the Ministry of Science and Higher Education of the Russian Federation (geochemistry and mineralogical composition of bottom sediments of the Siberia).

Conflict of interest

The authors declare no conflict of interests.

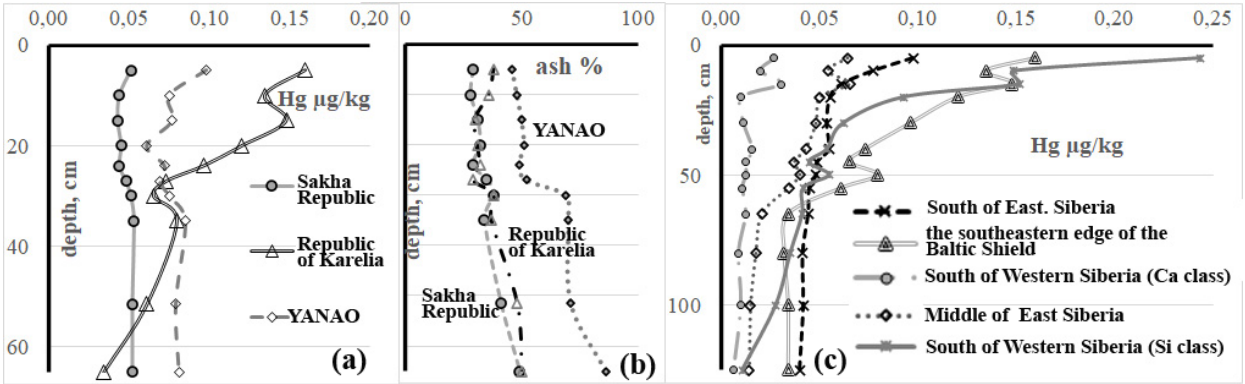

Fig.1. Vertical distribution of the contents of Hg (µg/kg) and ash (%) in bottom sediment cores from taiga lakes of various research areas: (a) the contents of Hg (µg/kg), (b) ash (%) for lakes located along 63° n. latitude; (c) the contents of Hg (µg/kg) for taiga lakes of various research areas

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Short communication

ISSN 2658-3518
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Hg in waste from mining and processing enterprises in the Republic of Khakassia

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ABSTRACT. The article presents the original data on the total Hg concentration in the waste of enterprises for the extraction of iron ore, coal and marble located in the Republic of Khakassia. Hg concentrations in the rocks of the dumps and the material of the tailings depend on the electrical conductivity and magnetic susceptibility. The concentration of this element increases in more acidic environmental conditions, and its higher concentrations are associated with particles having a size of 0.04 mm. Geoecological indicators demonstrate the enrichment of Hg waste from all enterprises studied, as confirmed by the calculation data of the enrichment factor.

Keywords: Hg, mining waste, Khakassia, soils, geoecology, iron ore, coal, marble

1. Introduction

The main cause of the negative impact of mining waste on the environment is associated with the migration of chemical elements formed through the placement and long-term storage of material during mining (overburden and enclosing rock dumps) and processing (tailing dumps and sludge ponds) of ores. The danger of waste can be exacerbated by the fact that they contain a large amount of toxic elements, including mercury (Hg). It is one of the priorities for the study of toxic elements (Alekseenko, 2000). Hg concentration exceeding the established standards is most often associated with tailings. The maximum Hg concentration is observed in the halo of the emission source, and the distribution is associated with the landscape and climatic conditions as well as the direction of the prevailing wind. A significant amount of Hg can enter the atmosphere, surface and groundwater from quarry dumps during blasting as well as during dusting and transportation of ores (Belan, 2005; Krupskaya et al., 2009; Zhuravleva, 2016; Gustaitis et al., 2016; Azarova et al., 2018).

2. Materials and methods

The object of the study were samples of dumps, tailings, sludge pits, ash and slag wastes, as well as soils located near dumps taken in the Teisky iron ore deposit, the Kibik-Kordon marble deposit and the Vostochno-Beisky coal mine. Waste and soil were sampled out using the envelope method (51 points) according to (GOST, 1984).

Hg concentration in the samples was determined on a RA-915 + Hg analyzer using the atomic absorption method with the PYRO-915 attachment (pyrolysis method; Hg detection limit 5 ng/g; determination accuracy 5 ng/g; element concentrations were calculated per 1 g of dry substances) in the educational and scientific laboratory on the basis of the School of Natural Resources Engineering at National Research Tomsk Polytechnic University (Shuvaeva et al., 2008). The granulometric analysis of the soils was carried out using laboratory sieves with diameters of 1. 0.5, 0.25, 0.125, 0.1, and 0.04 mm.

The method of the results processing included the calculation of ecological and geochemical indicators: the concentration coefficient relative to the average for the sample (K_M), maximum allowable concentration (MAC – 2100 ng/g) (Yanin, 1992), soils of the Earth (K_{SE}) (10 ng/g) (Alekseenko, 2000), clarke concentration (K_K) (Yanin, 1992) and enrichment factor (normalization by Sc, own data) (K_E).

3. Results and discussion

The mean Hg concentrations in the wastes of mining and processing enterprises of the Republic of Khakassia ranged from 69 to 126 ng/g (Table), with a range of absolute values of 10 to 1044 ng/g. The

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Received: June 20, 2022; ***Accepted:*** July 12, 2022;
Available online: July 31, 2022

Table. Geoecological indicators of Hg pressure near the tailings of mining and processing enterprises in the Republic of Khakassia

Sampling site	C_{Hg}, ng/g	K_M^*	MAC	K_E	K_K	K_{SE}
Tey	51-89	1	0.03	2.4	1.5	6.9
East Beyskoye	35-350	1	0.04	1.9	2	9.1
Kibik-Kordonskoye	10-1044	1.4	0.1	13.7	3.9	17.7

Note: * - see Materials and methods

distribution of Hg in tailings was uneven, as confirmed by the calculation of the variation coefficient (79-489%). The maximum mean concentrations were detected in the waste from the Kibik-Kordon marble deposit (171 ng/g), and the minimum - from the Tei iron ore deposit (69 ng/g). In the waste from the Vostochno-Beisky coal mine, the mean concentration was 91 ng/g.

The study of the dependence of element concentrations on the size of soil particles revealed that, in most cases, particles $^{>}0.04$ and <0.004 showed the maximum Hg concentration, i.e. the smallest particles (medium dust, according to (Kachinsky, 1958)). Their proportion was minimum in the soils of all studied tailings. The results obtained were consistent with the statement that the particles with the smallest size had the maximum Hg concentration.

In addition to the Hg concentration in waste samples, we determined such soil characteristics as electrical conductivity, magnetic susceptibility and pH (Fig. 1).

Taking into account the relationship of Hg with these characteristics, it is worth noting a rather high correlation between all factors for waste from the Vostochno-Beysky coal mine (Fig. 2). Therefore, to identify the strongest bonds, the critical value r = 0.8 (at P 0.05) was used, which revealed the strongest bond between the metal and the magnetic susceptibility. In the studied tailings, the connecting center for all indicators was precisely the magnetic susceptibility, through which Hg and other indicators were connected with each other. The magnetic susceptibility value indirectly indicated the presence of other metals in the samples. Thus, we assume that Hg is related to other metals, which requires additional studies. Hg concentration depends on the electric conductivity (both positively and negatively) and increases with the shift in the soil reaction towards oxidation (which is rather natural). The relationships obtained indirectly indicated the connection between Hg with other metals.

Calculations of environmental and geochemical indicators of Hg accumulation by waste from mining and processing enterprises of the Republic of Khakassia by different types of soils revealed an excess relative to the mean value for the sample (Table), the concentrations below MPC (2100 ng/g) and enrichment relative to the Clark of the Earth's crust (45 ng/g) and soils of the Earth (10 ng/g). The enrichment factor also indicates the enrichment of tailings materials and dump rocks in an element.

4. Conclusions

The studies of the concentration and geoecological features of the Hg distribution in the waste of mining and processing enterprises of the Republic of Khakassia revealed that the highest concentrations of this element were observed in the tailings of a marble mining enterprise. In the waste of all enterprises studied, Hg was had the maximum concentrations in the finest fraction, which is consistent with the literature data.

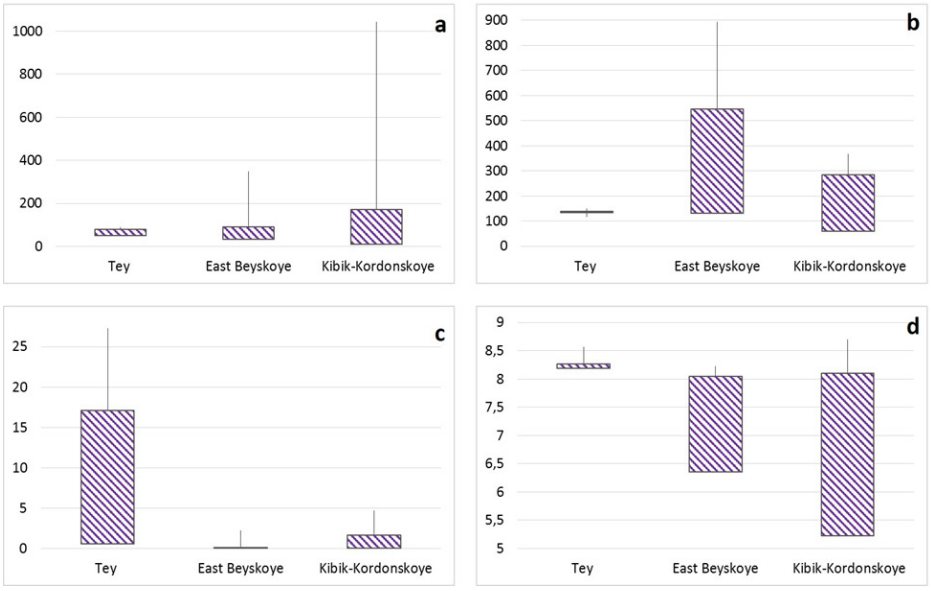

Fig.1. Hg concentrations and physical and technical characteristics of the material from tailings of mining and processing enterprises of the Republic of Khakassia: a - Hg concentration, ng/g; b - electrical conductivity, μS/cm; c - magnetic susceptibility 10-3 units, and d - the pH value of soil extract, pH units.

Furthermore, in the soils of tailings, Hg depended on the value of electric conductivity, magnetic susceptibility and increased with a change in the reaction of the environment towards acidification. The data from geoecological calculations testified to the Hg enrichment of the waste of enterprises extracting marble, iron and coal, as confirmed by the calculation of some indicators, including the enrichment factor relative to Sc.

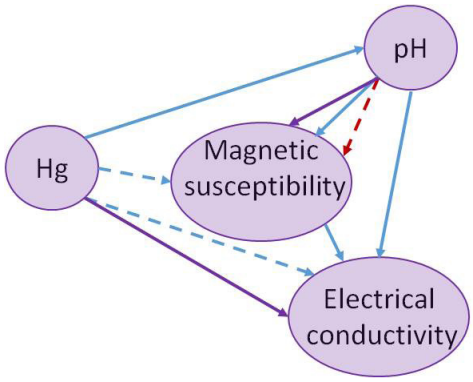

Fig.2. Graphs of the relationship of Hg with material properties of tailings of mining and processing enterprises of the Republic of Khakassia: solid line - positive relationship; dashed line - negative; red – Tey; blue - East Beyskoye and lilac - Kibik-Kordonskoye

Acknowledgments

This study was carried out within the framework of the state budget topic RK 121031300154-1 IK IMKES SB RAS. Research efforts were included in the development program of Tomsk Polytechnic University to make it more competitive among the world's leading research centers.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Mercury and hazard to health of the population of the Yamalo-Nenets Autonomous Okrug

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ABSTRACT. The aim of this study was to assess the mercury hazard to the health of the population in the Arctic zone on the example of the Yamalo-Nenets Autonomous Okrug (YaNAO). The study included two stages. At the first stage, we assessed the potential risk associated with the mercury intake in the body with local food products and water based on the hazard quotient (HQ). At the second stage, we examined the selected groups of the adult population living over 20 years in the Arctic and analysed the mercury concentrations in biological substrates to identify the dependence of the somatic and neuropsychic disorders on the mercury concentrations. The mean values of mercury intake in the body with food products were 0.001 mg/kg for adults per week, and 0.0015 mg/kg – for children. HQ was acceptable and correlated with the mercury concentrations in biological substrates. We identified the risk of low stress resistance (OR = 2.4 [1.3-6.2]) in people who had elevated mercury concentrations in their hair. In the risk group, the proportion of the examined people with elevated mercury concentrations in their hair was 46.0%, while in the comparison group it was 38.8%, and the mean concentrations of this toxicant were also higher, 2.51 μg/g and 1.69 μg/g, respectively. The risks of low self-assessment of health (OR = 5.7 [2.1-15.2]) and low stress resistance (OR = 3.3 [1.3-8.3]) were typical of people with low neuropsychic adaptation. Therefore, despite the absence of somatic health hazard for the newly arrived population of YaNAO, the people with elevated mercury accumulation showed a decrease in the neuropsychic adaptation, which determines the need to introduce biomonitoring in the medical examination system for the population of the Arctic.

Keywords: mercury, the Arctic, biological matrices, health hazard

1.Introduction

The global Convention on Mercury indicates that ecosystems and indigenous communities in the Arctic are especially vulnerable to toxicants, including through biomagnification and mercury pollution of traditional foods. It was shown that in the Arctic zone, between the polar sunrise and the end of snowmelt, the influx of Hg from the atmosphere to the terrestrial and aquatic ecosystems increases dramatically, leading to its accumulation in the food chains (Lindberg et al., 2002; Dudarev and Odland, 2017). This can explain the elevated concentrations of Hg in the tissues of Arctic fish and animals (Córdoba-Tovar et al., 2022). Selenium, zinc and other elements are mercury antagonists (Rahman et al., 2018; Castriotta al., 2020). In this regard, of special importance is the expansion of knowledge about the Hg accumulation in the bodies of the Arctic residents with a deficiency of essential elements and an excess of toxic ones. To prevent chronic non-communicable diseases and maintain health, it is necessary to preserve the specifics of the Arctic diet that should contain such products as fish and reindeer meet. The results of biological monitoring conducted previously by researchers from Arctic Research Center revealed that the Hg concentrations in biological matrices of the population of the Yamalo-Nenets Autonomous Okrug (YaNAO) varied greatly depending on gender, age and ethnicity (Agbalyan and Shinkaruk, 2018; Agbalyan et al., 2018).

The aim of the study was to assess the mercury hazard to the health of the Arctic population on the example of YaNAO.

2. Materials and methods

Hg quantification was carried out by inductively coupled plasma mass spectrometry (ICP-MS) and a sample preparation system based on microwave-assisted decomposition. A value of < 0.01 μg/mL was the upper

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Received: June 28, 2022; ***Accepted:*** July 13, 2022;
Available online: July 31, 2022

limit of the permissible Hg concentration in the blood (Skalny et al., 2004). The value of 0.01 μg/mL was the maximum safe mercury level for an adult. In addition to Hg, nutrients (Zn and Se) were determined in hair and blood. A risk for humans was assessed based on the maximum and mean exposition, taking into account an oral route as the most likely.

Clinical and psychological examinations, as well as a sociological survey, included 120 permanent representatives of the newly arrived population living over 20 years in the Arctic (in the cities of Labytnangi and Salekhard, and the Kharp settlement), among which 30% were men. Studies at the individual level included such blocks as general characteristics, chronic morbidity, psycho-emotional state, and concentrations of trace elements in the body. For statistical processing, methods of parametric and nonparametric analyses were used based on the approaches recommended for biomedical research (Medik and Tokmachev, 2007; Grzhibovsky, 2008). In comparing the frequency indicators in the cities studied, the significance criterion was adopted, taking into account the Bonferroni correction ($p < 0.017$). The closeness of the relationship was assessed by the Pearson and Spearman correlation coefficients. To identify factors that characterised the relationship between groups of parameters, factor analysis with varimax rotation was used. To determine the dependence of health disorders on the effect of some factors, the odds ratio was calculated with a 95 percent confidence interval (OR (CI)).

3. Results and discussion

Table 1 shows the distribution of the respondents by the frequency of consumption of certain food types in the Labytnangi and Salekhard cities as well as in the Kharp settlement. We found that only 7.5% of respondents from the Kharp settlement daily consumed fish from local water bodies. 73.33% respondents from Salekhard and 52.2% respondents from the Kharp settlement indicated that they consumed the local fish "several times a month".

Among the respondents, 8.57% of Labytnangi residents and 4.44% of Salekhard residents daily consumed venison, and 8.57 and 13.33%, respectively, consumed it several times a week. The proportion of respondents consuming venison several times a month was close in Salekhard and Kharp (37.78 and 30.3%). Concerning the consumption of offal (primarily liver), the differences were revealed in comparing the Labytnangi and Kharp groups ($p = 0.023$). The average daily consumption of offal was 0.005 kg/day.

Taking into account the intake of Hg from foods and drinking water, we determined that the mean weekly Hg dose for the population based on its maximum concentration in food was 0.003 mg/kg in adults. Calculating the average values indicated that the weekly Hg intake was 0.001 mg/kg, which reflects an acceptable risk and corresponds to the Hg concentrations in biological substrates. The hazard quotients for the consumption of food products (offal) of the local supply ranged from 0.19 to 0.9.

The Hg concentration in the blood of men varied greatly (Table 2). The mean concentration for the group was 0.0024 ± 0.0009 μg/mL. In groups of women, there were no differences in the concentrations, and the mean value was slightly lower than in men (0.0019 ± 0.0004 μg/mL). These values testified to a low health hazard to the population, which was caused by the presence of Hg in the blood. Previous studies indicated that the mercury concentration in the blood of indigenous residents of YaNAO was much higher. For example, it was 0.0131 ± 0.0096 μg/mL in residents of the Kharsaim settlement and 0.0142 ± 0.0085 μg/mL in residents of the Kutopiyugan settlement (Agbalyan et al., 2018).

The concentration of toxicants in hair better reflected long-term intake of toxicants (Tatsiy, 2013; Human biomonitoring..., 2015). In Salekhard, the mean group concentration of Hg in hair was two times higher than in Labytnangi and Kharp, and among women – 3.4 and 1.3 times, respectively. The mean value of Hg concentration in hair was 1.38 ± 0.47 μg/g among men, and 1.17 ± 0.30 μg/g among women (no significant differences were detected). The mercury concentration above 1 μg/g was identified in 20.0% of the examined Labytnangi residents, 60.0% of the Salekhard residents and 47.5% of the Kharp residents ($r^2 = 13.0$; $p = 0.002$). There were no cases of concentrations at the level of clinically significant values.

We determined that health had moderate feedback with the level of neuropsychic adaptation ($r = -0.35$; $r = -0.33$) and place of residence ($r = -0.32$; $r = -0.48$). Furthermore, the Labytnangi residents rated their health as good more often than the Kharp residents, which generally coincided with the health

Table 1. Distribution of the examined people by the consumption frequency of the main types of food in the studied groups (% of respondents).

Food type	Consumption frequency	1-Labytnangi (n = 35)	2-Salekhard (n = 45)	3-Kharp (n = 40)	Significance of differences
Fish from local water bodies	daily	0.00 (0)	0.00 (0)	7.50 (3)	p1/2 = 0.000 p2/3 = 0.077 p1/3 = 0.0002
	several times a week	28.57 (10)	8.89 (4)	2.50 (1)	
	several times a month	0,00 (0)	73.33 (33)	52.50 (21)	
	rarely/ never	71.43 (25)	17.78 (8)	37.50 (15)	

Table 2 . Mercury concentrations in biological matrices of the adult newly arrived population of YaNAO

Indicators	YaNAO settlements					
	Labytnangi		Salekhard		Kharp	
	women	men	women	men	women	men
n	24	11	30	15	30	10
blood, μg/mL						
*Geometric mean	0.0001	0	0.0001	0	0.0002	0.0001
Standard error	0.0002	0.0004	0.0002	0.0001	0.0005	0.0003
hair, μg/g						
*Geometric mean	0.4351	0.661	1.1476	1.1445	1.2022	0.5112
Standard error	0.0704	0.1601	0.2409	0.2994	0.1881	0.6138

Note: * the concentrations are presented as Log because the distribution is log-normal.

assessments of the respondents, which were carried out by specialists. There was a direct dependence of the stress level in men on the zinc to mercury ratio ($r = 0.47$) as well as an indirect dependence in terms of Se/As ($r = -0.37$). The correlation of the Se/Hg ratio in hair and stress assessment had the same direction both in men, $r = 0.38$ ($p < 0.017$), and in women, $r = 0.13$ ($p > 0.017$). Moreover, men showed a statistically significant dependence of neuropsychic adaptation on the balance of Zn/Hg ($r = 0.46$) and Zn/Pb ($r = 0.35$). All the variety of factors obtained during factor analysis revealed that the component-1 that determined 12% of the total dispersion was based on the circulation of toxic and assumed toxic elements in blood and hair. The concentrations of toxicants in hair had the greatest factor loading that was 0.97 for lead, 0.96 for mercury and 0.92 for manganese. The indicated elements had a negative effect on the nervous system, which led to certain limitations in our results and determined the future direction of research.

The calculation of the odds ratio for priority factors revealed the risk of low stress resistance (OR = 2.4 [1.3-6.2]) and a trend in the proportion of people under regular medical check-up (OR = 1.2 [0,4-3.5]) and having chronical diseases (OR = 1.1 [0.5-2.3]).

4. Conclusions

Therefore, the Hg concentrations in the hair and blood of the adult population living over 20 years in YaNAO confirm the long-term intake of this toxicant in the bodies of 20 to 60% of the examined people in an amount below a clinically significant level. There were no relationships between disorders of somatic health and circulation of Hg in the body (in existing concentrations), but there was a risk of a decrease in stress resistance and neuropsychic adaptation. Study of dependency of health characteristics and balances of nutrients and mercury in blood and hair revealed that the higher the selenium to zinc ratio in the blood, the lower the stress level and the higher the neuropsychic adaptation in men.

Acknowledgements

The authors are grateful to the colleagues from Arctic Research Center who took part in expeditionary research.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Vector field techniques for the detection of neuronal dynamics in the presence of mercury

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ABSTRACT. The role of mercury in the development of various neuropathologies is well known. The biogeochemical cycles of mercury indicate the possibility of its introduction into various organisms (including humans) through the corresponding trophic chains. However, as it turns out from the literature analysis, until recent years, there have been almost no works on the dynamic microscopic study (either *in situ* or *in vivo*) of the processes of connectome involution in aquatic organisms (including fishes, marine mammals, etc.) under the action of mercury. In this regard, we attempted to study the dynamics of morphogenesis and breakdown of the emerging connectome under the mercury exposure. A dynamic study of frames with the dynamics of the axonal path search was carried out in a series with an address-time code, on which it is possible to track the vector fields of displacements and reaction-diffusion processes in the cell culture immediately after the introduction of a drop of mercury or a mercury-containing liquid using capillary pipettes. This paper describes the observed effects and the possible mechanisms underlying them.

Keywords: mercury, ecotoxicology, axonal guiding, axonal pathfinding, motion estimation, vector fields

1. Introduction

The role of mercury in the formation of various neuropathologies is well known (O'Donoghue et al., 2020), including neurodegenerative diseases (Cariccio et al., 2019); it has been proven, in particular (Lee et al., 2018; Bjørklund et al., 2019; Siblerud et al., 2019; Azar et al., 2021), that mercury can cause the development of Alzheimer's disease. It can also lead to the development of brain tumors (Bjørklund et al., 2020) and the development of autism in children (Kern et al., 2020; Kaur et al., 2021), which is caused by disturbances in the machinery of neuro(morpho)genesis and impaired efficiency of connectome development (Abbot and Nigussie, 2021). Such effects may be due to exposure to mercury at the early stages of development, as well as at the most vulnerable stages of age-related physiology (Dórea et al., 2020). Effects of this type are also observed in marine mammals (López-Berenguer et al., 2020) inevitably exposed to mercury due to its presence in seawater (Brown et al., 2018; Wang et al., 2021; Jinadasa et al., 2021).

However, until recent years, there have been practically no works on the effects of mercury on the development of the neural structure of the brain of marine mammals during natural or model exposure to mercury, and, moreover, no works with dynamic observation of development with such exposure of their surviving brain slices under time-lapse microscopy and multi-angle 3D imaging techniques (confocal microscopy, SPIM, microtomography, holography, and holographic microscopy), which would answer the question of Hg-inhibitor diffusion in space and time. How does axonal guiding / axonal pathfinding change with introducing amounts of mercury characteristic of natural exposure into the nervous tissue? However, full-scale studies of this on marine mammals have not been conducted.

The situation is even worse with the study of the reactivity of the nervous system in fish to introducing mercury into the environment. Analyzing recent literature (because the author has not studied the nervous tissues of fish since 2015 (Gradov, 2015), due to the lack of equipment and infrastructural capabilities to maintain them), we came to a paradoxical, in fact, conclusion. Despite the increase in works postulating the toxic effect of mercury demonstrated on fish (up to its toxicokinetics and biotransformation at various stages of this effect) and works postulating mercury contamination under various hydrochemical conditions (Zheng et al., 2019; Jinadasa and Fowler, 2019; Wang and Wang, 2019; Mendes et al., 2019; Lahrich and El

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Received: June 10, 2022; ***Accepted:*** July 12, 2022;
Available online: July 31, 2022

Mhammedi, 2019; Rahmanikhah et al., 2020; Tamele and Vázquez Loureiro, 2020; de Paula Gutierrez and Agudelo, 2020; Askary Sary, 2020; Mahmudiono et al., 2020; Canham et al., 2021), the number of works describing and interpreting this effect at the cellular level, providing cytophysiological, immunohistochemical and morphometric data, allowing quantifying the effects with topographic reference, is extremely small (Pereira et al., 2019).

2. Materials and methods

Our approach implemented in this work was based on methods that provide for the dynamic study of frames with the dynamics of axonal pathfinding with a timecode, based on which it is possible to track vector displacement fields and reaction-diffusion processes in the culture immediately after introducing a drop of mercury or a liquid containing mercury using a capillary patch pipette. In this paper, we describe the method for the first time and test it on data, according to generally accepted ideas, proving (at a didactically understandable level) the presence of effects of exposure to mercury on neurogenesis. We initiated work on more complex neural structures, but their results, due to the multiplicity of interacting elements of the neural structure of the brain, are more difficult to describe and interpret and require reference to unpublished data. Therefore, we decided to start publication by a simpler version of the experiment known since the end of the past century.

Sequences of frames taken before the introduction of mercury were considered an episode for control. As an episode to control the intrinsic dynamics of disturbances in vector fields during mercury diffusion (under conditions of advection and convection that inevitably arise due to the temperature difference between the introduced substance and the cultivation medium), frames were taken for the first one and a half seconds after introducing the toxicant into the medium, until the currents were established, which allowed us to observe dynamics and own behavior of neurons, without “convective artifacts”. As an episode to control the vector fields of the intrinsic behavior of neurons, frames taken after the establishment of a stationary state of the medium up to the extreme stage of involution (denudation) and the decay of trends in the formation of the connectome were used.

3. Results

The results and their descriptions are shown in the figures, which shall be published in the latest issue of the journal. Briefly, the content of the experiment states is as follows:

1. The structure of the vector fields of axonal guidance in the control (before the introduction of mercury into the liquid) demonstrates the presence of a high “search activity” of axons, spreading over the entire field of view, a kind of “field probing”;
2. after introducing a drop of Hg into the area free from cellular structures using a patch pipette, there are high-speed convective and advective flows in the medium, indicating the beginning of the distribution of mercury in the medium;
3. when mercury reaches the ends of neuronal structures, denudation begins accompanied by the contraction of the lateral processes and protrusions, while the machinery of axonal path finding, the formation of connections (structural units of the connectome) is blocked and ceases to be active (since the vector fields of the dynamics of the structures corresponding to it cease to be registered);
4. retrograde vector fields indicate further structural involution: there is a reduction in the growth cones of axons of all neurons located at an accessible distance capable of participating in axonal search / axonal guidance (relative to each other);
5. the terminal stage of the development of denudation processes represents a stationary state; it is fixed by the absence of representative vector fields of motion estimation (however, in the initial period of it, residual oscillations / fluctuations can be observed: reversible short-wave contractions, which, apparently, are due to the automatism of the elements of the cytoskeleton and filopodia).

4. Discussion

The production of aquatic environments that simulate known freshwater and oceanic or marine environments with an arbitrarily high complexity of composition reproduction does not present significant technical problems at the moment - up to models that include microbiological components, fluid models for specific geographical locations, specific exposure levels - imitating the photochemistry and photohydrochemistry of mercury and the presence of specific dissolved or precipitated forms, etc. (Regnell and Watras, 2018; Zhu et al., 2018; Jinadasa and Fowler, 2019; Kimáková et al., 2019; Yan et al., 2019; Luo et al., 2020; Branfireun et al., 2020; Helmrich et al., 2021; Gallorini and Loizeau, 2021). Moreover, in the presence of modern models that reconstruct trends (which is a consequence of the analysis of “big data” about natural ecosystems), not only reconstruction is available for known environmental conditions, but also for arbitrary conditions for which a plausible calculation of the state in computational models is possible. That is, in fact, there are no obstacles to modeling not only statics and adaptation, but also possible forms of the norm of reaction to the content of mercury in the evolutionary process or in bio(geo/hydro-)chemical pathology.

5. Conclusions

Drawing parallels between the bioavailability of mercury for consumers of different levels, including humans (Broadhurst et al., 1998; Okpala et al., 2018; Ong and MacKenzie, 2018; de Almeida Rodrigues et al., 2019; Cosio, 2020), it is possible to implement multilevel schemes of model systems, in which the

conditions for the assimilation of mercury in ecological chains as a whole, and not only in individual organisms, will be reproduced. As a consequence, it is also possible to implement schemes of installations with a modified medium (analogues of stop flow or continuous flow, including their microfluidic implementations) to analyze the response of different neurons and for preparations of different types of aquatic organisms exposed to different (in terms of Hg content, at least) hydrochemical conditions. Applying to such "microchemostatic" systems vector-field methods for analyzing the results of microimaging obtained from inverted or lensless (which is suitable only for very large neurons) microscopes, it is possible to study the dependences of the search behavior of neurons in the process of axonal guidance depending on environmental conditions and the dynamics of its contamination. . In our opinion, such prospects can open a qualitatively new chapter in the history of mercury ecotoxicology, especially in terms of its neurophysiological and neuroembryological effects.

Acknowledgements

The author is very grateful to P.L. Aleksandrov (IBCh RAS) for automation of time-lapse recording at a given exposure, including camera modification for these purposes. The relevant data will be published in future papers. The author expresses his gratitude to E. Adamovich for the super-fast translation of the text of the article.

Conflict of interest

The author declares no conflict of interest related to this publication.

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Short communication

ISSN 2658-3518
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Comparative analysis of the sources of mercury concentration formation in the water of the Paatsjoki River basin

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ABSTRACT. We overview the content of mercury compounds in ore formations, the deposit development of which is the source of mercury compounds entering the environment. The vast majority of mercury in pyritic ores passes into concentrates and is taken in this composition for processing; only a small amount of it (up to 2–7% of the total amount in ores) goes into processing waste that is stored in tailings dams. We analyze the mercury concentrations in the water objects in the Paatsjoki River basin, the watershed of which is associated both with the Monchegorsk copper-nickel deposit where the mercury concentration can reach 9 g/t and with the production sites of PJSC MMC Norilsk Nickel. From 2017 to 2020, the concentration of mercury compounds in the water of the cascade of reservoirs on the Paatsjoki River, in the transborder sections of the Russian Federation border with Finland and Norway, increased evenly from the earlier to the later time of reservoir creation. The concentrations of mercury compounds in the waters of reservoirs generally exceeded the concentrations in the water of the Kolosjoki River at the observation site of the Nickel settlement in the area of the JSC Kola MMC activity. We conclude that the activation of microbial processes occurring in the bottom sediments during the formation of reservoirs with the increase in the amount of organic matter received and under certain geochemical conditions in the region affect the levels of mercury concentrations in the water.

Keywords: mercury compounds, the Paatsjoki River, reservoirs,the Kolosjoki River, river transborder sections

1. Introduction

Mercury is an accompanying element in most ore formations. In some deposits, e.g. copper-silver ones, mercury is present in the ore in mineral form. In platinoid deposits, mercury is part of complex minerals; in copper-pyritic, copper-nickel, sulfur-pyritic, and polymetallic deposits, mercury is present in a dispersed form. Sulfide deposits are distinguished by significant amounts of mercury, and zinc sulfideores are the most enriched in mercury (up to 10–100 g/t). The average content of mercury in ores of pyritic deposits is approximately 1 g/t and 1.1 g/t in polymetallic ores. The average content of mercury in sulfide copper-nickel ores is 1 g/t, although, for example, in ores of the Monchegorsk copper-nickel deposit, its concentration can reach 9 g/t. The bulk of mercury in ores is present in sulfide form as a finely dispersed admixture in ore-forming minerals. Sphalerite is the main concentrator and carrier of mercury. Additionally, fahlore, galena, bornite, chalcopyrite, and pyrite are mercury concentrators. During ore processing at concentrating plants, methods for crushing and grinding ores are used, followed by flotation and production of various industrial concentrates. The vast majority of mercury in pyritic ores passes into concentrates and is taken in this composition for processing; only a small amount of it (up to 2–7% of the total amount in ores) goes into the processing waste that is stored in tailings dams. Nevertheless, the presence of concentrating plants in the regions and significant volumes of waste containing mercury in one amount or another predetermines the potential for its inclusion in migration chains. The extraction of ores, especially those containing zinc, copper, nickel, lead, and gold, releases significant amounts of mercury into the environment. The bulk of mercury is mobilized with zinc and copper concentrates processed in Russian metallurgical enterprises. During the processing, mercury is either released into the air or goes into waste or byproducts such as industrial sulfuric acid. A very small amount of mercury is delivered with the produced metals to consumers (Bobrova et al., 1990; Rtutnoye zagryazneniye…, 2014).

At the end of 2020, PJSC MMC Norilsk Nickel, a diversified mining and metallurgical company, the world's largest producer of palladium and high grade nickel, as well as one of the largest producers of platinum and copper, stopped the work of the smelter

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Received: June 7, 2022; ***Accepted:*** July 12, 2022;
Available online: July 31, 2022

in the Nickel settlement (Murmansk Oblast). Todate, thiswastheoldestcompany'sproduction. Its shutdown was part of the Norilsk Nickel comprehensive environmental programme designed to significantly reduce the impact on the environment at all production sites. With the shutdown of the smelter, harmful emissions into the atmosphere at the Russian-Norwegian border were stopped. The company's management plans to modernize metallurgical production in the city of Monchegorsk. Analysis of the concentrations of mercury compounds in the surface waters of the region would reveal the contribution from each of the potential sources to the formation of their levels.

2. Materials and methods

Data on the concentrations of mercury compounds in the waters of reservoirs on the Paatsjoki and Kolosjoki rivers were obtained within the Programme for monitoring the pollution of surface waters of the land of federal monitoring network by hydrochemical indicators in the territory of operation of Murmansk Service for Hydrometeorology and Environmental Monitoring (Roshydromet) for 2017-2020 (Yezhegodnik…, 2017; 2018; 2019; 2020) (Fig. 1).

Fig.1. Layout of the sites of the Roshydromet federal monitoring network

3. Results and discussion

Based on the Murmansk Roshydromet data, the highest levels of water pollution were observed in the area of the JSC Kola MMC activity (Monchegorsk, Zapolyarny and Nickel) and in the city of Murmansk. The Kolosjoki River in the Nickel settlement is the most polluted watercourse in the watershed basin. A characteristic feature of water objects located in the area of the Kola MMC activity is the presence of nickel and copper compounds in natural water (according to Roshydromet data). An analysis of the data obtained by Roshydromet from 2017 to 2020 (five-year period before the shutdown of the smelter in the Nickel settlement) indicated the presence of dissolved mercury compounds in the water of the Paatsjokibasin in the river transborder sections near the state border with Norway and Finland. Notably, in the Kolosjoki River (Nickel settlement)polluted by wastewater from Kola MMC, the water of which is characterized by the fourth class with interannual fluctuations in grades from "a" and "b" ("dirty") to "c" and "d" ("very dirty"), the concentrations of mercury compounds were much lower than in the Paatsjoki River, the water of which in the sections upstream of the confluence with the Kolosjoki River is characterized as "roughly clean" of the first quality class or "weakly polluted" of the second quality class (Fig. 2).

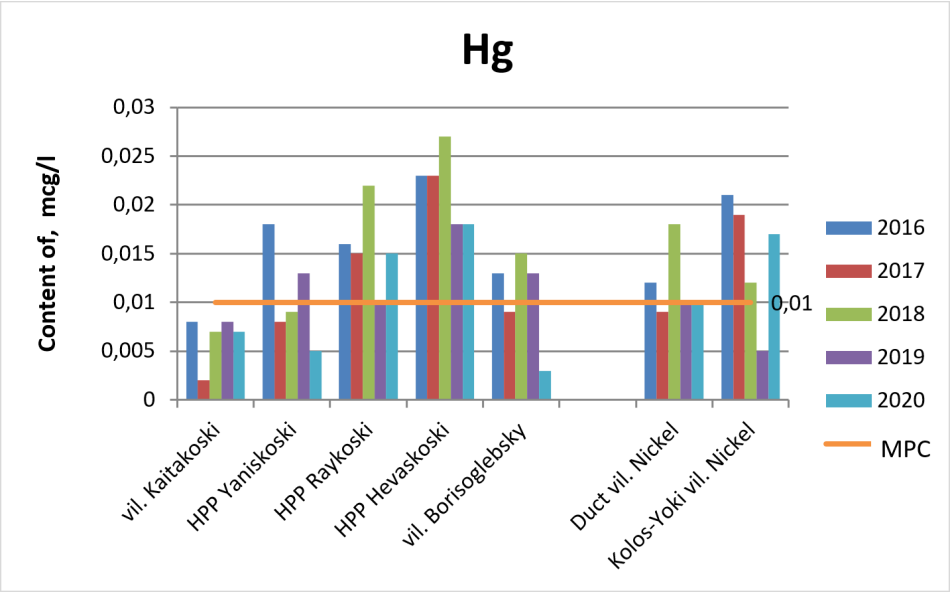

Fig.2. Histogram of the average annual concentrations of mercury in the water of the Paatsjoki River basin

Near the dam of the Hevaskoski Hydroelectric Power Plant (HPP), there were the most significant concentrations of mercury compounds. As this is the border with Norway, and there are no production facilities in this area, we can state that this is the consequence of the natural accumulation of mercury in the bottom sediments as well as of relatively recently created reservoir (the Hevaskoski HPP was the last constructed in the cascade of reservoirs) that was dispersed in the geochemical landscape of the region. In the Borisoglebskaya HPP of the Paatsjoki River, which is the last downstream and located farther off the confluence with the Kolosjoki River, the concentrations of mercury compounds were almost the same as in the Kolosjoki River, and the water quality varied from the third class of grade "a" ("polluted") to the second class ("weakly polluted"). Hence, the elevated concentrations in the surface waters of the region were due to the geochemical conditions.

Previously, it was shown that the creation of new or expansion of existing artificial reservoirs significantly increased the production of methylmercury, although in the new lakes in Finland, this increase was rather short-term. A similar phenomenon of the increase in mercury in new reservoirs, which fish and mammals that feed on them consume, was also observed when the runoff of the Churchill River in the province of Manitoba was diverted. Methylation levels in one of the reservoirs, which was flooded 20 years ago, returned to baseline. Mercury in all these artificial reservoirs, apparently, was also of natural rather than anthropogenic origin. The flooding of a large amount of organic matter and subsequent activation of microbial activity were considered the causes of the increased involvement of mercury in the methylation process (Gigiyenicheskiye kriterii..., 1992).

4. Conclusions

As over 50 years have passed since the commissioning of the youngest reservoir from the cascade on the Paatsjoki River, the Hevaskoski HPP, and the rate of bottom sediment formation has stabilized, we can more likely conclude that the mercury methylation process in the bottom sediments has also returned to its original volumes there. The increased geochemical background of the concentrations of mercury compounds in the surface waters of this region requires a more detailed study of microbial activity in the bottom sediments of the cascade of reservoirs on the Paatsjoki River located along the state border of the Russian Federation with Finland and Norway.

Conflict of interest

The authors declare no conflicts of interest.

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Short communication

ISSN 2658-3518
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Variations in mercury concentrations in the muscles of fish in biotopes within the water body and in different water bodies of Russia

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ABSTRACT. In recent decades, researchers from Papanin Institute for Biology of Inland Waters Russian Academy of Sciences have been studying mercury concentrations in the muscles of fish from water bodies situated in different natural and climatic zones. Overall, more than 5000 fish samples from 102 lakes and 35 rivers in Russia were analysed. In the absence of local sources of mercury entering the water body, its concentrations in the fish muscles varied in wide ranges, exceeding two orders of magnitude. Minimum concentration (<0.03 mg/kg wet weight) was recorded in the muscles of omul, rotan (Chinese sleeper), minnow, and bleak (Lake Baikal, Transbaikalia and European Russia). Maximum mercury concentration (2-3 mg/kg wet weight) was recorded in the muscles of perches from lakes in the northwest of Russia (Vologda and Novgorod regions, Karelia). Most of the measurement results ranged from 0.05 to 0.30 mg/kg wet weight. Differences in mercury concentrations in the muscles of fish of the same species, similar in size and from one water body, as a rule, did not exceed ranges of one order of magnitude. In the absence of local mercury sources, mercury concentrations in fish muscles from closely spaced water bodies could have more than tenfold differences.

***Keywords*:** mercury, fish, muscles, rivers, lakes

1. Introduction

In the Russian Federation, there are a great number of various water bodies that differ in morphometric, hydrological, hydrochemical, and hydrobiological parameters. Fish inhabit many water bodies, which are traditionally an object of fishing and an essential part of the diet of the population. However, the concept of the nature of mercury distribution in muscles of different fish species from different water bodies of the Russian Federation has not yet been formulated. In this regard, the aim of this analysis was to compare mercury concentrations in the muscles of fish caught at closely spaced stations of one or several water bodies situated in different geographical regions.

2. Materials and methods

Fish were caught by all possible legal methods depending on the conditions and tasks: fixed nets, seine nets and fishing rod. The caught fish were weighed; the length was measured, and a muscle sample was taken below the dorsal fin. If the conditions did not allow us to do this, the fish was frozen and stored until analysis at -14 to -4 C^0. During long expeditions, muscle samples were dried in air (in the absence of refrigerators), then stored in a freezer under laboratory conditions and dried in a thermostat before analysis. Mercury was determined on the Russian analysers: Yuliya 2 until 2007 and RA-915 with the PYRO attachment since 2007. For data control, a certified reference material for trace metals, Dorm II (dogfish muscles, Canadian Institute of Environmental Chemistry), with a standard mercury concentration, was used.

3. Results and discussion

Rybinsk Reservoir. The difference between minimum and maximum mercury concentrations in the muscles of the perch from the Rybinsk Reservoir was almost tenfold. Over the past thirty years, there has been a four- or fivefold decrease in mercury concentrations in the muscles of perch from the Sheksna reach (up to 0.10-0.20 mg/kg wet weight) and an increase (up to 0.20-0.30 mg/kg wet weight) in fish from Mologa and Volga reaches. A decrease in mercury concentration in the muscles of perch can be explained by technological reequipment of production in Cherepovets, which was conducted in the 1990s. For all parts of the reservoir, we determined a statistically significant dependence

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Received: July 7, 2022; A***ccepted:*** July 14, 2022;
A***vailable online:*** July 31, 2022

of mercury concentration in muscles on the size and weight characteristics. There was a correlation between mercury concentration in the muscles of perch and its concentration in the bottom sediments ($r = 0.95$; $p < 0.047$). The complex multi-component ecosystem of the Rybinsk Reservoir, as well as the interaction of many abiotic and biotic factors that have been poorly controlled and even ignored until recently, did not allow us to propose a simple explanation of the change in mercury concentration in muscles of perch in recent decades. Furthermore, mercury was accumulated in different directions in separate parts of the water body (Gremyachikh et al., 2019).

Lakes of Darwin Nature Reserve, Vologda Region. For the first time in Russia, high mercury concentrations (>0.5 mg/kg wet weight) in the muscles of perch from lakes that do not have local mercury sources in the watershed were recorded in 1989 during the expedition to Darwin Nature Reserve (Haines et al., 1992). The difference between the minimum mercury concentrations in the muscles of perch from the lake with neutral water pH values (~0.10 mg/kg wet weight) and the maximum ones (3.01 mg/kg wet weight) in perch from the acidotrophic (pH<5.0) dark-water lake was more than 30-fold (Haines et al., 1992). At the same time, the size and weight characteristics of the perch from acidotrophic lakes were lower than in the perch from the lake with neutral water pH values. In the perches from acidotrophic lakes, mercury concentrations in muscles did not depend on size and weight characteristics. Long-term changes in mercury concentrations in the muscles of fish from different lakes were multidirectional. For 25 years, mercury concentration in the muscles of perch increased (acidotrophic clear-water lakes Dorozhiv, Temnoye and Motykino), decreased (acidotrophic dark-water Lake Dubrovskoye) or did not change (neutral Lake Khotavets, acidotrophic dark-water lakes Uteshkovo and Zmeinoye) (Komov et al., 2015). Based on data from 1989, there was a statistically significant negative relationship between mercury concentration in perch muscles and the maximum chlorophyll concentration in lake waters during the vegetation period.

Lakes of Rdeysky Nature Reserve, Novgorod Region. The Polistovo-Lovatsky raised bog landscapes are one of the largest areas in Europe. Any economic activity and the presence of humans here are minimal or absent. The lakes in this bog area are shallow and inhabited primarily by perches. Only in some lakes, pikes are also found. At the same time, the variability of mercury concentrations in the muscles of the perches from these lakes was very high. The lowest recorded mercury concentrations in the muscles of perches from lakes Dolgoye, Domshinskoye and Ostrovistoye (0.04 to 0.07 m/kg wet weight) were 30 to 60 times lower than the maximum concentrations in the muscles of the perch from Lake Bolshoye Goretskoye (2.40 mg/kg wet weight). As a rule, the differences in mercury concentrations in the muscles of perches from each lake were 1.5- to 4-fold. Mercury concentrations in muscles did not depend on size and weight characteristics. Maximum accumulation of mercury was detected in fish from lakes with minimum specific watershed (Bolshoye Goretskoye Lake and Maloye Goretskoye Lake), and the minimum mercury concentrations in muscles were typical of lakes with a specific watershed exceeding 8 (Komov et al., 2009). The role of the watershed basin as a factor influencing the intensity of mercury accumulation in fish may include: i) evaporation of mercury from the area uncovered by water; ii) mercury absorption by peatlands; iii) change in the amount of nutrients in the surface runoff of water entering the lakes.

Rivers and lakes of Oka Nature Reserve, Ryazan Region. Mercury concentrations in the muscles of the perches from water bodies and watercourses of the Oka basin in Oka Nature Reserve varied in a wide range of values: from the minimum concentrations (0.01 mg/kg wet weight) recorded in rotan and bream to the maximum concentrations (1.94 mg/kg wet weight) in pike (Gremyachikh et al., 2012). As a rule, mercury concentrations in the muscles of the perches inhabiting lakes were lower than in the fish from rivers. Mercury concentrations in the muscle of perch and pike depended on size and weight characteristics as well as on age of perch. Higher mercury concentrations in the muscles of the perch from the Pra River compared to fish from other rivers and lakes of the reserve, as well as the Volga reservoirs, may be due to the influence of the surface runoff from wetlands. In predatory fish species, mercury concentrations were higher than in non-predatory ones. However, high mercury concentrations in the muscles of silver bream (non-predatory species) and moderate concentrations in the muscles of burbot may indicate the dietary habits of these species.

The Kuybyshev Reservoir, the largest in the Volga River basin, has a length of more than 500 km and is located in five regions of the Russian Federation. Mercury concentrations in the muscles of the perch from the Kuybyshev Reservoir ranged from 0.05 to 0.59 mg/kg, averaging 0.20 mg/kg wet weight throughout the reservoir, which corresponded to the results obtained in other Volga reservoirs (Telezhnikova et al., 2020). Mercury concentration had statistically significant positive correlation with weight and age of the perch. There was no correlation between mercury concentration and the abundance /biomass of aquatic organisms at the sampling sites. The perches inhabiting river areas of the reservoir accumulated more mercury than the perches inhabiting lake part of the reservoir.

The Selenga River basin and Lake Baikal. The identified differences between the mercury accumulation levels in the muscles of the fish from lakes Gusinoye and Karasinoye (Selenga basin) and the fish from the Selenga River may indicate insignificant amount of mercury entering the aquatic ecosystems with precipitation and larger-scale migration of mercury with river runoff. Minimum mercury concentrations (<0.15 mg per 1 kg dry weight) were recorded in the muscles of the rotan from Lake Karasinoye and Baikal omul; the maximum concentrations (1.0 to 2.3 mg/kg dry weight) were recorded in predators (pike, catfish and perch) and euryphages (roach and ide) from the Selenga River delta (Komov et al., 2014). The mercury

accumulation in the muscles of the dace decreased downstream the river.

4. Conclusions

Mercury concentrations in the muscles of fish from rivers and lakes in the central and northwestern parts of European Russia were, as a rule, higher than in the muscles of fish from water bodies in the Selenga River basin. High mercury concentrations (>0.5 mg/kg wet weight) were recorded in the muscles of the fish inhabiting i) rivers and lakes in areas with high waterlogging degree, ii) large reservoirs and iii) the Selenga River delta.

Conflict of interest

Authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Adaptation of cryomicrobiocenoses to mercury pollution

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ABSTRACT. This article presents the results of a layer-by-layer study of the ice thickness in the main channel of the Amur River (Khabarovsk city area) and Pemzenskaya and Amurskaya channels. Spectral and microbiological methods were used to assess the nature of ice contamination with organic compounds. The study of suspensions from ice melts by mass spectrometry (ICP MS) confirmed mercury pollution. Among the cultivated heterotrophic bacteria from the ice mass (cryomicrobiocenoses), there were communities adapted to high mercury concentrations (up to 0.001 mg/L). In some layers of the ice, we recorded a high portion of sulfate-reducing bacteria involved in mercury methylation. In the mainstream of the Amur River, a layer of ice (70-117 cm) had a high content of mercury, dissolved organic matter, plant detritus, and the maximum number of bacteria resistant to mercury pollution. This ice layer was formed during the period of technological discharges from reservoirs to combat the consequences of a major flood in the Amur River Basin. The indicator of resistance of cryomicrobiocenoses to high mercury concentrations was due to the adaptive potential of heterotrophic microorganisms, including active mercury methylators, i.e. sulfate-reducing bacteria. This indicator can be used for a retrospective assessment of mercury pollution of rivers during the freeze-up period.

Keywords: mercury pollution, cryomicrobiocenoses, methylation, sulfate reduction, organic matter

1. Introduction

Mercury is a dangerous toxicant for humans and aquatic organisms due to its high accumulation capacity. There are numerous data on its accumulation in bottom sediments and living organisms (Wiener et al., 2006). The risk of mercury pollution depends on many factors, including its occurrence in the environment. The migration ability of mercury is due to its transformation into a toxic form, methylmercury (CH_3Hg^+), resulted from microbial activity in the presence of organic substances (OS) (Ermakov, 2010; Liu et al., 2012). Dissolved OS play a more significant role in mercury methylation than pH or Eh (Feyte et al., 2010). The main mechanism of resistance of microorganisms to mercury, including cryomicrobiocenoses (CM) developing in the ice mass, is associated with the metabolism of specialized groups of microorganisms (iron- and sulfate-reducing bacteria) (Kerin et al., 2006). These bacteria from the Arctic ice and permafrost were adapted to mercury pollution. They can maintain their metabolic activity at low temperatures (Rivkina et al., 2000; Moller et al., 2011).

Previously, an increased resistance of CM to mercury ions was recorded in the transboundary section of the Amur River downstream the mouth of the Sungari River (right-bank tributary from the territory of China). Heterotrophic bacteria isolated from the ice in the study of river runoff from the territory of China were resistant to high concentrations of mercury, lead and cadmium salts (up to 0.1 g/L). In the control section, CM growth was inhibited by a lower content of these metals (0.001 g/L).

This article presents the results of experimental studies of the cryomicrobiocenoses resistance from the Amur River near Khabarovsk to mercury pollution after a major flood.

2. Materials and methods

The ice cores were sampled in March 2014 during a complex expedition by specialists from Institute of water and ecology problems, Far Eastern Branch, Russian Academy of Sciences. Ice was sampled using an annular drill with an inner diameter of 16 cm. Melts

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Received: June 22, 2022; ***Accepted:*** July 14, 2022;
Available online: July 31, 2022

of different layers of ice sampled along the transverse profile of the Amur River near the city of Khabarovsk and in large tributaries (Amurskaya and Pemzenskaya) were used for chemical and microbiological analyzes. The thickness of the ice layers was determined by its heterogeneity: transparency, turbidity, presence of detritus, etc.

For microbiological studies, the ice samples were melted at room temperature according to asepsis rules. The abundance of cultivated heterotrophic bacteria (CHB) was determined on a dense nutrient medium (fish-peptone agar diluted 10 times); that of sulfate-reducing bacteria (SRB) – by deep inoculation of 1 mL of ice melt on Postgate agar medium. The growth activity and adaptation of SRB to mercury pollution were assessed by the change in the optical density (OD) of the culture liquid at 600 nm on a KFK-3-01 photometer. Cultivation was carried out in a liquid medium with calcium lactate. Water-soluble mercury salt ($HgNO_3$) was added at concentrations of 0.0005 (Hg1) and 0.001 mg/L (Hg2).

Total concentrations of dissolved OS in the ice melts samples after separation of suspensions was determined by the spectrophotometric method at 254 nm (Shimadzu UV-3600) and expressed as a spectral absorption coefficient (SAC_{254}, abs. units). Suspended substances were separated from the melts by filtration through a double paper filter (blue ribbon treated with freshly prepared 1% HNO_3). The solid precipitate was washed off the filters with an acidified nitric acid solution into glassy carbon crucibles and decomposed. The elemental composition in ice melts and suspended matter was determined according to Federal environmental normative document (PND F 16.1:2.3:3.11-98) by inductively coupled plasma spectrometry on a Perkin Elmer instrument (USA) at the Khabarovsk Innovation and Analytical Center for collective use at the Yu.A. Kosygin Institute of tectonics and geophysics FEB RAS.

3. Results and discussion

Studies were carried out during the freeze-up period after the flood in the summer of 2013, when large reservoirs in the Russian territory (Zeyskoye and Bureyskoe reservoirs) were overfilled, and technological discharges were carried from them in winter. It is important to emphasize that during the period of ice core sampling, the mercury content in the under-ice water and in ice melts was below the detection limits. A completely different situation was observed with suspended matter (SM) from different ice layers (Table 1). The maximum concentration of mercury was in the 70–117 cm layer, which was characterized by a high content of detritus and mineral suspensions. The finely dispersed part of SM from this layer was a complex conglomerate of diatoms, bacterial complexes and a lithogenic component on SEM images (Golubeva et al., 2020).

Microbiological studies were carried out with ice melts with a high concentration of dissolved OS sampled in the mainstream of the Amur River, Pemzenskaya and Amurskaya channels. A high abundance of CHB and SRB was characteristic of the melt of 70-117 cm ice layer that was brown in color, high in SAC_{254}, detritus, and aromatic compounds due to the presence of phenol-resistant bacteria (Table 2). High abundance of CHB and SRB in the ice is one of the important prerequisites for the formation of conditions for mercury methylation in ice.

Cryomicrobiocenoses from the ice layer of 70-117 cm sampled in the main channel of the Amur River, 272 m from the left bank, under the influence of the Bureya River, were distinguished by the maximum adaptive potential to mercury pollution. Growth on calcium lactate in the presence of mercury (0.0005 and 0.001 mg/L) did not actually differ from the control. In other parts of the main channel of the Amur River, the growth of CM on calcium lactate was weaker, but no inhibition by mercury was observed.

In the Pemzenskaya channel, with a lower concentration of dissolved OS, there were the maximum abundance of CHB and a high abundance of SRB in the ice layer of 60-85 cm. It was comparable to the abundance of the unique ice layer in the main channel of the Amur River. This may be due to the fact that part of the water masses of the Amur River enters the Pemzenskaya channel. Selected mercury concentrations inhibited the growth of cryomicrobiocenoses (Table 2).

Interesting pattern was noted in the study of ice in the Amurskaya channel, which receives the Ussuri River runoff from the territory of China. The OS concentrations in the ice melts were comparable to their values in the ice melts of the Pemzenskaya channel. However, the phenomenon of mercury stimulation of CM growth on calcium lactate from the surface layer

Table 1. Mercury concentrations in suspended matter of ice melts from the cores sampled in the mainstream of the Amur River in the winter of 2013-2014

Ice core, 20 m from the left bank		Ice core, 272 m from the left bank		Ice core, 80 m from the left bank	
Layer, cm	**Concentration, μg/g**	**Layer, cm**	**Concentration, μg/g**	**Layer, cm**	**COncentration, μg/g**
0-30	0.32	0-40	0.30	0-12	-
30-45	0.03	40-50	0.22	12-27	0.70
45-60	0.15	52-72	0.50	27-57	0.72
60-70	b.l.	70-117	0.91	57-82	0.11
120-132	b.l.	117-139	b.l.	-	-

Note: «b.l.» - below the detection limits of the device; «-» - only four ice layers.

Table 2. Integrated assessment of ice melt and resistance of microorganisms to different mercury concentrations (Hg1 = 0.0005 mg/L; Hg2 = 0.001 mg/L)

Sampling site of ice cores	Ice layer, cm	SAC_{254}, absorbance units	Abundance, CFU/mL		Growth activity on lactate, OD, 600 nm		
			CHB	SRB			
Mainstream of the Amur River, Khabarovsk city area					Control	Hg1	Hg2
Lb	70-117	0.982	68600	25070	0.85	1.1	0.8
Middle	190-200	0.127	6600	60	0.28	0.35	0.30
Rb	10-30	0.443	13800	7130	0.58	0.65	0.6
Pemzenskaya channel							
Lb	10-35	0.319	23000	17800	0.35	0.42	0.15
Middle	60-85	0.352	83000	23700	0.65	0.55	0.36
Rb	90-102	0.192	360	120	0.20	0.25	0.20
Amurskaya channel							
Lb	90-100	0.312	12600	7560	0.25	0.30	0.34
Middle	0-20	0.256	2330	2257	0.32	0.36	0.35
Rb	0-10	0.264	10000	3500	0.45	0.60	0.67

Note: CFU/mL - number of colony-forming units in 1 mL of melted ice; Lb/Rb - on the left/ right bank.

of ice sampled from the right bank was revealed for both mercury concentrations. Previously, an elevated mercury concentration in water was repeatedly recorded on the right bank where the rice fields were located, which can be treated with mercury-containing pesticides. Such CM growth stimulation by elevated mercury concentrations may be associated with chronic pollution of the Amurskaya channel.

4. Conclusions

The adaptive potential of cryomicrobiocenoses that develop in the ice column can be used to indicate the contamination of river waters with organic substances and heavy metals, including mercury, during the ice formation on rivers. The study of layer-by-layer chemical characteristics of ice and the resistance of heterotrophic bacteria, including sulfate-reducing bacteria, to mercury pollution, allows us to assess the degree of environmental risk in case of chronic pollution of the water and bottom sediments of watercourses by toxic substances and to identify technological discharges from reservoirs and the impact of surface runoff from agricultural fields contaminated with mercury-containing pesticides.

Acknowledgments

The authors are grateful to the staff of the Laboratory of Hydrology and Hydrogeology, IWEP FEB RAS, Dr. A.N. Makhinov, Ph.D. V.I. Kim, S.V. Shmigirilov for sampling ice cores.

Conflict of interest

Authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Total Hg level in hair, its predictors and relationship with health risk of Chelyabinsk residents

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ABSTRACT. We studied the total mercury concentration (T-Hg) in the hair of people living in Chelyabinsk. Hair analysis was combined with a survey evaluating relationships and variations among subgroups and potential metal exposure predictors. We determined the influence of factors such as age, gender, location of residence, smoking, hair color, T-Hg contents in soil, road dust, household dust as well as fish and potato consumption in the diet. The mean value of T-Hg in the hair for the subjects under study (0.402 μg/g) was lower than the value referred from the World Health Organization (WHO) (1–2 μg/g). There was no linear correlation between mercury hair levels and age or gender. We found a significant positive correlation between T-Hg concentration in hair and health cardiometabolic risk as well as the Hg content in road dust and the Hg of potato consumption in the diet. The data from this study can be used to develop prevention strategies for the health of residents.

Keywords: biomonitoring, human hair, total mercury, trends, health risk

1. Introduction

Mercury (Hg) is a volatile metal that is naturally present in the Earth's crust. Mercury has both natural and artificial sources. Natural sources of Hg include volcanic activity, erosion and the largest emissions as a result of degassing of the Earth's crust (Zhang et al., 2022). But in most cases, the main source of Hg is anthropogenic impact (Driscoll et al., 2013). The level of Hg in the environment is increasing due to emissions from the hydroelectric, mining and pulp and paper industries. Combustion of municipal and medical waste and emissions from coal-fired power plants also contribute to high levels of Hg (Sundseth et al., 2017).

It is important to note that there may not be a direct correlation between blood Hg concentration and the severity of its poisoning because Hg can be rapidly removed from the blood, redistributed and sequestered into various tissues (Halbach et al., 2008). Shortly after ingestion, Hg is believed to rapidly become tightly bound in the brain, spinal cord, ganglia, autonomic ganglia, and peripheral motor neurons (Yoshida et al., 1980). However, although the nervous system is the main repository for Hg exposure, transient and residual systemic distribution of Hg can cause symptoms in many organ systems. Hg accumulation in the heart is believed to contribute to the development of cardiomyopathy (Ivanova et al., 2021). The level of Hg in the heart tissue of people who died from idiopathic dilated cardiomyopathy was 22,000 times higher than in human heart of people who died from other forms of heart disease (Nyland et al., 2012).

Human biomonitoring studies assess human exposure to elements through the measurement of chemicals in body fluids and tissues such as blood, plasma, serum, breast milk, urine, saliva, lung fluid, nails, and hair (Astolfi et al., 2020). Hair has some advantages over other biological matrices. Elements can accumulate in hair at higher concentrations and for longer than other biomarker media such as urine and blood. The ability of hair to consistently accumulate chemicals within its internal structure, together with the ability to perform retrospective analyses, means that hair analysis can be used for screening and confirmation purposes in various application contexts such as forensic and clinical. Another advantage of using hair is the painless and non-invasive sampling and no need for experienced staff. Hair samples can be transported and stored at room temperature, and small sample sizes are required for analysis. The results of hair examination are a useful screening tool for assessing exposure, developmental and nutritional studies, and possible pathological processes.

The aim of this study was to investigate the levels of Hg in the hair of people living in Chelyabinsk, an industrial city in Russia. We observed the influence

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Received: June 16, 2022; ***Accepted:*** July 14, 2022;
Available online: July 31, 2022

of some factors on the variability of Hg concentration in hair and determined the relationship of Hg in hair with risk cardiovascular factors.

2. Materials and methods

A questionnaire was prepared to collect data on age, gender, location of residence, smoking, hair coloring, health, and diet. All participants gave free informed written consent in accordance with the World Medical Association Code of Ethics (Helsinki Declaration) to conduct experiments with human participation and to publish the results obtained. Only adults participated in the study. The privacy rights of participants were of paramount importance. The presence of metabolic syndrome was assessed according to Ivanova et al. (2021).

Hair strands from each participant were collected according to Grandjean et al. (1994) and then placed in plastic bags. We collected soil, road dust, and household dust in all locations and households. The main source of mercury and its compounds in the human body is fish (Bradley et al., 2017). We asked the frequency of eating fish per week. However, as the residents of the Chelyabinsk region eat little sea fish (rarely more than twice a week), they buy it in supermarkets, where it was tested for safety, we chose potatoes as a food product. We collected samples of potatoes; the source of Hg in them may be pesticides.

Soil and dust samples were taken and dried in an oven at 60 ˚C for 3 days and then crushed and sieved through a 1 mm polyethylene sieve to remove stones. After that, the dusts were sieved through a 63 μm sieve. Potato samples were washed in freshwater. A freeze dryer was used for drying potato samples.

The total Hg concentration (T-Hg) was determined by the atomic absorption pyrolysis method without preliminary **sample preparation** on a RA-915M mercury analyzer with PYRO (for hair and potato samples) and URP (for soils and dusts) attachments.

We used certified biological material (DOLT-5) to control the accuracy. Data analysis was carried out using the IBM SSPS Statistics 27. Correlations were assessed using the nonparametric Spearman coefficient.

3. Results

Table 1 gives some statistical parameters for the T-Hg concentrations in hair for all subjects in the study.

The correlation coefficients of several predictors with the measured T-Hg concentrations in hair were considered useful for understanding to what extent these factors influence the accumulation of mercury in the hair of the subjects. The data are presented in Table 2.

4. Discussion

The overall mean value of the mercury concentrations in the hair samples (0.402 μg/g) was within the range (1–2 μg/g) that WHO considers normal for populations that do not consume fish with high methylmercury concentrations.

Table 1. T-Hg concentrations in hair.

Parameter ($n = 71$)	Hg value (μg/g)
Mean	0.402
Minimum value	0.092
Maximum value	0.931
Standard deviation	0.210

Table 2. Correlation coefficients of T-Hg concentrations in hair with other factors

Correlation type ($n = 61$)	R value
Hg concentration in hair	
Health cardiometabolic risk	**0.29***
Gender	-0.039
Age	-0.026
Place of resident	-0.113
Frequency of eating fish in a week	0.160
Smoking	0.105
Hair color	-0.104
Road dust	**0.291***
Soil	0.159
Household dust	-0.086
Potato	**0.338****

Note: * Correlation is significant at 0.05 (two-tailed)
** Correlation is significant at 0.01 (two-tailed)

There was no linear correlation between mercury hair levels and age or gender. This could be explained by the relatively short biological half-life of Hg. We detected the positive significant correlations between T-Hg hair levels and road dust and potato. Our research revealed that mercury concentration in hair was significantly correlated with health. Mercury is currently considered a pollutant with a high human health risk and it has high toxicity and mobility in ecosystems. According to the literature, there are more than 250 symptoms associated with Hg exposure, which can make an accurate diagnosis difficult (Paduraru et al., 2022). The values of cardiometabolic risk factors of health (systolic blood pressure, diastolic blood pressure, cholesterol, and glucose) indicated a statistically significant dependency on T-Hg in hair.

5. Conclusions

The mean value of mercury in hair for the combined population is well within the range that WHO classifies as normal. The positive results of potato consumption in the diet proves its importance in the mercury content in the body and hair. More reliable conclusions require a greater number of cases to be sampled.

Acknowledgments

The study of Hg concentrations in the environment was funded by the Russian Science Foundation (RSF), project number 22-17-20006 (https://rscf.ru/en/project/22-17-20006/) and the Chelyabinsk Region. The relationship of T-Hg in hair with cardiometabolic risk factors was supported by the Ministry of Science and Higher Education of the Russian Federation (government order FENU-2020-0022).

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Geoecological features of mercury pressure on the south coast of the Republic of Crimea based on the study of needles

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ABSTRACT. The article presents the original data on the total Hg concentration in the needles of different tree species in the recreational zones of settlements on the south coast of the Republic of Crimea. Mean Hg concentrations were lower than in the Tomsk Region and the Republic of Sakha-Yakutia but higher than in Southern Siberia. Hg concentrations increased from west to east along the south coast of Crimea. Pine needles showed increased sorption properties relative to mercury, juniper needles had the least sorption. There was no dependence of the element input on height relative to sea level. Calculated indicators indicated elevated Hg concentrations in needles relative to the background, the temporary allowable concentration and the mean value for terrestrial plants.

Keywords: mercury, needles, Republic of Crimea, geoecology, bioindication

1. Introduction

Needles, as a bioindicator of the ecological condition of the atmospheric air, together with epiphytic lichen species and poplar leaves, reflect even weak effects of anthropogenesis due to the cumulative effect. They show the total effect of all the impacts of human activity, which are important for the natural environment and the geochemical features of the territories. They indicate the trends and degree of negative impact on humans through the biota. They allow for predicting the state of the individual components and the environment as a whole in the future. Needles reflect the state of atmospheric air for one growing season and up to five years. During the destruction of the coniferous litter, its accumulated substances are involved in the formation of the chemical composition of the soil cover, surface and groundwater (Anoshin, 1995). Plants can not only accumulate mercury (Hg) to very high concentrations but also release it back into the atmosphere during respiration (Chernenkova, 2002).

Hg is recognized as one of the most dangerous environmental pollutants strictly regulated in its components (Vinogradov, 1988; Alekseenko, 2000). This element belongs to the group of thiol poisons; it constantly transforms under changing environmental conditions with the formation of highly toxic compounds; it is hazardous even at very low concentrations (Ermakov, 2010). Atmospheric transport contributes the most to Hg migration (Saukov, 1966).

The aim of the study was to determine Hg concentrations in needles from the recreational zones of settlements on the south coast of the Republic of Crimea (hereinafter referred to as the South Coast) as well as to identify the characteristics of the mercury pressure depending on the type of coniferous and landscape conditions (height above sea level and location relative to sea).

2. Materials and methods

Needles were sampled in the recreational areas (parks, embankments and avenues) of the settlements on the South Coast of the Crimea: Sevastopol (including the Balaklava area), Yalta (embankment, Massandra winery), Bakhchisaray, and the Miskhor village (embankment, Ai-Petri) (8 sites) according to (Alekseenko, 2000). Overall, 15 samples of needles of Crimean pine (Pinus pallasiana), common spruce (Picea abies), European larch (Larix decidua Repens), Algerian fir (Abies numidica), and stink juniper (Juniperus foetidissima) were selected.

Hg concentrations in the samples were determined on a RA-915+ Hg analyzer using the atomic absorption method with the PYRO-915 attachment (pyrolysis method; Hg detection limit 5 ng/g; determination

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Received: June 20, 2022; ***Accepted:*** July 12, 2022;
Available online: July 31, 2022

accuracy 5 ng/g; element concentrations are calculated per 1 g of dry substances) in the educational and scientific laboratory on the basis of the School of Natural Resources Engineering at National Research Tomsk Polytechnic University (Shuvaeva et al., 2008).

The method of results processing included the calculation of ecological and geochemical indicators: the concentration coefficient relative to the background (C_F - 4 ng/g) (Yanin, 1992), temporary allowable concentration (TAC - 8 ng/g), Clark of living matter (K_{LM} - 50 ng/g g) (Vinogradov, 1988), noosphere (K_N – 180 ng/g) (Glazovskaya, 1988), mean dry matter concentration in terrestrial plants (K_{LP} – 15 ng/g) (Kovalsky, 1974), and sample mean value (K_M – 18.5 ng/g).

3. Results and discussion

The mean Hg concentrations in the needles from all studied recreational areas, regardless of the tree species, differed significantly from each other and ranged from 8 to 47 ng/g. Hg distribution in the needles from the South Coast was uneven, as confirmed by the calculation of the variation coefficient (59%). The Hg maximum concentrations were observed at the easternmost sampling site, the Massandra winery (Yalta), and the minimum - at the western: Balaklava area (Sevastopol) as well as in the park areas of Sevastopol, Balaklava, Bakhchisaray, and at the Ai-Petri peak (Table). On average, Hg accumulates better in the needles of pine, fir and larch (24-27 ng/g); juniper needles contained the lowest concentration of the pollutant (10 ng/g).

A more detailed analysis indicated the maximum Hg concentrations in pine needles from the city of Yalta (Massandra - 47 ng/g), and the minimum ones - in the city of Sevastopol (Grafskaya Wharf - 14 ng/g). In larch needles, the highest concentrations of the pollutant were in the city of Sevastopol (Grafskaya Wharf - 31 ng/g), in the lowest concentrations - in the city of Yalta (embankment - 14 ng/g). Maximum and minimum Hg concentrations were detected in the needles of spruce in Sevastopol (15-24 ng/g). Juniper needles were distinguished by the lowest Hg accumulation at all sampling sites compared to other studied coniferous species. Elevated concentrations of the pollutant in juniper needles were identified in the park of the Miskhor village, the lowest ones – on the embankments of Sevastopol and Yalta as well as at the Ai-Petri peak.

In addition to species diversity, landscape conditions of tree growth also influence the degree of mercury accumulation. The mean Hg concentration in the needles, regardless of the tree on the coast, was 17 (8-31 ng/g). In the mountains, the range of values was much wider, 8-47 ng/g, averaging 22 ng/g. At the same time, it should be noted that the mercury accumulation by conifers did not depend on their height, as confirmed by calculations of the correlation coefficient (0.1), except for the city of Yalta where such a relationship was found (0.88).

The obtained Hg concentrations in the coniferous trees on South Coast were significantly lower than the literature data on other bioindicators of the condition of the atmospheric air: epiphytic lichen species and poplar leaves (Evstafieva et al., 2021). The mean mercury concentration in lichens was from 3 to 15 times higher, and in poplar leaves - from 1.5 to 2 times higher (Fig.). It is preferable to compare the Hg concentrations in needles with data on poplar leaves, as they reflect the level of mercury impact on the atmosphere of the region in one season, while lichens show the long-term input of the element. At the same time, the mean mercury concentration in the air of the Republic of Crimea was 2 ng/m^3; background concentrations in soils - 8-3000 ng/g; bedrock - 12-10000 ng/g and sea water - 3-680 ng/g.

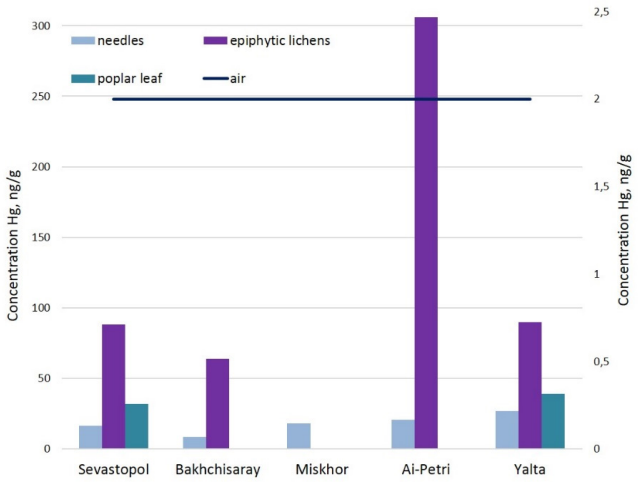

Fig. Hg in adjacent environments on the South Coast of Crimea.

Table. Geoecological indicators of mercury pressure on the South Coast of Crimea

Sampling site	C_{Hg}, ng/g	K_C*	TAC	K_M	K_N	K_{LM}	K_{LP}
Sevastopol	18 ± 0.8	4.6	2.3	0.4	0.1	0.4	1.2
Balaklava	17 ± 0.9	4.2	2.1	0.3	0.1	0.3	1.1
Bakhchisaray	8 ± 1.5	2.1	1.1	0.2	0.05	0.2	0.6
Miskhor	18 ± 0.9	4.5	2.1	0.4	0.1	0.4	1.2
Yalta	27 ± 0.5	6.7	3.3	0.5	0.1	0.5	1.8
Ai-Petri	21 ± 1.7	5.1	2.6	0.4	0.1	0.4	1.4

Note: * - see materials and methods

The average Hg concentration in needles from the recreational zones on the South Coast was lower compared to the data on the Tomsk Region and the Republic of Yakutia but higher than in the Altai Territory, the Irkutsk Region and the Republic of Buryatia (Lyapina et al., 2018).

The data on the Hg concentration in the needles on the South Coast were comparable with those in other regions of Russia and the world (Lyapina et al., 2018). Since the concentration of element No. 80 in all studied samples was not high, background concentrations from the literature were used to calculate geoecological indicators (Lyapina et al., 2018). The results of the calculations revealed that the concentrations in the needles were up to 6.7 times higher than the background (4 ng/g); VDC - up to 3.3 times, and the mean value for terrestrial plants - up to 1.8 times, which indicates the accumulation of this metal. However, compared to Clarke, the noosphere and living matter were lower (Table).

4. Conclusions

The of studies of the concentration and geoecological features of Hg accumulation in needles from recreational zones on the south coast of the Republic of Crimea revealed that Hg concentrations corresponded to the data obtained by other researchers in Russia. The highest mercury concentrations were observed in the needles of pine, fir and larch, and the lowest - in the needles of juniper. Eastwards along the coast, Hg concentrations increased. Moreover, there was no increase in pollutant influx to the needles with height relative to sea level, except for the city of Yalta. The data of geoecological calculations testified to the cumulative nature of the Hg levels in the needles in comparison with the Clark of the noosphere and living matter. However, it was significantly lower compared to the concentration of element No. 80 in epiphytic lichen species and poplar leaves in the study area.

Acknowledgments

This study was carried out within the framework of the State Budget Topic RK 121031300154-1 IK IMKES SB RAS.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Mercury pressure in the Tomsk Region based on biomonitoring studies

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ABSTRACT. The article presents the original data on the total Hg concentration in needles of different tree species and aspen foliage in the Tomsk Region. Mean Hg concentrations were lower than in the Republic of Sakha-Yakutiya but higher than in Southern Siberia. Hg concentrations increased from the southeast to the northeast of the Tomsk Region. Cedar needles had increased sorption properties relative to this metal, and pine needles had the lowest ones. Aspen foliage accumulated mercury better in one growing season compared to needles. The calculated indicators indicated elevated Hg concentrations in needles relative to the background, the temporary allowable concentration and the mean value for terrestrial plants.

Keywords: mercury, needles, Tomsk Region, geoecology, bioindication

1. Introduction

Needles, epiphytic lichen species, poplar leaves, and aspen leaves are the most popular and frequently used representatives of vegetation for biomonitoring and bioindication both in Russia and abroad. They are convenient and informative as bioindicators of the ecological condition of the atmospheric air. These representatives of the diagnostics of the state of environmental components are distinguished by a wide range of growth, species diversity, collection ease, sample preparation, and analysis. The data obtained with needles allows us to accurately and representatively assess the quality of the surface atmosphere both for one growing season and up to five years. Furthermore, coniferous and leafy litter is involved in the formation of the soil, and the chemical elements accumulated in it contribute to the formation of the chemical composition of the soil, surface and groundwater (Anoshin et al., 1995). Plants can release accumulated mercury (Hg) back into the atmosphere during respiration (Chernenkova, 2002).

Hg is extremely toxic and pathological; it belongs to the group of thiol poisons and is an element of hazard class I, which is recognized as one of the most dangerous environmental pollutants. Therefore, it is rigidly normalized in its components (Saukov, 1966). During migration, it methylates, forming highly toxic compounds (Ermakov, 2010). The main pathway of Hg migration in the environment is atmospheric transport.

The aim of the study was to determine Hg concentrations in needles and aspen leaves from the Tomsk Region as well as to identify the characteristics of the mercury pressure depending on the type of bioindicator, the area of the region and the calculation of geoecological indicators.

2. Materials and methods

Needles were sampled in the Tomsk Region (TR) from 2018 to 2020, according to (Alekseenko, 2000). A total of 113 samples of bioindicators of mercury exposure were taken: 85 samples of needles of Scots pine (Pinus sylvestris L.), Siberian pine (Pinus sibirica L.), Siberian larch (Larix sibirica L.), and Siberian fir (Abies sibirica) as well as 28 samples of aspen trembling (Populus tremula).

Hg concentrations in the samples were determined on a RA-915+ Hg analyzer using the atomic absorption method using the PYRO-915 attachment (pyrolysis method; Hg detection limit 5 ng/g; determination accuracy 5 ng/g; element concentrations were calculated per 1 g of dry substances) in the educational and scientific laboratory on the basis of the School of Natural Resources Engineering at National Research Tomsk Polytechnic University (Shuvaeva et al., 2008).

The method of results processing included the calculation of ecological and geochemical indicators: the concentration coefficient relative to the background

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Received: June 20, 2022; ***Accepted:*** July 12, 2022;
Available online: July 31, 2022

(CS - 4 ng/g, needles; 8 ng/g, leaves) (Yanin, 1992), temporary allowable concentration (TAC - 8 ng/g, needles; 16 ng/g, leaves) (Yanin, 1992), Clark of living matter (KLM - 50 ng/g) (Vinogradov, 1988), noosphere (KN - 180 ng/g) (Glazovskaya, 1988), mean concentration in dry matter of terrestrial plants (KLP - 15 ng/g) (Kovalsky, 1974), mean value for the sample (KM - 24.5 ng/g, needles; 21.9 ng/g, aspen leaf), and enrichment factor (normalization by Sc, own data) (KE).

3. Results and discussion

The mean Hg concentrations in the needles from all studied areas of TR, regardless of the tree species, differed significantly from each other and ranged from 11 to 51 ng/g, averaging 26 ng/g; in aspen leaves, it ranged from 12 to 24 ng/g, averaging 22 ng/g (Fig.). Aspen foliage accumulated the element better in one growing season compared to needles.

The distribution of Hg in needles and aspen leaves of the studied areas was homogeneous, as confirmed by the calculation of the variation coefficient (C_V = 7% and 28%, respectively).

The Hg maximum concentrations in needles are observed in the Verkhneketsky (32 ng/g) and Pervomaisky (34 ng/g) Districts that are located in the northeast and east of TR and border with each other. The minimum Hg concentrations were recorded in Krivosheinsky District (13 ng/g) located in the central part of TR (Table). In the aspen foliage, the maximum (25 ng/g) and minimum (15 ng/g) Hg concentrations were detected in the central Kolpashevskiy and Molchanovskiy districts of TR, which also border with each other (Table).

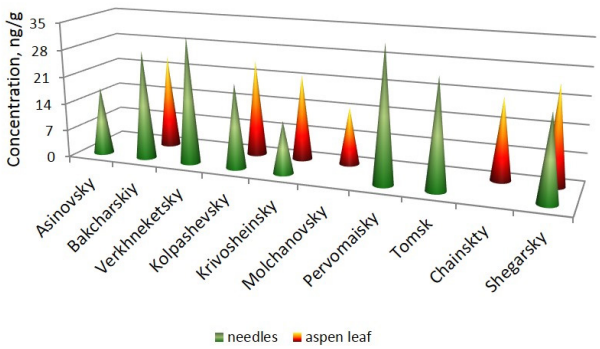

Fig. Hg in aspen needles and leaves from TR.

Mean Hg concentration in the needles from TR was lower than in the Republic of Sakha-Yakutiya (47 ng/g) but higher than in the Altai Territory (15 ng/g), Irkutsk Region (14 ng/g), Republics of Buryatia (15 ng/g). d) and Crimea (18 ng/g) (Lyapina et al., 2018).

A more detailed analysis of the Bakcharsky District indicated that Hg concentration both in needles and in poplar leaves was significantly lower than in adjacent environments: sphagnum peat and swamp waters (Domarenko et al., 2017). The excess ratio of the mean mercury concentration in peat to needles ranged from 1.5 to 46 times, and in swamp waters - from 4 to 39 times. For aspen leaves, the indicators were as follows: in peat - from 1.3 to 3.5 times and in swamp waters - from 3.4 to 29 times. Among the wide species diversity of coniferous tree species in the region, the data on Hg concentrations in pine and cedar needles are the most widely presented.

Table. Geoecological indicators of mercury pressure in the districts of the Tomsk Region

District	C_{Hg}, ng/g	K_C [2]	TAC	K_M	K_N	K_{LM}	K_{LP}	K_E
Asinovsky	17.3[1] n/d[3]	4.3 n/d	2.2 n/d	0.7 n/d	0.1 n/d	0.3 n/d	1.2 n/d	0.1 n/d
Bakcharskiy	27.9 24	7.0 3	3.5 1.5	1.1 1	0.2 0.1	0.6 0.5	1.9 1.6	0.3 0.004
Verkhneketsky	32.4 n/d	8.1 n/d	4.1 n/d	1.3 n/d	0.2 n/d	0.6 n/d	2.2 n/d	0.3 n/d
Kozhevnikovsky	1 n/d	1.8 n/d	0.9 n/d	0.3 n/d	0.04 n/d	0.1 n/d	0.5 n/d	1.4 n/d
Kolpashevsky	21.6 24.7	5.4 3.1	2.7 1.5	0.9 1	0.1 0.1	0.4 0.5	1.4 1.6	0.08 0.02
Krivosheinsky	13.3 22	3.3 2.8	1.7 1.4	0.5 0.9	0.1 0.1	0.3 0.4	0.9 1.5	0.02 0.01
Molchanovsky	n/d 14.7	n/d 1.8	n/d 0.9	n/d 0.6	n/d 0.1	n/d 0.3	n/d 1	n/d 0.01
Peromaisky	34.2 n/d	8.6 n/d	4.3 n/d	1.4 n/d	0.2 n/d	0.7 n/d	2.3 n/d	0.2 n/d
Tomsk	27.5 n/d	6.9 n/d	3.4 n/d	1.1 n/d	0.2 n/d	0.6 n/d	1.8 n/d	0.2 n/d
Chainskty	n/d 20.7	n/d 2.6	n/d 1.3	n/d 0.8	n/d 0.1	n/d 0.4	n/d 1.4	n/d 0.02
Shegarsky	21.5 25	5.4 3.1	2.7 1.6	0.9 1	0.1 0.1	0.4 0.5	1.4 1.7	0.2 0.02

Note: 1 – needles/aspen leaf; 2 - see Materials and methods; 3 n/d - no data

The data on Hg concentration in the needles and leaves of the aspen from TR were comparable with those in other regions of Russia and the world (Lyapina et al., 2018). As the concentration of element No. 80 in all studied samples was not high, background concentrations from the literature were used to calculate geoecological indicators (Lyapina et al., 2018). The calculation results indicated that the concentrations in the needles were up to 8.6 times higher than the background (4 ng/g), and in aspen leaves (8 ng/g) - up to 3.1 times; VDC - up to 4.3 times in needles and up to 1.6 times in aspen leaves; the mean value up to 2.3 times for terrestrial plants and up to 1.7 times in aspen leaves, which indicated the Hg accumulation. However, compared to Clarke, the noosphere and living matter were lower (Table). The calculation of the enrichment factor revealed the absence of Hg enrichment in both aspen leaves and needles, except for the Kozhevnikovsky District.

4. Conclusions

The studies of the concentrations and geoecological features of the Hg accumulation by bioindicators (needles and aspen leaves) in the Tomsk Region revealed that the Hg concentrations were comparable with the data obtained in other regions of Russia. Aspen foliage accumulated this element better in one growing season compared to needles. Elevated Hg concentrations were detected in the northeast of the Tomsk Region. Moreover, there was no pollutant enrichment in aspen leaves and needles, except for the Kozhevnikovsky District. The data from geoecological calculations indicated the cumulative nature of Hg levels in needles and aspen leaves for all calculated indicators, except for the Clarke of the noosphere and living matter.

Acknowledgments

This study was carried out within the framework of the state budget topic RK 121031300154-1 IK IMKES SB RAS. Research efforts were included in the development program of Tomsk Polytechnic University to make it more competitive among the world's leading research centers.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
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Distribution of mercury concentrations in lichens, mosses and larch needles in Western Siberia (according to the 2019 data)

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ABSTRACT. This paper presents data on mercury concentrations in samples of lichen and moss, as well as needles of trees (larch, cedar and pine), taken in September 2019 along a rare sampling network on the meridional transect from the Novy Urengoy area in the north to Tobolsk in the south. The mean Hg concentration (ng/g) in samples of moss, lichen and larch needles was 26, 15 and 17, respectively. The Hg concentrations in samples of annual needles of pine and cedar were below the detection limit of the method (<10 ng/g). We discuss possible factors that affect the heterogeneity of the Hg distribution in biomonitors and the discrepancy between the Hg concentrations for samples taken at the same sites. There was a systematic increase in background mercury concentration near the Novy Urengoy city and the Gubkinsky town. We assume a possible decrease in the Hg concentration in the mosses of the middle part of Western Siberia compared to its northern part.

Keywords: Hg, Arctic, Western Siberia, lichen, moss, needles, larch

1. Introduction

Mercury is a heavy metal that is hazardous for the ecosystem, which makes it relevant to identify cases of its elevated concentrations in ecosystem components. The high volatility of elemental mercury determines the dependence of its migration and distribution in ecosystem components on atmospheric transport (Carpi, 1997; De Simone et al., 2014). Covers of lichens, mosses and tree needles are natural atmospheric fallout biomonitors, and their study provides an assessment of the state of the geochemical background of some elements, including mercury (Bargagli, 2016; Vosel et al., 2021). This paper presents data on mercury concentrations in samples of lichen and moss, as well as (larch, cedar and pine), taken in September 2019 along a rare sampling network, the meridional transect from the Novy Urengoy area (north) to Tobolsk (south).

2. Material and methods

The study area includes several landscape zones: tundra, forest-tundra, taiga, and forest-steppe. Epigean lichen (*Cladonia rangiferina* (L.) Weber ex F.H.Wigg.), moss (*Hylocomium splendens* (Hedw.) Schimp., and *Cladonia stellaris* (Opiz) Pouzar & Vezda), as well as annual needles of larch (*Larix sibirica* Ledeb.), pine (*Pinus sylvestris* L.) and cedar (*Pinus sibirica* Du Tour), were selected as end-to-end objects of study. From Novy Urengoy, sampling was carried out along the highways in the direction of Omsk (south), Nadym (west), Yamburg (north), and Tazovsky (north-east). Samples were taken at a distance of 100–200 m from the road. The distance between the sampling sites in the Yamal-Nenets Autonomous Area (YNAA) ranged from 20 to 60 km, and within the Khanty-Mansi Autonomous Area – Yugra (KMAA) and the Tyumen Region, it was 80 to 150 km. In the region of the Arctic tundra, lichen covers were ubiquitous. In more southern regions lichen was less common and found in the form of small islands. Moss was less common at the sampling sites; in the northern sampling sites, areas covered with moss were represented by rare patches, and in the southern sampling points, longer moss covers could be found. Larch was most often found in the arctic and subarctic regions; in the more southern regions, there were not larch trees suitable for needle sampling at sampling sites. Pine and cedar were widespread south of Novy

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Received: June 23, 2022; ***Accepted:*** July 13, 2022;
Available online: July 31, 2022

Urengoy and almost never met further north, in the tundra zone.

Lichen and moss samples were collected in plots of 0.04-0.09 sq.m. Needle samples were taken at a height of 1-2 m. Larch needles were sampled along the entire length of the branches, and during the sampling of cedar and pine needles that formed in one season, only the meristem ends of the branches were involved. Before the determination of mercury, the samples were kept at room temperature until they acquired an air-dry state.

The bulk contents of Hg in the plant samples were measured by flameless AAS on a Lumex RA-915M Hg analyzer with a RP-91C pyrolysis attachment (analyst M.A. Gustaitis). Prior to analyses, the plant samples were reduced to a fine powder in a mortar. The technical specifications of the instrument allowed avoiding special preconditioning of solid samples. The national standard of birch leaf (LB-1) certified for heavy metals and mercury was used to calibrate the spectrometer and check the quality of analyses. Relative analytical errors did not exceed 20%. The detection limit for Hg concentrations in samples was 10 ng/g.

3. Results

The results of the mercury determination in biomonitors are presented in the sampling scheme (Fig.). Hg concentrations in the samples of annual needles of pine and cedar was below the detection limit of the method (<10 ng/g) and would not be considered further.

There was a difference in the distribution of mercury concentrations in biomonitors. The mean Hg concentrations (ng/g) in samples of moss, lichen and larch needles were 26 (min-max 17-54, SD 9, n 23), 15 (min-max (<10)-29, SD 5, n 47) and 17 (min-max 10-27, SD 4, n 28), respectively. Estimates of the mean, minimum and maximum Hg contents in moss samples were 1.5-2 times higher than the corresponding estimates in the case of lichen or larch needles. The distribution of mercury concentration in larch needles was more homogeneous (variation coefficient 24%) compared to lichens or mosses (33 and 35%, respectively). Based on the mercury concentration in lichen, there was no difference between samples taken in the north (YNAA) and in the central (KMAA, Tyumen Region) parts of Western Siberia. Based on the mercury concentrations in moss samples, there was a trend to decrease in the central part of Western Siberia. However, it should be noted that the number of samples in the central part was small.

The spatial distribution of Hg concentrations in all biomonitors indicated an increase in Hg concentration in the Novy Urengoy area. In some cases, north of Novy Urengoy towards Yamburg, elevated mercury levels in biomonitors were observed: for mosses, these sites were closer to Yamburg, and for lichens and larch needles, the corresponding sited were closer to Novy Urengoy. The area of Gubkinsky stands out: an increased Hg concentration in moss was observed to the north, and an increased Hg concentration in lichen – to the south of the town.

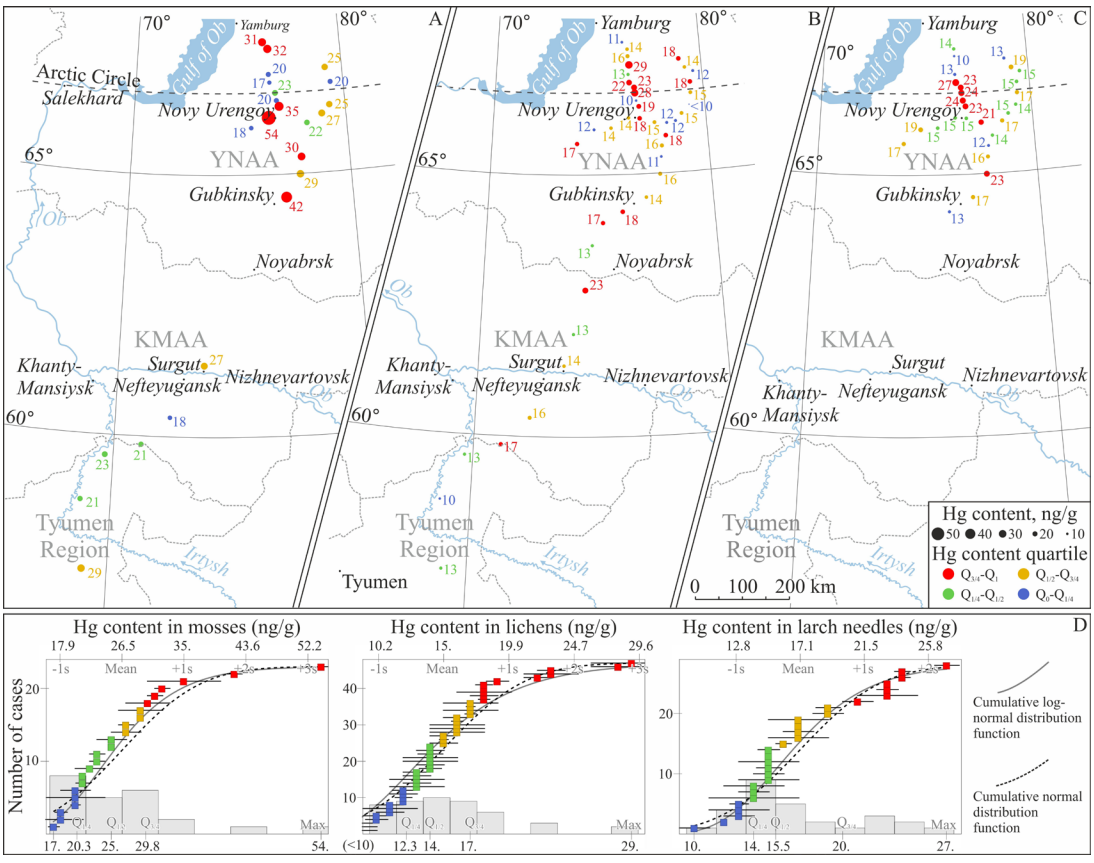

Fig. The sampling scheme (A, B and C) and distribution of mercury concentrations (D) in mosses (A), lichens (B) and larch needles (C) collected in September 2019 along the Novy Urengoy - Tobolsk transect.

4. Discussion and conclusions

We assume that the data obtained characterize the background values of Hg concentrations in the studied samples, without traces of significant pollution. It should be noted that previously (in 1998 to 2002), for lichens collected in the YNAA (without dividing into background and polluted areas), higher Hg concentrations were detected: mean value 56 (min-max 10-310, n 210) ng/g (Strakhovenko et al., 2005). Below, there is a comparison with three neighboring regions. In the eastern direction, at the Taimyr Peninsula (Krasnoyarsk Territory), according to the generalized data for 1986-2004 (Zhulidov et al., 2011), Hg concentrations in mosses and lichens were lower or comparable with the data of this study. The mean background concentrations of Hg for the mosses in this area were 14 to 21 ng/g, and for the lichens - 11 to 26 ng/g (Zhulidov et al., 2011). Shevchenko et al. (2013) and Elsakov et al. (2018) described higher background mercury levels in lichens from more western region. For lichens sampled in 2004–2006 in the White Sea catchment area in Murmansk and Arkhangelsk Region, as well as the Republic of Karelia, the mean Hg concentration was 33 (min-max 13-68, SD 14, n 25) ng/g (Shevchenko et al., 2013). For lichens sampled in 2014 and 2015 in the Kola Peninsula (Murmansk Region), in the Pasvik Nature Reserve, mean Hg concentration was 27 (min-max 14-46, SD 8, n 15) ng/g (Elsakov et al., 2018). In the southeast direction of the study area, in the Tomsk Region, higher Hg concentrations were determined in mosses and lichens collected in 2003 to 2013 (Lyapina, 2015). The mean Hg concentration was 59 (min-max 35-95) ng/g in lichen and 58 (min-max 27-90) ng/g in mosses.

Two points could explain the difference in the homogeneity of the distributions of Hg concentrations in moss and lichen samples, on the one hand, and in larch needle samples, on the other hand: i) the difference in the history of the interaction of samples with the atmosphere and ii) finding samples in different tiers of biocenosis. Mosses and lichens, unlike larch needles, are indicators of long-term Hg influx from the atmosphere with interruptions for periods of snow cover formation (October-April). Moreover, the surface position of mosses and lichens, unlike larch needles, firstly, entails a more intense effect of dust particles raised by the wind from the soil surface, and secondly, leads to the possibility of the influence of meltwater during the spring flood. In turn, one-year tree needles are an indicator of seasonal (May-September) accumulation of mercury from the atmosphere, which are not directly affected by snowmelt waters. Notably, the more than a twofold excess of Hg concentrations in larch needles compared to cedar and pine needles is fully consistent with our previous assumption about more efficient capture of dust and aerosol microparticles from the atmosphere of larch needles based on the concentration distribution of atmospheric isotopes ^{210}Pb and ^{7}Be (Belyanin et al., 2021).

The difference in the distributions of Hg concentrations in biomonitor samples in the same areas can be considered random and associated with the heterogeneous (mosaic) distribution of mercury from the atmosphere. Since in this study, during the selection of moss and lichen samples, there was no clear documentation of the age of the identified areas, this could lead to an additional complication of the result obtained. The time spent by mosses and lichens in contact with the atmosphere and episodes of spring floods should be considered factors contributing to the leaching and redistribution of Hg accumulated from the atmosphere (Bargagli, 2016). For lichens, there is a known description of mercury removal indicators for different levels of pollution, depending on the time of further staying in a clean atmosphere (Vannini et al., 2021).

The increase in mercury concentrations in biomonitors in the area of Novy Urengoy city and Gubkinsky town is possibly associated with human economic activity. It is impossible to draw a conclusion about significant regional differences in the Hg concentrations in mosses and lichens of Western Siberia based on the presented data from an irregular sparse network. However, there is a trend to a decrease in the Hg concentrations in mosses sampled in the central part of Western Siberia compared to its northern part.

Acknowledgments

The authors are grateful to V.A. Khodko for his assistance in fieldwork, and M.V. Rubanov and A.S. Shavekin for assistance in sample preparation. The study was supported by a grant from the Russian Science Foundation (project no. 18-77-10039) (including fieldwork, sample preparation). Part of the study on the determination of Hg was carried out within the framework of the state project of Institute of Geology and Mineralogy SB RAS with financial support from the Ministry of Science and Higher Education of the Russian Federation. Analytical work was carried out at the Analytical Center for multi-elemental and isotope research SB RAS.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
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Hg^{2+} incorporation in Andean Patagonian ultraoligotrophic lakes: insights into the role of pelagic protists

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ABSTRACT. In ultraoligotrophic lakes of Andean Patagonia, microbial assemblages at the base of pelagic food webs bear high THg concentrations compared to planktonic consumers. In this study, we evaluate experimentally the passive and active (trophic) uptake of Hg^{2+} using $^{197}Hg^{2+}$ to trace Hg incorporation in picoplankton (autotrophic and heterotrophic bacteria), in the photoautotrophic phytoflagellate, *Gymnodinium paradoxum*, and in the mixotrophic ciliates, *Stentor araucanus* and *Ophrydium naumanni*. The studied protists were found to incorporate substantial amounts of dissolved Hg^{2+}; however, their potential for Hg transference to higher trophic levels depends on their degree of Hg internalization (cytoplasmatic Hg), which varied widely among species.

Keywords: Andean Patagonian lakes, microbial assemblages, Hg^{2+} incorporation

1. Introduction

Andean North Patagonia has numerous deep clear ultraoligotrophic lakes (Queimaliños et al., 2012; 2019) with catchments impacted by active volcanoes of the Southern Volcanic Zone (Rizzo et al., 2014). Most of these lakes have very low levels of dissolved organic carbon (DOC < 0.7 mg L^{-1}) and, depending on the proximity to the volcanic source, show moderate to high levels of total mercury (THg), resulting in elevated THg:DOC ratios and thus, remarkable high availability for fractionation/bioaccumulation (Soto Cárdenas et al., 2018a). In the pelagic food webs of Andean Patagonian lakes, THg levels are consistently higher in the smaller planktonic fraction 10-53 μm comprising picoplanktonic and nanoplanktonic species, the main constituents of the microbial loop (Arribére et al., 2010; Rizzo et al., 2014; Soto Cárdenas et al., 2014). Larger planktonic fractions up to 200 μm, including protists and mixotrophic ciliates, rotifers and small crustaceans, show comparatively lower THg but higher levels than the fraction >200 μm (Rizzo et al., 2014; Arcagni et al., 2018).

In this investigation, we experimentally evaluate the uptake of Hg^{2+} in key components of microbial assemblages of Andean lakes, including the picocyanobacteria *Synechococcus* sp., and three protists, the photoautotrophic phytoflagellate, *Gymnodinium paradoxum* (Chromista, Dinophyceae), and the mixotrophic ciliates, *Stentor araucanus* and *Ophrydium naumanni* (Protozoa, Ciliophora, Heterotrichida), both bearing the endosymbiotic green alga *Chlorella*. We hypothesize that the passive incorporation of Hg by the different species is determined by morphological traits [surface (S), volume (V), S:V], while the active Hg^{2+} incorporation depends on the trophic transfer through picoplankton consumption.

2. Materials and methods

2.1. Sample collection and processing

Water samples for experimental purposes were collected with a Kemmerer bottle at 20 m depth in Lake Moreno West (Nahuel Huapi National Park, Patagonia, Argentina). Organisms were collected sweeping with a 10 μm plankton net from 40 m depth to surface. Water samples were sterilized by filtration (0.22 μm, PVDF membranes, Millipore) and used as the experimental culture medium. Individuals of *Gymnodinium*, *Ophrydium* and *Stentor* were separated manually with a micropipette and put in filtered water. At least 30 individuals of each species were measured under the microscope. Natural picoplankton was obtained by sequential filtration of lake water through 20 μm and 2.7 m membranes, concentrated on 0.22 μm filters and resuspended in sterile lake water. The picocyanobacteria, *Synechococcus* sp., was obtained from laboratory cultures kept in the BG-11 culture medium.

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Received: June 30, 2022; ***Accepted:*** July 14, 2022;
Available online: July 31, 2022

2.2. Experimental design

A first series of experiments was performed to study the passive Hg^{2+} incorporation (absorption and/or adsorption) in *Synechococcus*, *Stentor*, *Ophrydium*, and *Gymnodinium*. Organisms were placed in sterile lake water amended with Hg^{2+} (~8-16 ng L^{-1}) using the radioisotope $^{197}Hg^{2+}$. A second series of experiments was set up to evaluate the active uptake of Hg^{2+} in *Stentor*, *Ophrydium* and *Gymnodinium*, through similar incubations, except that we provided radiolabelled natural picoplankton (heterotrophic and autotrophic bacteria). After completing the incubations (14°C), organisms were recovered, and the activity of ^{197}Hg was evaluated according to Ribeiro Guevara et al. (2007). Three different Hg uptake factors were calculated, following Soto Cárdenas et al. (2014): a- the bioconcentration factor (BCF) based on individual Hg accumulation; b- the surface concentration factor (SCF) based on cell surface area; and, c- the volume concentration factor (VCF) indicative of the internalization of Hg^{2+}. The VCF to SCF ratio was calculated to characterize the degree of internalization.

3. Results

The S:V ratio indicated higher values in picoplankton (auto- and heterotrophic bacteria and *Synechococcus*; ca. 7.4 μm^{-1}), followed by *Gymnodinium* (ca. 0.2 μm^{-1}), *Ophrydium* (ca. 0.16 μm^{-1}) and *Stentor* (ca. 0.04 μm^{-1}).

In the passive Hg uptake experimental series, the BCF showed higher Hg^{2+} uptake in *Ophrydium*, followed by *Gymnodinium* and *Stentor*, whereas *Synechococcus* showed much lower uptake ($p < 0.001$; Fig. 1A). The SCF showed similar and much higher values in *Gymnodinium* and *Ophrydium* compared to *Stentor* and *Synechococcus* ($p < 0.001$; Fig. 1B). In terms of the VCF, *Synechococcus, Gymnodinium* and *Ophrydium* showed overall higher values than those measured in *Stentor* (Fig. 1C). The active uptake of Hg^{2+} recorded through the SCF and VCF resulted similarly higher in *Ophrydium* and *Gymnodinium* ($p > 0.05$) compared to *Stentor* ($p < 0.05$, respectively).

Stentor displayed higher active Hg^{2+} incorporation through the different bioconcentration factors compared to the passive ones ($p < 0.05$), indicating that consumption of Hg-bearing picoplankton enhanced its Hg uptake. In the case of *Gymnodinium*, the passive uptake of Hg was much higher than the active incorporation ($p < 0.05$). In contrast, *Ophrydium* had similar passive and active Hg uptake, suggesting that it can incorporate Hg from the dissolved phase and also through ingestion.

4. Discussion and conclusions

Overall, the results obtained showed that the protists studied can incorporate substantial amounts of dissolved Hg^{2+}, although their passive and active incorporation differ among species. Different patterns of Hg^{2+} incorporation were detected in the studied protists.

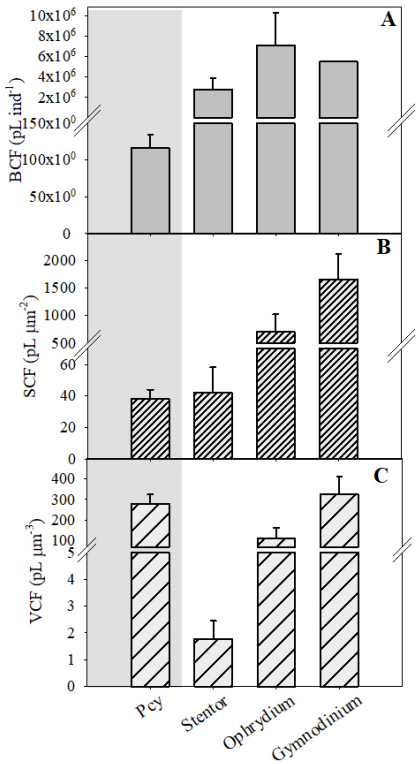

Fig.1. Hg^{2+} uptake ($^{197}Hg^{2+}$passive adsorption^{-1}) by different pelagic microbial species of Andean Patagonian lakes, measured in laboratory trials using natural lake water amended with $^{197}Hg^{2+}$ (THg:DOC = 21 ng mg^{-1}): **A**- Abundance-based Hg bioconcentration factor (BCF); **B**- Surface-based Hg concentration factor (SCF), and, **C**- Volume-based Hg concentration factor (VCF).

In autotrophic bacteria (picoplankton), Hg uptake was characterized by high internalization. The other protists showed particular Hg uptake characterized by: a- higher active than passive incorporation efficiency (*Stentor*), b- similar active and passive incorporation (*Ophrydium*) and c- higher passive incorporation (*Gymnodinium*), likely depending on their degree and mode of mixotrophy. Active Hg incorporation likely depends on bacteria consumption in *Stentor* and at a lesser extent in *Ophrydium.* In the case of *Gymnodinium*, the passive uptake clearly prevails, and the values of active incorporation recorded could be atributted to bacteria attachment to its surface rather than bacteria ingestion (Soto Cárdenas et al., 2018b).

The differences detected in the internalization of Hg^{2+} through the VCF in the different organisms tested would determine their potential for Hg transfer from the dissolved phase to the pelagic food web through consumption (Fig. 2). Higher internalization means a high potential for trophic transfer, as cytoplasmatic Hg can be more efficiently incorporated in consumers than Hg adsorbed to membranes (Wang, 2002; Twining and Fisher, 2004). These species may also transfer Hg to the benthic food web through their senescence and sinking and also regenerate Hg to the dissolved phase by excretion (Fig. 2) (Twiss and Campbell, 1995; Soto Cárdenas et al., 2014; 2018b; 2019). Thus, protists of pelagic microbial food webs of Andean lakes contribute to transfer Hg from the dissolved phase to higher trophic levels of pelagic and benthic lake food webs,

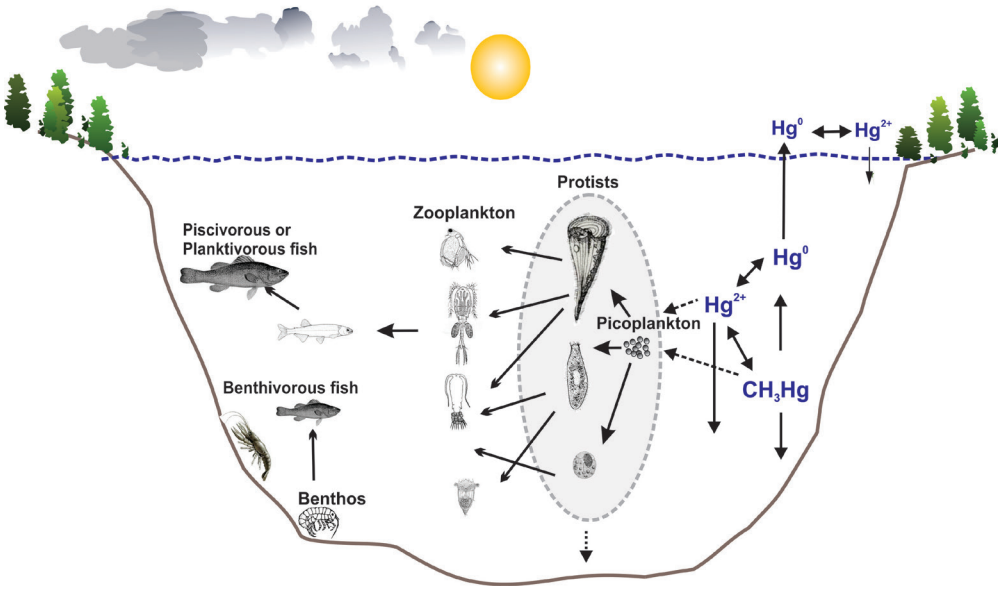

Fig.2. Schematic Hg^{2+} pathways involving pelagic microbial organisms of Andean Patagonian lakes.

linking the abiotic and biotic compartments in the Hg cycle.

Acknowledgments

This work was supported by Agencia FONCyT through the grants PICT 2018-00903 and PICT 2020-00068. The National Bureau of National Parks and the Town Council of San Carlos de Bariloche (Río Negro, Argentina) granted permission to collect samples in Lake Moreno West.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
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Mercury in the Baikal aquatic ecosystem (Lake Baikal, its tributaries, Angara River source)

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ABSTRACT. This article discusses the features of mercury distribution in the water of the Baikal ecosystem. We present an analysis of Hg concentrations in the surface and deep water of Lake Baikal, its outflow, the Angara River, and the largest tributaries of Lake Baikal. The study revealed that all significantly elevated mercury concentrations in Baikal water were preceded by earthquakes or geodynamic impacts. We propose a death of Baikal endemic species, Baikal seal, due to mercury intoxication.

Keywords: mercury, earthquake, water, Lake Baikal, tributaries, Angara River source

1. Introduction

Lake Baikal is located in the Baikal Rift Zone (BRZ) (Fig. 1.) characterized by frequent earthquakes and geodynamic impacts (Grebenshchikova et al., 2020; 2021). An average thickness of the Earth's crust under the central part of the Baikal basin is about 36 km. The basement within the southern Baikal depression appears to have a very imbricate structure due to many faults and frequent earthquakes occurring here.

Previous studies in the Baikal region revealed that significant changes in climate and water level of Lake Baikal can occur approximately in the space of a single century. It was also shown that surface water in Lake Baikal moves horizontally counterclockwise, and the water movement in its three basins is even more complex. The dynamic uplift of deep water was suggested for Lake Baikal previously (Didenkov et al., 2006; Troitskaya et al., 2022). Scientific research proved the rise of deep waters and the lowering of surface waters along the coasts (upwelling/downwelling) (Shimaraev et al., 2012).

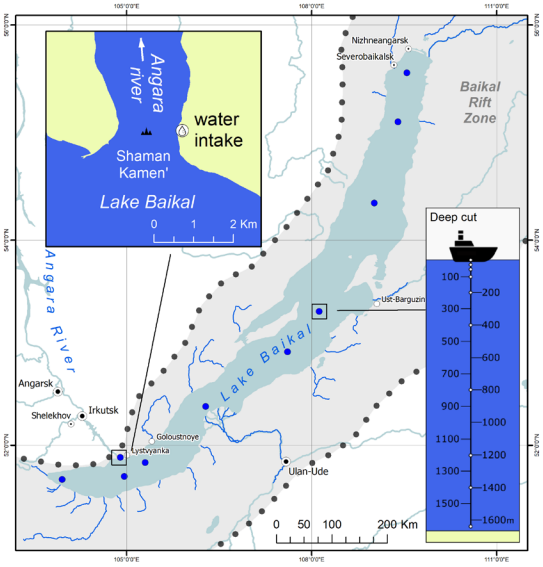

Fig.1. Scheme of water sampling in the Baikal aquatic ecosystem (Angara River source, surface and deep Baikal water, and water from the tributaries) for chemical analyses (Grebenshchikova et al., 2021).

2. Materials and methods

In winter, Lake Baikal freezes, but the water of the source of the Angara River does not freeze because warm water comes from under the ice Baikal thermocline to the Angara River. This feature makes water sampling at the river source possible all year round and, hence, long-term geochemical monitoring studies (1950-2022).

Measurements of mercury concentrations in water samples were carried out using the atomic absorption method with flameless determination of vapors of reduced atomic mercury on an RA-915+ instrument with an RP-91 attachment. The measurement accuracy was controlled by annual testing and adjustment of the instrument by the manufacturer (LUMEX, St. Petersburg). Chemical analysis of water samples was performed using the equipment of the certified Center of Collective Use for Isotope-Geochemical Research at the Institute of Geochemistry, SB RAS (Irkutsk, Russia)

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Received: June 17, 2022; ***Accepted:*** July 12, 2022;
Available online: July 31, 2022

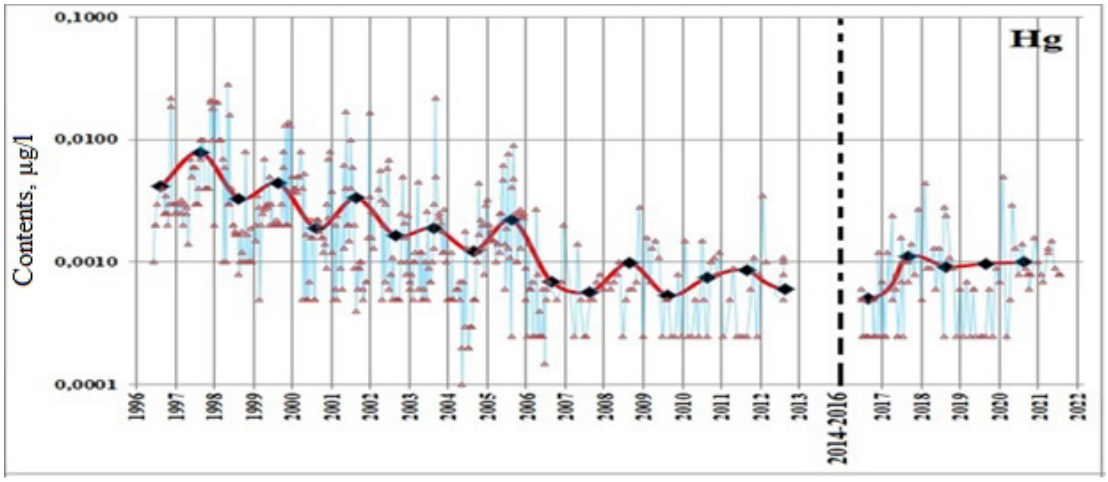

Fig.2. Distribution of Hg concentrations in the Angara River source water in 1996 to 2022.

(Skuzovatov et al., 2022). The accuracy of the results was confirmed by the analysis of reference samples of the Baikal water composition.

Monitoring (monthly) studies to analyze mercury concentrations in the water of the Angara River source have been conducting in Institute of Geochemistry SB RAS since 1997 (Fig. 2). The water samples from Lake Baikal and 30 tributaries were taken within the time span from 2007 to 2022 in the warm seasons, mainly in spring and autumn. Analytical information for about 1000 water samples from the Baikal aquatic ecosystem has been acquired by the present time. Of special interest is the study of mercury concentrations in the water of the Baikal ecosystem related to its specific chemical properties, high bioactivity, and the possible entry of mercury from the faults of the Baikal Rift Zone (Koval et al., 2003).

3. Results and discussion

The plots of time variations in the mercury concentrations in the Angara River source indicate that the most significant maxima and increased data spread were recorded between 1997 and 2000 (Fig. 2). P.V. Koval (Koval et al., 2003) called this time span a “mercury breath of Lake Baikal”. Deaths of seals were recorded on the shores of Lake Baikal during this time span. In 2001 to 2006, data volatility gradually decreased, and there were individual maxima of mercury concentrations in 2002, 2004, and 2006. Since 2007, there was a low mercury level in the water; data spread was minimum, and the small maxima were observed in 2007, 2009, and 2012 against the general quasi-stationary background.

The maximum level and increased volatility of mercury concentrations in the Angara River source between 1997 and 2000 coincided with the strong earthquake in the southern basin of Lake Baikal (February 25, 1999).

During extrapolation of the plot towards the decrease in time, the mercury concentration increased: over intervals of one month and half a month, the predictive values of the mercury concentrations amounted to approximately 0.36 and 0.64 µg/l, which exceeds the maximum permissible concentration of water bodies for fish farming (0.01 µg/l) and drinking water (0.5 µg/l) purposes. Predictive estimates differed from the actual measurements, in which the mercury concentration did not exceed 0.028 µg/l. However, these Hg concentrations indicated that, after a strong geodynamic impact or a strong earthquake, the mercury concentration may increase significantly for a short time in a local area the fault fluid discharge. Over time, the maxima of mercury concentrations dissipate through the water column to elevated and then background values (Fig. 3). The background mercury concentration in the water of Lake Baikal and the Angara River source amounts to ≤ 0.0005 µg/l.

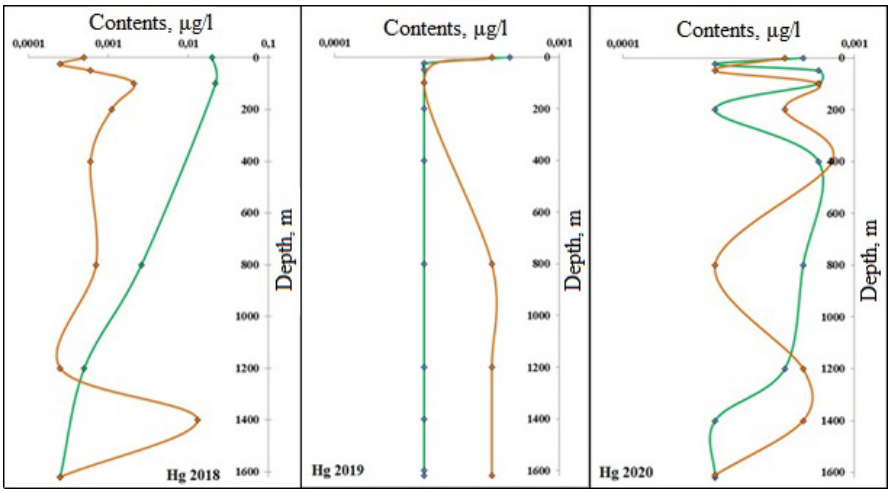

Fig.3. Distribution of Hg concentrations in Baikal water throughout the depth in 2018 to 2020.

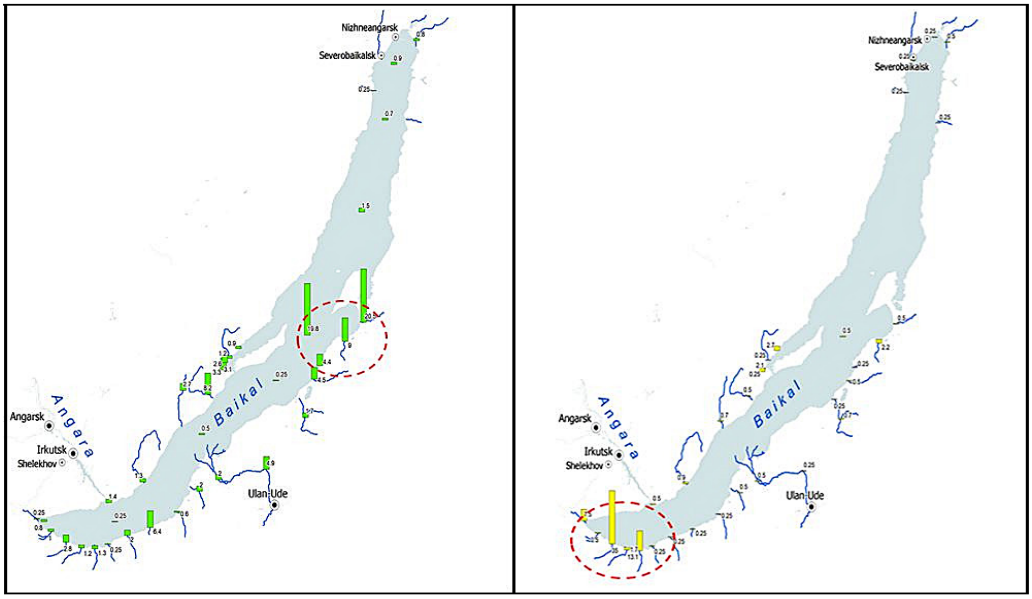

Fig.4. Distribution of mercury concentrations (n·10^{-3}) in the water of Lake Baikal, the Angara River source and the mouths of tributaries in spring (25 May 2018; green) and autumn (27 August 2018; yellow).

Sampling and analysis of water samples taken from Lake Baikal and its tributaries in the spring and autumn of 2018 during significant earthquakes and geodynamic impacts in BRZ revealed that significant maxima of mercury concentrations in the waters of Lake Baikal and some of its tributaries (Barguzin, Kultuk) coincided with earthquakes occurring here as well as with deaths of Baikal seals (red dotted line) (Fig. 4). The intoxication due to the transformation of mercury into methyl mercury in living organisms can possibly explain poisoning and death of seals.

4. Conclusions

We compared the results of estimating the mercury concentrations in the water of the Baikal ecosystem with the timing of the earthquakes of different magnitudes, which occurred at various distances from the water sampling sites. All significant maxima of mercury concentrations in the water appeared to be responses to strong geodynamic impacts. Predictive estimates of the trend for average annual mercury concentrations suggested the possibility of considerable increases in mercury concentrations in the local area of fault fluid discharge under a strong geodynamic impact. We proposed that the opening of deep faults under strong geodynamic impacts leads to decompression with boiling, degassing of mercury, and a rapid rise onto the surface along the zones of open faults.

The results obtained indicate that the state and preservation of the water in the Baikal ecosystem depend on both natural cataclysms (intoxication of seals), and anthropogenic impact. Consequently, it will be necessary to continue constant geochemical and geodynamic studies in the monitoring regime.

Acknowledgements

The studies were carried out within the framework of the State Program (Project No 0284-2021-003) and were supported by RFBR ofi_m (№ 17-29-05022).

Conflict of interest

The authors declare they have no conflict of interest.

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Short communication

ISSN 2658-3518
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Membrane analytical test system for highly sensitive determination of Hg^{2+} ions in natural waters

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ABSTRACT. A membrane test system has been developed for sensitive and specific detection of Hg^{2+} ions in natural waters. The test system uses gold nanoparticles synthesized by citrate reduction and a nitrocellulose membrane with a band of the conjugate of mercaptosuccinic acid (MSA) and bovine serum albumin (BSA). In the presence of Hg^{2+} ions, they are reduced by citrate and adsorbed on the surface of gold nanoparticles. The resulting product moves along the membrane of the test strip under the action of capillary forces and specifically binds to the MSA-BSA conjugate with the formation of a visually detectable colored band. The analysis takes 20 minutes without requiring additional manipulations or instrumentation. Under optimized conditions, the detection limit for Hg^{2+} ions was 0.13 ng/mL. The efficiency of the proposed approach was confirmed by its approbation for the control of natural waters; Hg^{2+} recovery ranged from 70 to 120%.

Keywords: non-laboratory analysis, membrane tests, environmental monitoring, control of natural waters, determination of mercury ions

1. Introduction

Currently, mercury pollution of natural objects is becoming an essential problem, which has been significantly intensified due to urbanization and the increase in industrial waste volumes. The movement and accumulation of mercury in the food chains of ecosystems cause risks to human health. The high toxicity of mercury determines the need for its monitoring in environmental objects (Gworek et al., 2020). The maximum permissible concentrations of Hg^{2+} ions in drinking water have been established by various organizations and vary from 0.5 to 6 ng/mL (US EPA, 2009; GOST, 2011; WHO, 2017). Chromatographic and electrochemical methods are mainly used to detect such low concentrations (Saleh et al., 2020). However, their implementation requires stationary expensive equipment, which limits productivity and increases the cost of testing, significantly lengthening the time required for decision making. These limitations can be overcome only with the widespread introduction into the practice of highly sensitive, productive, and simple methods of non-laboratory testing.

Membrane test systems seem to be promising tools for the rapid and selective detection of various analytes, in particular, Hg^{2+} ions (Bhang and Patel, 2021). Membrane tests make assaying extremely easy: immersion of the test strip in the sample initiates all subsequent interactions and ensures obtaining the final result. Enzymes, aptamers, and antibodies are used in such tests as recognition molecules conjugated with marker nanoparticles. Chelating agents such as derivatives of ethylenediaminetetraacetic acid are effective additional means to bind metal ions. The possibility of Hg^{2+} ions detection through the formation of an amalgam with another metal, Ag or Au, was also shown, and the selectivity of Hg^{2+} detection in this way is ensured through its high affinity to gold nanoparticles (Mertens et al., 2011).

The principle implemented in this study consists of the interaction of mercury ions with gold nanoparticles (AuNPs) and citrate ions immobilized on their surface, followed by complexation with mercaptosuccinic acid (MSA) in the test zone of the membrane. Thus, contact of the test strip with the sample without any additional action leads to the appearance of a colored zone on the membrane.

2. Materials and methods

Aqueous solutions of metal ions (Hg^{2+}, Cd^{2+}, As^{3+}, Cu^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Fe^{3+}, and Pb^{2+}) were prepared by diluting the initial standards (Center for Standardization of

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Received: July 12, 2022; ***Accepted:*** July 14, 2022;
Available online: July 31, 2022

Samples and Highly Pure Substances, Russia) with a concentration of 1 mg/mL.

AuNPs were synthesized by mixing 100 mL of 0.01% $HAuCl_4$ (Sigma-Aldrich, USA) with 1.5 mL of 1% sodium citrate (Sigma-Aldrich, USA) and incubating at 100°C for 15 min. 10% Tween-20 (10 μL per 1 mL of AuNPs) was added to the resulting product, cooled to room temperature, and incubated for 1 h. The resulting preparation was separated by precipitation at 8,000 g for 15 min and redissolved in deionized water.

The MSA-BSA conjugate was synthesized by adding 450 μL of MSA solution (4.4 mg/mL in citrate buffer, pH 4.0) and 10 mg of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (Sigma-Aldrich, USA) to 200 μL of an aqueous solution of BSA (10 mg/mL). The reaction mixture was incubated for 2 h at room temperature with continuous stirring. The resulting conjugate was dialyzed against 10 mM phosphate-buffered saline (PBS, pH 7.4) with a three-fold wash using Amicon-30 membrane (Merck Millipore, USA).

The test strips were made using the CNPH-90 nitrocellulose membrane as the working membrane, the PT-R7 glass fiber membrane as the membrane for the nanoparticle conjugate, and the AP045 adsorbing membrane as the final absorbent membrane. All membranes were manufactured by Advanced Microdevices, India. To form a test zone, the MSA-BSA conjugate (0.5 mg/mL in 10 mM PBS) was applied to the working membrane using IsoFlow automatic dispenser (Imagene Technology, USA). To cut the test strips 3.5 mm wide, an Index Cutter-1 automatic guillotine cutter (A-Point Technologies, USA) was used.

To carry out the testing, the edge of the test strip was immersed in the sample for 10 min and then placed to dry for 10 min on a horizontal surface. The CanoScan 9000F scanner (Canon, Japan) was used to register the assay results. The staining intensity of the test areas was calculated using the TotalLab TL120 program (Nonlinear Dynamics, UK).

3. Results and discussion

The scheme for the colorimetric determination of Hg^{2+} ions is shown in Fig. 1. Citrate ions located on the AuNPs surface ensure the reduction of Hg^{2+} to Hg^0 (Ojea-Jiménez et al., 2012). In the presence of Hg^{2+}, reduced elemental mercury is deposited on the AuNPs' surface due to its high affinity to gold. Additionally, gold atoms act as catalysts of the amalgamation process. Due to this, the mercury-modified nanoparticles, passing along the test zone with the liquid flow, bind to the thiol groups of the immobilized MSA-BSA conjugate. In the absence of Hg^{2+} ions, AuNPs stabilized with Tween-20 detergent migrate along the membrane, passing the test zone.

In the course of the work, the optimal conditions for Hg^{2+} ions detection were established: the concentration of the MSA-BSA conjugate applied to the test zone was 0.5 mg/mL; medium for the standard (calibration) solutions preparation – citrate buffer, pH 4.0; concentration of detergent Tween-20 – 1%; color development time – 10 min.

Solutions of Hg^{2+} ions with concentrations of 0.1 to 100 ng/mL were tested under the given optimal conditions. The intensity of the test zone is correlated with the concentration of Hg^{2+} ions. Fig. 2 shows the calibration curve for the detection of Hg^{2+} ions in the range from 0 to 25 ng/mL, which a linear approximation with high accuracy describes. The detection limit for Hg^{2+} ions calculated by the 3σ method was 0.13 ng/mL (0.64 nM).

The selectivity of the proposed technique was characterized using solutions of other toxic metal ions (Pb^{2+}, Ag^{+}, Ba^{2+}, Co^{2+}, Sb^{3+}, Cd^{2+}, Sn^{4+}, Fe^{3+}, Cu^{2+}, As^{3+}, and Ni^{2+}) and cations that are present in large amounts in natural waters (Ca^{2+} and Mg^{2+}). Even with a 100-fold excess of alternative cations, the specific signal exceeds the nonspecific one more than 9 times, demonstrating the high selectivity of the developed test system with respect to Hg^{2+} ions.

To evaluate a practical application, water samples (waterfall and spring) with added known concentrations of Hg^{2+} ions were analyzed. Photos of the test strips after sample analysis are shown in Fig. 3. The recovery of Hg^{2+} detection was within the acceptable limits of 113-120% and 70-100% for spring water and waterfall, respectively. These results confirm the suitability of the developed test system for the detection of Hg^{2+} ions in natural waters.

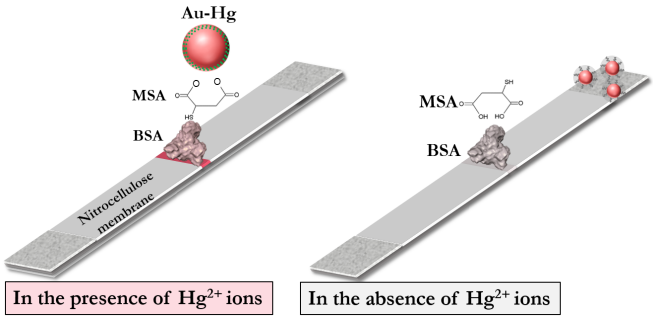

Fig.1. The proposed principle of operation of the test-system for the Hg^{2+} ions detection.

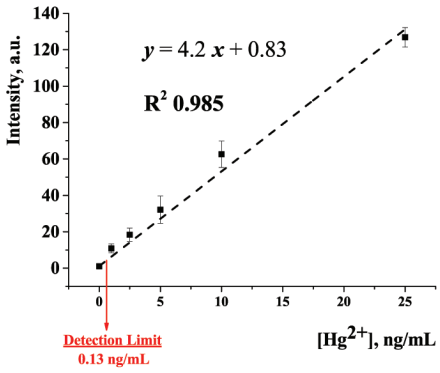

Fig.2. Calibration curve of Hg^{2+} ions.

4. Conclusions

We have proposed a membrane analytical test-system for selective and highly sensitive determination of Hg^{2+} ions. This technique combines the maximum simplicity of analysis, the clarity, and reliability of its results. Analytical characteristics were determined under the optimized conditions, demonstrating the prospects of the developed approach for Hg^{2+} ions determination in natural waters. Moreover, comparison with conventional analytical methods has revealed that the proposed approach is simple to perform, more economical, and exhibits high sensitivity and excellent selectivity.

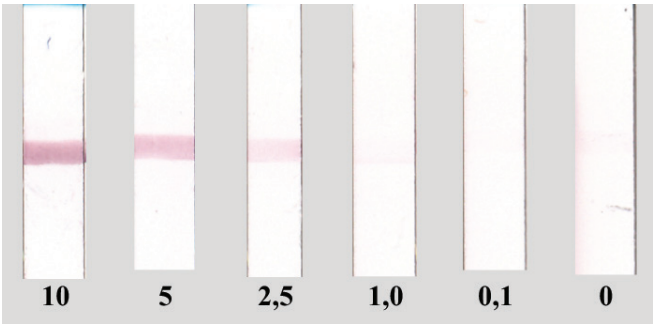

Fig.3. Results of testing spring water samples with different concentrations of Hg^{2+} ions (ng/mL).

Acknowledgments

This work was financially supported by the Russian Science Foundation (grant no. 22-23-00859).

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
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Characteristics of Hg accumulation in mushrooms and fish in areas disturbed by mining activity (Western Siberia)

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ABSTRACT. We studied the distribution of Hg in mushrooms and fish on the example of three objects (Kurai mercury zone, Ursk ore field and Saralinsk ore field) located in the area with the elevated geochemical background of this element (Altai-Sayan province) and affected by the mining waste. Maximum mercury concentrations in mushrooms and fish were observed in the Ursk ore field. Both in mushrooms and in fish, Hg concentrations exceeded MPC, posing significant human health risks if consumed.

Keywords: mercury, fish, mushrooms, bioconcentration factor

1. Introduction

The impact of food polluted by potentially toxic elements on human health is recognised as a global problem (Franco-Uría et al., 2009; Machado et al., 2017). Anthropogenic activity and industry led to a significant release of heavy metals and other pollutants into the environment (Hajeb et al., 2009).

Mushrooms and fish, being a source of various minerals and vitamins, can actively accumulate heavy metals, which allows considering them a source of chronic poisoning of people (Racz et al., 1996). Mercury occupies a special position among toxicants because it has a wide variety of chemical forms in nature, and its compounds are extremely toxic, especially in the form of methylmercury (Kuzubova et al., 2000). World Health Organization established the values of the maximum weekly human intakes of total mercury and methylmercury at a level of 300 and 200 μg, respectively. However, some species of higher fungi accumulate mercury in their sporocarps in higher concentrations, up to 32 μg/g (Gustaitis et al., 2016). Also, these food products can be indicators of mercury pollution in the environment. This study aimed to identify the characteristics of Hg accumulation in food products in areas with elevated geochemical background of this element and additional technogenic activities.

2. Materials and methods

Three objects within the Altai-Sayan mercury province were selected for the study. The first object belongs to the Kurai mercury zone of Gorny Altai (Ulagan District, Aktash settlement) where the deposits and ore occurrences of Hg are located with a high density. Near the Aktash settlement, there are remains of the Aktash Mining and Metallurgical Enterprise (AMME) that develops the mercury deposit of the same name. This area is recognised as a territory with a high level of accumulated environmental damage. The AMME dumps of are stored on the banks of the Yarly-Amry River and are carried into it by rains, melt water and wind. Soils of intermountain basins are used in agriculture, but their formation occurs with active participation of matter brought from other geomorphological positions (Robertus et al., 2015).

The second object is located within the Salair mercury zone in the Ursk volcanoplutonic structure of the Salair Ridge (Kemerovo Region, Ursk settlement), in the area of Novo-Ursk gold-bearing sulfide ore deposit and its tailings dumps. Cyanidation and amalgamation waste are carried to a waterlogged ravine (Myagkaya et al., 2022). Initially, Hg was present in ores in the form of cinnabar, thin inclusions of mercury telluride and mercury selenide in pyrite and barite. We also assume that Hg is present in pyrite in the form of an isomorphic admixture and as a physically sorbed form ($HgCl_2$ and Hg^0) that, according to some data, can be localised in crystal defects (Gustaitis et al., 2010).

The third object is located within the Saralinsk ore field in the area of the Kuznetsk Alatau (Ordzhonikidzevsky District, Priiskovy settlement and Ordzhonikidzevsky settlement, the Republic of Khakassia) and has belonged to the mining industry

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Received: July 14, 2022; ***Accepted:*** July 15, 2022;
Available online: July 31, 2022

(Au mining) since 1834. Initially, Au was mined from placers and ores by amalgamation (Shirokikh et al., 1998). The Saralinsk tailings dump of gold-bearing sulfide ores is situated in close proximity to the Priiskovy settlement; nearby areas (Ordzhonikidzevsky settlement) experience the anthropogenic impact of the mining industry.

Samples of fish and mushrooms were taken for the study within the selected study objects. Fish samples were divided according to the food type (predators and nonpredators); mushroom samples – according to the species (agaricales and spongy). To calculate the bioconcentration factor (BCF) (BCF; Formula 1), soil and water were sampled together with mushrooms and fish, respectively.

$$BCF = \frac{C_{foodproduct}}{C_{habitat}} \qquad \text{Formula 1,}$$

where $C_{food\ product}$ is Hg concentration in mushrooms or fish (μg/g), and $C_{habitat}$ –Hg concentration in soil or water (μg/g or μg/L).

In the Kurai mercury zone, four sites were tested (Lake Cheybekkel, Lake Geizernoe and water bodies in the Aktash settlement and Kurai steppe). The Kurai steppe was considered a background site because it is a zone of removal of matter from the surrounding areas. In the Ursk ore field, three sites were tested (water bodies above the influence of the tailings dump considered as background, water bodies in the area of the tailings dump and water bodies in the influence zone of the tailings dump). In the Saralinsk ore field, three sites were tested (water bodies in the surroundings of the Priiskovy settlement, including the Bezymyanny stream, and water bodies near the tailings dump in the Priiskovy settlement).

Muscle tissue weighing 20 to 25 gram was sampled immediately after catching fish with a plastic tool (Popov et al., 2018). Soil was sampled using a ring with a diameter of 10 cm in depth by the indentation technique. The samples (soil, mushrooms and fish) were dried under laboratory conditions to an air-dry state at 20–22 °C, avoiding exposure to sunlight.

The Hg concentration in water was determined by the cold vapor method, followed by atomic absorption detection (AAS; RA-915M analyzer with the RP-92 attachment manufactured by Lumex (Russia) (ISO 12846-2012). Detection limit was 0.02 μg/L; the method error was up to 20%. The total Hg concentration in solid samples was determined by AAS (RA-915M analyzer with the RP-91C pyrolytic attachment according to the PND F 16.1:2:2.2.80-2013 (M 03-09-2013) method). The detection limit was 0.01 μg/g; the method error was less than 20%. The correctness of Hg measurements was controlled using standard samples of the SDPS-3 composition (sod-podzolic soil) and ERM-CE464 (Tuna fish).

3. Results and discussion

Edible mushrooms tend to accumulate toxic elements in areas of industrial emissions. Moreover, this ability is manifested in them much greater than in higher plants and other organisms (Gorbunova, 1999). Hg concentration in mushrooms from the studied sites varied from 0.052 to 32 μg/g (Fig. 1). Mushrooms from the studied areas were divided into agaricales and spongy, but we did not detect any difference in Hg accumulation. Notably, Hg concentrations did not exceed MPCs at all studied sites. MPCs were 1.2 to 34 times exceeded in the Saralinsk ore field, 4 to 80 times – in the Kuray mercury zone, and from 3.4 to 642 times (the maximum value among all objects) – in the Ursk ore field.

The BCF values for mushrooms indicated (Fig. 1) that the highest Hg concentration was observed in the Ursk ore field. Within the Kurai ore zone, active mercury accumulation occurred near Lake Geizernoe; within the Usk ore field – near ore dumps. In the Saralinsk ore field, the maximum BCF was recorded in the vicinity of the Priiskovy settlement located near the tailings dump. The concentration degrees in the studied objects varied from low to moderate.

Hg concentrations in fish of all objects ranged from 0.02 to 1.35 μg/g (Fig. 2). In the Kurai mercury zone, there was no excess of MPC in fish, while mercury concentrations in fish from the studied sites in the Ursk ore field and the Saralinsk ore field exceeded MPC (2-4 times and 2.4 times, respectively, according to SanPiN 2.3.2). BCF values for fish (Fig. 2) indicated the active mercury accumuation in the area of the Ursk ore field both at background sites and in water bodies subjected to technogenic impact. In the Saralinsk ore field, mercury absorption in fish was active only in water bodies subjected to technogenic impact. The concentration degree in the studied objects was classified as low. Notably, individuals of predatory fish species sampled in the water bodies of the Saralinsk

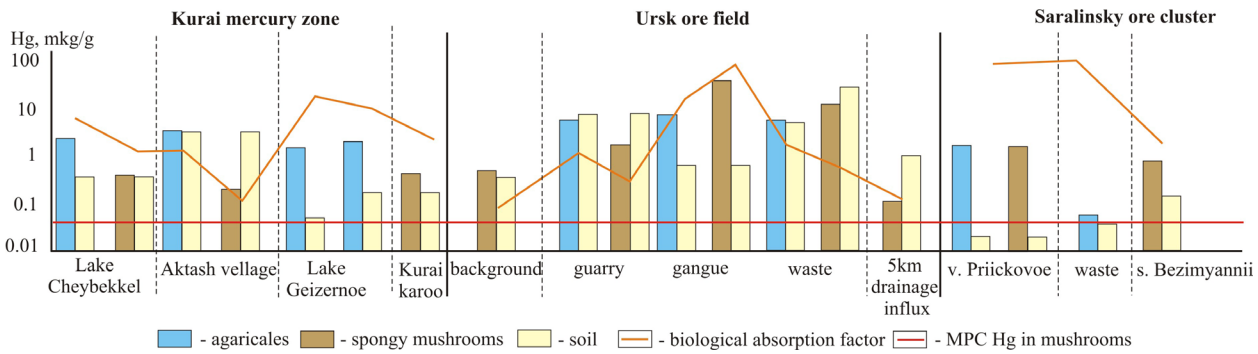

Fig.1. Mercury distribution in soil-mushrooms of the studied areas.

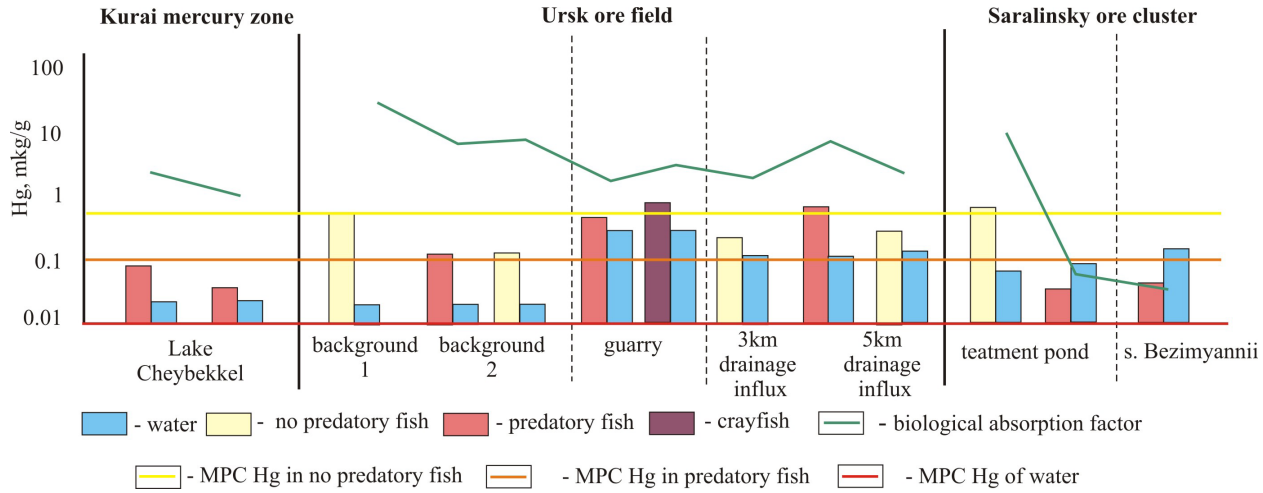

Fig.2. Mercury distribution in the water-fish system of the study areas.

ore field had much lower mercury concentrations than other studied species. This was likely due to the small length of the studied fish (8-10 cm) than the peculiarity of this species. However, according to the literature, 95% of the organic mercury in fish was present in the methylated form (Watras and et al., 1995). Therefore, the consumption of fish in the studied areas is extremely dangerous.

4. Conclusions

This study revealed that in areas subject to technogenic pressure in the form of mining waste, Hg was actively accumulated in mushrooms and fish. In areas with elevated geochemical background of Hg (mercury province) without technogenic pressure, there was less active mercury accumulation in mushrooms and fish.

Acknowledgements

This study was partially carried out within the framework of the IGM SB RAS State Project at the Analytical Centre for multi-elemental and isotope research of IGM SB RAS. Samples of the Kurai mercury zone were studied with the support of the RSF project No 18-77-10056.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

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Technology for the treatment of mercury-containing wastes

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ABSTRACT. We have developed an efficient and environmentally friendly technology based on a combination of mechanical treatment and chemical immobilization to demercurize mercury-containing waste.

Keywords: mercury-containing wastes, gravitational concentration, chemical immobilization of mercury

1. Introduction

The development of technologies for demercurization of mercury-containing wastes is an extremely urgent problem, as mercury is a known super-toxicant. Mercury pollution in Russia is related to the activity of industrial facilities that produce mercury and its compounds, manufacture mercury-containing products (e.g. light bulbs), or use mercury in production cycles. These facilities produce mercury-containing wastes (MCW) that have the potential to poison the environment.

Moreover, the abrupt closure of companies that have used mercury in production cycles, and, hence, the "abandoned" state of facilities with unused raw materials and other chemicals results in mercury pollution of production buildings and facilities and the environment. In these cases, the prevention of mercury pollution depends mainly on the effectiveness of the technologies used to neutralize mercury-containing waste. Currently, the methods based on the combination of the extraction of metallic mercury from MCW and subsequent conversion of sorbed non-recoverable mercury into an insoluble compound, with the final product not exceeding the fourth hazard class, are considered the most promising and environmentally friendly (Levchenko L.M. 2010, 2012, 2014; Minin V.A. 2015, 2021).

The aim of this work was to develop a technology for the demercurization of solid waste based on gravity separation combined with subsequent chemical treatment. In this technology, metallic mercury is supposed to be extracted with a centrifuge-like equipment, and the non-recoverable mercury is to be converted into mercury sulfide that belongs to the fourth hazard class according to the Russian classification.

2. Materials and methods

2.1 Materials

Mercury-containing waste (MCW) with low mercury content (three or four groups according to the national standard GOST R 52105-2003) was used to develop a technology for the demercurization of solid waste. The technology was developed based on the requirements of GOST 12.3.031, taking into account that, according to the requirements of GOST 17.2.3.02 and GOST 12.1.005, the developed technology should ensure the conversion of mercury or its compounds into low volatile and low soluble states.

The MCW used were soils, construction debris, metal parts, and other materials generated from the removal of buildings and facilities where mercury production cycles were conducted. All industrial wastes containing mercury are classified as extremely hazardous wastes (Hazard Class I) according to the Federal Waste Classification Catalog (approved by the Order of the Ministry of Natural Resources of Russia dated 02.12.2002 No. 786). Most of the MCW were construction wastes: fragments of various sizes resulting from the destruction of reinforced concrete and bricks or other parts of buildings and their plastered surfaces. Soils heavily contaminated with mercury were materials of various grain sizes, in which mercury was present in the form of liquid droplets. The coarse clastic fraction consisted of crushed stone and construction debris fragments; in this part, the mercury content was close to the MPC. The fine-grained fraction consisted of clay-sand material, in which most of the mercury was accumulated (> 100 MPC). Metallic mercury and its compounds were present in this material as fine particles in a "free" or adsorbed state. The bulk density

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Received: June 15, 2022; ***Accepted:*** July 15, 2022;
Available online: July 31, 2022

ranged from 1.5 t/m^3 (gypsum and soil) to 3.0 t/m3 (reinforced concrete), depending on the composition of the waste.

2.2. Methods used

The following methods were used in this study to determine mercury concentrations and the component composition of MCW.

Powder diffractograms of MCW were recorded using a Shimadzu XRD-7000 diffractometer. The IR transmission spectra were recorded in the range of 350 to 4000 cm-1 using a Fourier IR spectrophotometer SCIMITAR FTS 2000 series (DIGILAB). Samples for the FTIR studies were prepared by mixing and grinding 1.0 mg of sample with 3 g of dried KBr, followed by tableting.

The analysis of mercury concentration in MCW was carried out by the AAS method (Yuliya analyzer) in accordance with GOST Z 51768-2001 and PNDF 14.1.2.20-95. The microelement composition of the studied MCW samples was characterized using atomic emission spectrometry with arc excitation (DPT AES). The analysis was performed using a PGS-2 spectrometer (Carl Zeiss Jena, Germany) with a diffraction grating as a dispersion element and a photodiode array to record the spectra. A double-lens slit illumination system with 20μm width was used. The magnitude of the arc discharge current was 10 A, and the exposure time was 18 seconds. Prior to analysis, the electrodes were cleared of surface contamination by preignition at a current of 12 A for 20 seconds.

3. Results

3.1. Material composition

Typical production waste (construction waste and soil) was powders, various colors from brick to dark brown. In the diffraction patterns of RSO powders (construction waste and soil), only the crystalline phase of SiO_2 was detected. Waste composition based on chemical analysis, % wt.: silicon oxide - 92; aluminosilicates 6-8; mercury - 10-0.0004; iron - 0.1; calcium - 0.1; magnesium - 0.3; manganese - 0.1, and titanium - 0.15.

In the IR spectra, intense bands were observed in the region of 1084-1036 cm-1, which corresponds to the stretching vibrations of Si-O. Additionally, the presence of water was observed; absorption bands were recorded in 3437 cm-1 and 3432 cm-1, which was related to the stretching and bending vibrations of H_2O. In soil samples, calcium hydroxide (3618 cm-1) was also observed. In the region of 600-400 cm^{-1}, oscillations of the aluminosilicate frame appeared. Vibration bands in 420-534 cm^{-1} were vibrations of the SiO_4 layer, tetrahedra. Bands in 797 cm^{-1} and 779 cm^{-1} were bending vibrations of Si-O. The absorption bands in 1422–1432 cm^{-1} and the shoulder in 876 cm^{-1} referred to vibrations of the C = O bond in carbonate. Quartz, aluminosilicates, carbonates and calcium hydroxides represented the mineral composition of RSO (construction waste and soil) was represented.

To determine the mercury concentration in RSO, the method of dissolving mercury in nitric acid was used. The procedure was as follows: five parallel weighings of 1 g of soil (G1-G5) were repeatedly washed alternately with nitric acid and water, then the washing solutions were brought to the mark in volumetric flasks of 100 ml. For analysis, the resulting solutions were diluted 5000 times. The mean mercury concentration in the soil determined by the AAS method was 3.94 ± 0.40 mg/g. In WRS samples, mercury concentrations varied from 0.05-0.06 mg/g to 50-60 mg/kg, while the MPC level for soils was 2.1 mg/kg, i.e. there was an excess of MPC.

3.2. RSO demercurization technology

The technological scheme for the neutralization of RSO is based on the gravitational method of separation of metallic mercury in water and the method of chemical immobilization of mercury in a pilot plant. According to the scheme, construction waste and soils initially pass through two stages of crushing (jaw and roller crushers); in the case of large blocks of construction waste, additional separation is carried out in a butare. Crushed material with a particle size of less than 2 mm from the crusher in the form of pulp is supplied by a sand pump for gravity enrichment to the Itomak KG-2.0 centrifugal concentrator with the production of metallic mercury, concentrate, cake and tailings. The concentrate is used to isolate metallic mercury, and the remaining tails and cake after filtration are immobilized in two stages: oxidation and the formation of mercury sulfide in waste. The enrichment tailings are constantly washed and transported by the stream into a transfer tank with a volume of 0.2 m^2 and are fed for dehydration by the PVP 12.5 / 12.5 sand pump, while the concentrate remains in the conical bowl and is periodically unloaded into the concentrate tank, from where it enters for finishing at the concentration table SKO-0.5. Cake, material dehydrated to 20-30% moisture content, is removed with a knife device from the surface of the drum fabric into a receiving funnel and then enters the immobilizer into the mercury immobilization apparatus through the chute, in which the process of chemical immobilization of mercury adsorbed on the surface of construction waste is carried out. From the container, the decontaminated waste is reloaded into the container; samples are taken from which the hazard class of the waste is determined.

4. Discussion

We have demonstrated that the MCW processing consists of four stages. Stage 1. Mercury contaminated soils, wastes or sludges are separated according to their size (particles larger than 2 mm and smaller). Particles from the larger fraction are crushed to a size of less than 2 mm, then particles from both streams are combined and processed into slurry. Stage 2. The slurry enters the gravity separator (series ITOMAK KG) where metallic mercury is extracted by gravity separation. Stage 3. The slurry separated from metallic mercury is sent to the

reactor for chemical immobilization of the remaining mercury with calcium polysulfide. Stage 4. Dehydration of the slurry with a filter press. The cake is taken to the MCW landfill as waste of hazard class IV -V, and the water is returned to the technological process, with the aspiration system ensuring that possible mercury vapor emissions in the work area and beyond are removed and neutralized.

The mercury remaining after gravitational separation is chemically inactivated by converting it to the ionic form (Hg^{2+}) with an oxidant containing active chlorine and then treated with a solution of calcium polysulfide. The resulting compound, mercury sulfide, HgS(II), is sparingly soluble and volatile and does not pose an environmental hazard.

The technological performance indicators of the treatment plant are as follows: maximum productivity for the feedstock up to 0.2 t/h; maximum fineness of the source material is 70 mm; circulating water supply, maximum water consumption of the process water, m3/h; maximum power consumption (3 x 220/380V, 50Hz), kW 55.6; outside air temperature +1°C - + 45°C.

5. Conclusions

The processing 500 kg of processed soils and 800 kg of processed construction waste revealed that MCW demercurization technology enabled extraction of up to 98% of metallic mercury from soils and up to 80% from construction waste.

The residual amounts of mercury in construction waste and soils were converted into low- soluble mercury sulfide using a solution of calcium polysulfide whereupon the content of unbound mercury in the water extracts from the demercurized samples turned out to be below the detection limits of the AAS method (0.0005 mg/l). According to the results of biotesting, the demercurized wastes were classified as hazard class IV wastes.

Ackhowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, NIIC SB RAS No. 121031700321-3.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Air mercury monitoring in the Baikal area (2011-2021)

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ABSTRACT. We present long-term (2011 – 2021) data on air mercury monitoring that was started within the GMOS (Global Mercury Observation System) project (2011-2015) at the Listvyanka station located on the shore of Lake Baikal, Siberia. Monitoring shows an obvious seasonal variation in the background mercury concentration in the air, which increases in the cold season and decreases in the warm season. Short-term anomalies are associated with the wind carrying air from industrial areas where several large coal-fired power plants are located (Irkutsk and Angarsk). A positive correlation between mercury, SO_2 and NO_2 concentrations is observed both in short-term variations and in average monthly concentrations. The analysis of the forward and backward trajectories obtained with the HYSPLIT model demonstrates possible mercury emission sources. Concentration-weighted trajectory (CWT) analysis has revealed potential remote regions of mercury emissions from where mercury can be transported by air masses to the area of Lake Baikal, including the territories of Transbaikalia and Mongolia (Erdenet). During the 2018 cruise, the continuous air mercury survey above Lake Baikal covered 1800 km. The mean mercury concentration above Lake Baikal is significantly lower than the mean value obtained at the onshore Listvyanka station during the same days of the cruise. That can lead to the conclusion that Lake Baikal is a sink of atmospheric mercury.

Keywords: Lake Baikal, air mercury monitoring, seasonal and short-term variability, sources of emissions, coal-fired power plants

1. Introduction

Within the GMOS project, air mercury monitoring has been running since November 2011 at the Listvyanka station located on the SW shore of Lake Baikal (Sprovieri et al., 2016). In July 2018, for the first time, air mercury survey was carried out throughout the Baikal area during the cruise onboard the research vessel (RV) "Akademik Koptyug" (Mashyanov et al., 2021).

2. Materials and methods

Long-term air mercury measurements at the Listvyanka station were carried out using a Lumex RA-915AM air mercury monitor; air measurements during the RV cruise – with a RA-915M multifunctional portable analyzer. The principle of operation of both systems is based on differential atomic absorption spectroscopy with the Zeeman background correction (Sholupov et al., 2004) that provides continuous background GEM (gaseous elemental mercury) monitoring in compliance with EN 15852 standard. During the cruise around Lake Baikal, the air mercury survey was performed with two portable RA-915M mercury analyzers operating concurrently. Data were collected continuously with a response time of 1 s, averaging over 4 min, and zero control every 5 min; the detection limit was 0.6 ng/m^3. The RA-915M analyzer with the PYRO-915$^+$ attachment was also used for PBM (particulate bound mercury) determination. The following atmospheric gases were monitored together with GEM at a time resolution of 1–2 min: SO_2, NO, NO_2, CO, CO_2, O_3, and some others (Obolkin et al., 2014).

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Received: July 12, 2022; ***Accepted:*** July 15, 2022;
Available online: July 31, 2022

3. Results and discussion

Continuous automatic monitoring of mercury at the Listvyanka monitoring station shows the mean GEM concentration of 1.59 ng/m^3 throughout the 2011-2021 observation years. PBM amounts to 0.7 % of GEM.

3.1. Seasonal variations

The obtained data show an obvious seasonal variation in the background mercury concentration in air (both GEM and PBM), increasing in the cold seasons (November – February) with the mean GEM of 1.74 (1.56 - 1.95) ng/m^3, and decreasing in warm seasons (June – September) averaging 1.43 (1.12 – 1.63) ng/m^3 (Fig. 1A); the same seasonal variation shows PBM since January 2016 to March 2017 (Fig. 1B).

Seasonal variations of both GEM and PBM types are obviously due to elevated mercury emissions from coal combustion during the cold season, giving rise to background mercury concentrations at regional and global levels.

3.2. Short-term variations

Short-term (minutes – hours) anomalies of the mercury concentration can reach values of 5-7, sometimes 15-20 ng/m^3. Long-term monitoring shows a positive correlation of GEM peaks with the local anomalies of acid gases typical of coal combustion emissions such as SO_2 and NO_2.

To assess the relationship between mercury and acid gas anomalies recorded at the Listvyanka station and the sources of industrial emissions, we used the HYSPLIT model (Cheng et al., 2013; 2015; Rolph et al., 2017) with air mass trajectory calculation at the three vertical levels of 50, 150 and 500 m. An example of long-distance transport of air pollutants is shown in Fig. 2. The correlated maxima of SO_2 and GEM concentrations at the Listvyanka monitoring station are observed during superposition of air masses carrying plumes of coal-fired power plants from the Angarsk, Irkutsk and Shelekhov cities (Mashyanov et al., 2021).

The monitoring data also indicate that forest fires could be a significant source of mercury and can contribute to the increase in the average monthly concentration, for example, 1.73 and 1.94 ng/m^3 in June 2019 and July 2020, respectively.

3.3. Mercury in the air above Lake Baikal

In July 2018, the air mercury survey was carried out throughout the Baikal area during the cruise onboard the RV “Akademik Koptyug”. The continuous air mercury survey above Lake Baikal covered 1800 km. During the cruise, there no significant anomalies of mercury concentration in the air above the lake (Fig. 3A). Concentration-weighted trajectory (CWT) method based on the backward trajectories of air masses (Cheng et al., 2015; Kalinchuk et al., 2021) revealed several potential areas of mercury emissions (Fig. 3B).

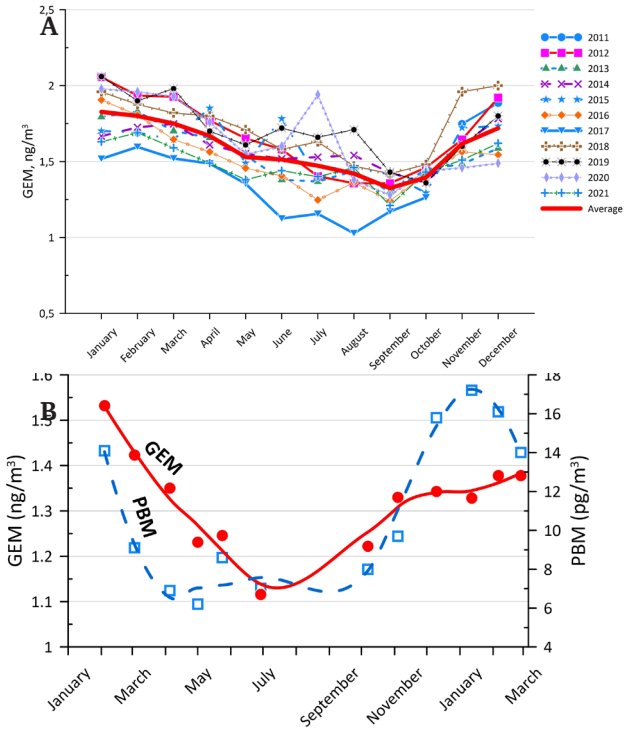

Fig.1. Seasonal variation in GEM between 2011 and 2021 (**A**) and PBM between 2016 and 2017 (**B**); average monthly value.

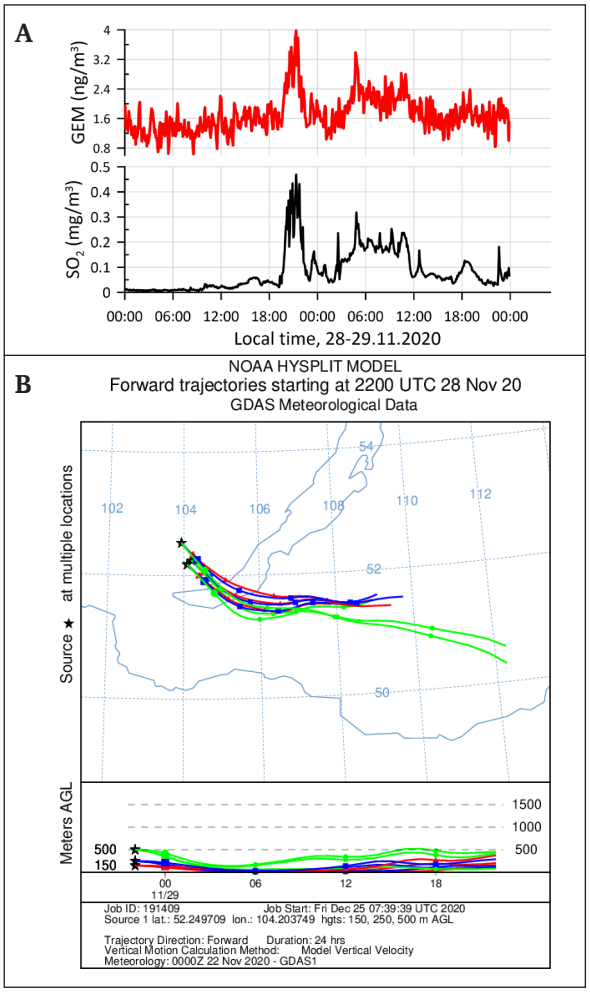

Fig.2. Superposition of the plumes from industrial emissions sources: SO_2 and Hg concentration (**A**); forward air trajectories modelling (**B**).

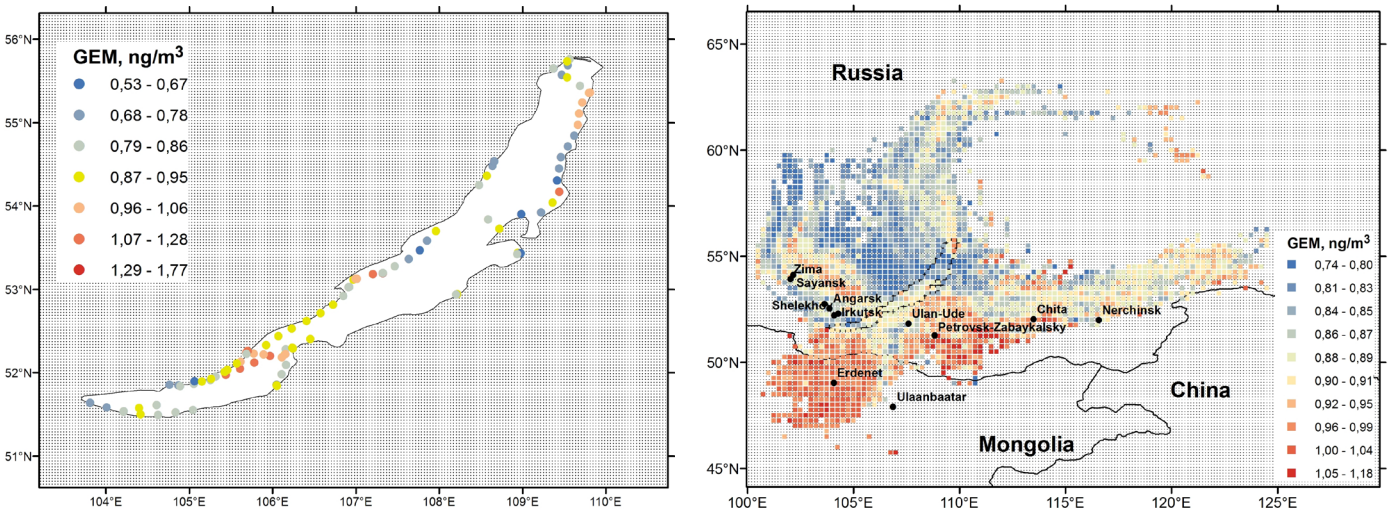

Fig.3. Local mercury anomalies in the air above Lake Baikal (**A**). Gridded (0.25° × 0.25°) concentration-weighted trajectory (CWT) values for GEM (**B**). Cruise onboard the RV "Akademik Koptyug", July 2018.

The cruise data confirmed the conclusion derived from stationary monitoring of the mercury air transport from industrial areas (Irkutsk, Angarsk, Shelekhov, and others) along the Angara River valley. Additionally, there were areas of mercury emissions on the southern side of Lake Baikal (Fig. 3B). The southwestern area is located on the territory of Mongolia and coincides with the position of the largest copper-molybdenum deposit and smelter (Erdenet). Sources of mercury located to the east, on the Ulan-Ude - Chita line, may be associated with the influence of cities and mining plants in Buryatia and Transbaikalia regions.

The mean mercury concentration of 1.10 ng/m^3 recorded above Lake Baikal is significantly lower than the mean value of 1.60 ng/m^3 obtained at the onshore Listvyanka monitoring station during the same days of cruise. The explanation for this phenomenon may be the specific air circulation over the Baikal water area in summer. An inverted layer is formed in the atmosphere above the cold lake surface, preventing the mixing of air above the surface with air masses coming from the continent. Under such conditions, Lake Baikal can be considered as a sink of atmospheric mercury.

Conclusions

The total mean (GEM) concentration at the Listvyanka station in 2011 to 2021 of the observation was 1.59 ng/m^3. PBM comprised about 0.7 % of GEM.

The average daily concentration of GEM ranged from 1.2 to 1.9 ng/m^3 and that of PBM from 7.8 to 15 pg/m^3 in the warm and cold seasons, respectively, indicating the elevated mercury emissions from coal combustion during the cold season.

The coal combustion plants are the main sources of the elevated mercury concentration at Listvyanka station, as confirmed by the clear correlation between the mean concentrations of Hg and SO_2, NOx, and O_3.

Wildfires can contribute to the increase in the average monthly GEM concentration.

The mean mercury concentration measured above Lake Baikal during the Baikal cruise was 1.10 ng/m^3, which is significantly lower than the mean value of 1.60 ng/m^3 obtained at the onshore Listvyanka GMOS station during the same days of the cruise. Thus, Lake Baikal can be a sink of atmospheric mercury due to air temperature inversion in the warm season.

CWT analysis of the 2018 cruise data revealed the areas where the sources of mercury anomalies were located: industrial areas along the Angara River (Irkutsk, Shelekhov, Angarsk, probably Usolye-Sibirskoye, Sayansk, and Zima), Mongolia (Erdenet), Buryatia and Transbaikalia.

Acknowledgements

This study was carried out within the framework of the FP7 project "Global Mercury Observation System", grant agreement SPSU No 265113 (2011-2015); and the LIN SB RAS projects of the Ministry of Science and Higher Education of the Russian Federation No 0279-2021-0014 and POI FEB RAS No AAAA-A20-120011090005-7.

Conflict of Interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Atmospheric gaseous elemental mercury and its sea-air evasion fluxes from the Sea of Okhotsk to the South China Sea: results of cruise studies in 2019

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ABSTRACT. At present, the behavior of mercury in the sea-atmosphere system in the north western Pacific Ocean is poorly understood. From September to December 2019, continuous measurements of atmospheric gaseous elemental mercury (Hg(0)) and point measurements of Hg(0) evasion fluxes from the sea to the atmosphere were carried out during two adjacent cruises from the South China Sea to the Sea of Okhotsk. The median concentration of Hg(0) (1.1 ng/m^3) was below both the background of the Northern Hemisphere and the average values previously recorded in these areas. There was a trend of increasing Hg(0) concentration with decreasing latitude. The Yellow Sea with adjacent territories and northeast China were the Hg(0) source area for the Sea of Japan and the Sea of Okhotsk. The Kuril sector of the Pacific Ocean was identified as a source of Hg(0) for the Sea of Okhotsk. East China, Southeast China and Indochina were sources of Hg(0) for the East China and South China seas. A winter increase in Hg(0) concentrations was observed in the Sea of Japan and the East China Sea. Our data showed significant relationships between Hg(0) fluxes, latitude, and water temperature.

Keywords: mercury, atmosphere, fluxes, marginal seas of the Pacific Ocean

1. Introduction

East and Southeast Asia, mainly China, is the largest exporter of anthropogenic mercury in the atmosphere (AMAP/UN Environment, 2019). Atmospheric transport of Hg(0) from China was previously observed in the South China Sea, East China Sea, Yellow Sea, and Sea of Japan(Wang Y. et al., 2017; Wang C. et al., 2016; Kalinchuk et al., 2021). Transport of Hg(0) from East Asia by westerly winds was recorded in North America (Jaffe et al., 2005). Apparently, mercury from East Asia can be transported by air masses into the atmosphere over the Sea of Okhotsk and, possibly, further north, but experimental confirmation of this phenomenon has not yet been obtained.

To identify the source regions that affect the concentrations of Hg(0) in the atmosphere over the marginal seas of the northwestern Pacific Ocean, we conducted a study covering the water area from the South China Sea to the Sea of Okhotsk during two adjacent cruises on board the R/V Akademik M.A. Lavrentev.

2. Materials and methods

Hg(0) concentrations in the atmosphere at a height of about 2 m above the sea surface were continuously measured using a RA915M analyzer (Lumex Ltd, St. Petersburg, Russia) with a detection limit of 0.1–0.2 ng/m^3 at a 30-minute averaging (Mashyanov et al., 2021). Ambient air was supplied to the analyzer through a 20 m Teflon hose. The air intake was installed in the bow of the vessel in such a way as to take air that had not yet come into contact with the vessel. For analysis, all data were combined into 1-hour values.

Additionally, continuous current data on meteorological and hydrological parameters were obtained using a Davis Vantage Pro weather station (Davis Instruments Corp., USA), SBE45 MicroTSG thermosalinograph (Sea-Bird Scientific, USA), and 10-AU-005-CE fluorimeter (Turner Designs, USA).

Hg(0) emission fluxes were measured using a mercury analyzer in combination with a dynamic flux chamber. Briefly, the standard method is based on the difference between the Hg(0) concentrations in the

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Received: June 17, 2022; ***Accepted:*** July 13, 2022;
Available online: July 31, 2022

ambient air entering the chamber and the air leaving the chamber (Qureshi et al., 2012). We modified this method by using mercury-free air instead of ambient air entering the chamber (Kalinchuk et al., 2021). This approach is explained by the fact that the ship is a source of Hg(0) to the ambient air, which can distort the flux measurements.

To study the effect of air mass movement of Hg(0) concentrations at the measurement points and to identify areas potentially influenced by atmospheric Hg(0) concentrations in the studied seas, we used backward trajectory analysis and the concentration weighted trajectory (CWT) analysis, respectively.

The backward trajectories of air mass movement were calculated on the READY website using the model of a hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) (Stein et al., 2015). CWT analysis was performed based on the formula presented by Cheng et al. (2015).

3. Results and discussion

During the two expedidions, Hg(0) concentrations ranged from 0.5 to 2.98 ng/m^3 (N = 1916) with mean (± SD) and median values of 1.23 (± 0.38) ng/m^3 and 1.09 ng/m^3, respectively. As seen in Fig. 1, atmospheric Hg(0) concentrations over the marginal seas of the western Pacific decreased with increasing latitude. The highest concentrations were recorded in the South China Sea, and the lowest – in all water areas surveyed during the northern cruise. The decrease in Hg(0) concentrations ranged from 5 to 12%, with an average of 8% for every 5 degrees from 10 to 55 degrees north latitude.

During the northern cruise, elevated CWT values were detected over northeastern China, southern Primorsky Krai (Russia), the Kuril sector of the Pacific Ocean, and the Sea of Okhotsk (Fig. 2). Atmospheric transport of Hg(0) from northeast China was repeatedly observed in the Sea of Japan and was likely associated with anthropogenic emissions (Kalinchuk et al., 2021). Elevated concentrations of Hg(0) were previously recorded over the Kuril sector of the Pacific Ocean, which were presumably caused either by volcanic emissions (Kalinchuk et al., 2019) or an increased flux of Hg(0) emissions from sea water in this region (Kalinchuk et al., 2021).

During the southern cruise, elevated CWT values were detected over the Korean Peninsula in the northwestern and southeastern parts. Higher CWT values were found above Pohang, a major industrial center in South Korea. The area extending from the southwestern coast of the Yellow Sea to southern Indochina was identified as the largest potential source region. Elevated CWT values over the South China Sea were likely caused by the spread of Hg(0) from continental sources. The release of Hg(0) from the sea into the atmosphere could an additional impact be.

Lower CWT values were identified over the Philippine Sea, the Yellow Sea, and northeast China. Although the latter, according to the northern cruise, was characterized by increased CWT values. This

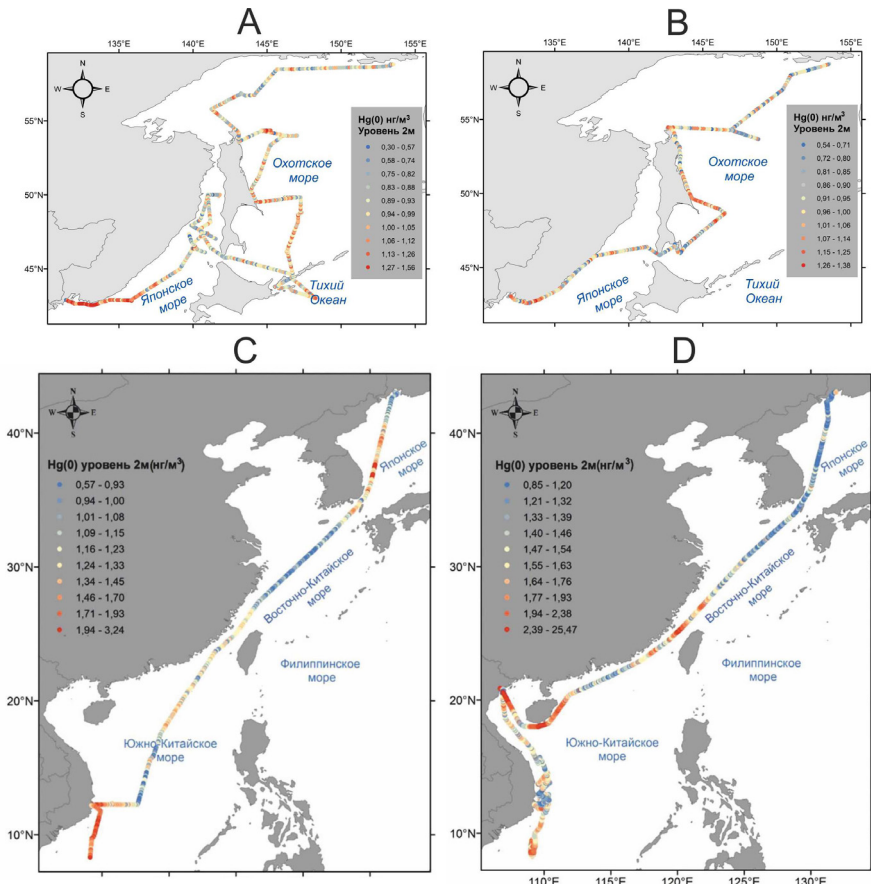

Fig.1. Spatial distribution of Hg(0) concentrations in the atmosphere measured from September to December 2019. Letters A and B show the stages of the northern voyage from Vladivostok to the Sea of Okhotsk and back. Letters C and D designate the stages of the southern voyage from Vladivostok to the South China Sea and back.

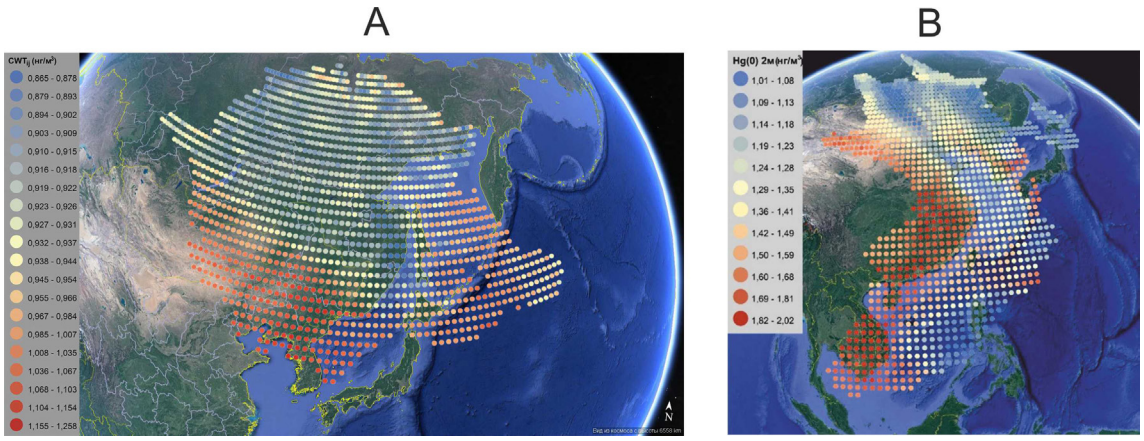

Fig.2. Distribution of the CWT values according to the data obtained in: A – northern cruise; B - southern cruise.

indicates that northeast China is a significant source region for areas north of it, but for more southerly areas it is a minor source.

During the two expeditions, Hg(0) fluxes varied from 0.6 to 2.5 ng/m^2/h with an average value of 1.7 ± 0.6 ng/m^2/h and a median of 1.6 ng/m^2/h (Fig. 3). Lower values with a mean value of 1.2 ± 0.4 ng/m^2/h and a median value of 1.3 ng/m^2/h were observed during the northern cruise. The South China Sea was characterized by fluxes with mean and median values of 2.0 ± 0.5 ng/m^2/h and 2.1 ng/m^2/h, respectively. The highest positive correlation was found between Hg(0) flux and latitude ($R^2 = 0.46$) and the highest negative correlation – between flux and water temperature ($R^2 = 0.48$).

4. Conclusions

In the Sea of Japan, Hg(0) concentrations increased with the arrival of air masses from northeast China and the Korean Peninsula. For the Sea of Okhotsk, the source area was the Kuril region and northeastern China with the Korean Peninsula. Northeast China and the Korean Peninsula were an important source of Hg(0) for the Sea of Japan and the Sea of Okhotsk, while they were a minor source for the East China and South China Seas. For these two seas, the most significant potential source area was the vast area from the southwestern coast of the Yellow Sea to southern Indochina. In the marginal seas of the northwestern part of the Pacific Ocean, there was a trend towards a decrease in Hg(0) concentrations from south to north.

Hg(0) emission fluxes showed a similar trend. The fluxes had a positive relationship with the water temperature and a negative relationship with the latitude. Presumably, such relationships could be due to the combined action of two factors: i) the effect of water temperature on the formation of dissolved Hg(0) and the rate of its diffusion; ii) an increase in anthropogenic mercury emission in southern latitudes, followed by the precipitation of elevated concentrations of oxidized mercury from the atmosphere and its transformation into dissolved Hg(0) in seawater.

Acknowledgments

The authors thank S.A. Gorbarenko and R.B. Shakirov for organizing and managing the northern and southern cruises, respectively. The study was financially supported by the Ministry of Science and Higher Education of the Russian Federation (project Nos AAAA-A20-120011090005-7, 121021700342-9, 121021500055-0, and 121021700346-7). With the support of the Russian Science Foundation (RSF), data processing and interpretation (project No19-77-10011) as well as preparation of the text of the article (project No 18-77-10017) were carried out.

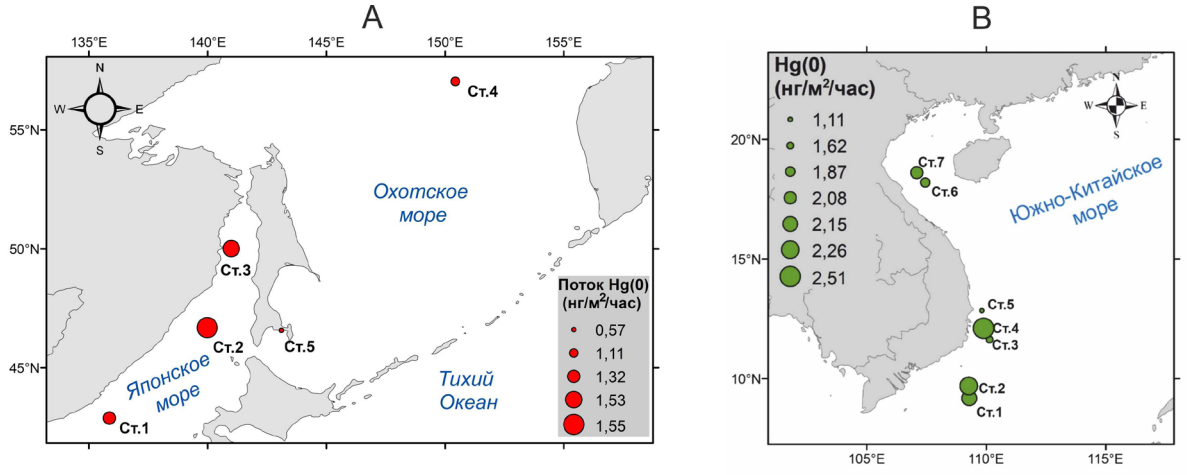

Fig.3. Hg(0) emission fluxes measured in September to December 2019.

Confict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Sea fog increases the total mercury level in the terrestrial ecosystem (on the example of the tiger *Panthera tigris altaica* Temminck, 1844)

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ABSTRACT. This study discusses one of the aspects of the mercury problem, which is the relationship between aquatic and terrestrial ecosystems. We indicate that the mercury concentration in the Amur tiger fur (*Panthera tigris altaica*) is higher in the coastal area than in the inland area because the coastal areas are exposed to the impact of marine atmospheric fog, a potential source of monomethylmercury. The total mercury concentration from the Khasansky District varied from 0.16 to 0.45 mg/kg, on average 0.22 ± 0.04 mg/kg, in tiger fur, from 0.07 to 1.01 mg/kg, on average 0.64 ± 0.05 mg/kg, in leopard fur (*P. pardus orientalis*) and from 0.055 to 1.233 mg/kg, on average 0.336 ± 0.056 mg/kg, in Himalayan bear fur (*Ursus thibetanus*). The total mercury concentration in the fur of the last predators from the inland areas is unknown. Further research is needed.

Keywords: aquatic and terrestrial ecosystems, total mercury, *Panthera tigris altaica, P. pardus orientalis, Ursus thibetanus*

1. Introduction

The Russian Far East is a region where gold is mined, or the deposits of mercury-containing minerals are found. At the same time, the southern regions of the Russian Far East are unique in the number of Mesozoic relics, species that require special conservation measures. The Amur tiger is on the list of rare animals. Tigers 'crown' ecological pyramids and, therefore, have the potential for bioaccumulation. We have studied the mercury concentration in the body of a tiger, the top link of the food web of coastal and inland ecosystems of the south of the Russian Far East. This is a continuation of our pioneering research on the assessment of mercury concentrations in the fur of Amur tigers. The diet of animals of this tiger subspecies includes 85 species of vertebrates, the main part of which consists of five species of ungulates, while bears, pheasants, hares, and badgers are much less likely to be involved (e.g. Yudin and Yudina, 2009; Poddubnaya and Kolomiytsev, 2016; Salkina et al., 2018). Tigers can eat reptiles, fish, small mammals, and, sometimes, domestic animals. In recent years, tigers have been consuming more and more carrion and food waste collected and left by humans in certain places. It is a generally recognized fact that different fish species are the main source of mercury supply into the predator body and the trophic web of the ecosystem. In some areas of the Far East, the seasonal abundance of salmon can provide tigers with protein. Amur tigers can take fish from fishermen. However, our observations and data on mercury concentration indicate that tigers do not often eat salmon (especially compared to bears), and they definitely do not hunt the redfin dace (*Tribolodon hakonensis*) (Poddubnaya et al., 2021).

2. Materials and methods

The total mercury (Total Hg, THg) concentration was analyzed in 29 tiger fur samples collected from animals killed by poachers until 2014 from different locations in the south of the Russian Far East (Fig. 1).

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Received: June 17, 2022; ***Accepted:*** July 15, 2022;
Available online: July 31, 2022

As one sample of tiger and that of Far Eastern leopard fur (*Panthera pardus orientalis*) with the highest mercury level were from the south-western Primorye, we collected additional samples of tiger (n = 8), Far Eastern leopard (n = 8) and Himalayan bear (n = 22) fur (*Ursus thibetanus*) from this area (Khasansky District). The analysis was carried out on a RA-915M mercury analyzer (Lumex).

3. Results and discussion

The mean individual concentrations of total mercury in the tiger fur from the coastal area of the Sea of Japan ranged from 0.115 to 0.918 mg/kg, on average 0.434 ± 0.067, while the tiger fur from the inland areas had lower THg concentrations (from 0.057 to 0.950 mg/kg, on average 0.239 ± 0.075); the differences between the mean values of the two plots were statistically significant (P = 0.02) (Poddubnaya et al., 2021). Despite the small amount of sampling, there were significant differences in pairs: tiger fur from the coastal and inland areas; young and adult tiger fur; female fur from the coastal and inland areas (Fig. 2). The total mercury content in the *Usnea* sp lichens from the coastal and inland subregions was additionally analyzed; the results averaged 0.170 ± 0.017 mg/kg and 0.065 ± 0.004 mg/kg, respectively. The only sample with the maximum mercury concentration of 1.402 mg/kg (age and gender unknown) was from the southwestern Primorye, which is located on the coast with nearby cinnabar deposits. This sample was not used in the total analysis. Interestingly, the available sample of a young female Far Eastern leopard fur from the same site had practically the same mercury concentration (1.456 mg/kg). Local increased mercury concentrations in the body of tigers can be associated with deposits of mercury-containing minerals (Poddubnaya et al., 2021).

The total mercury concentration in the tiger fur collected in the Khasansky District of the Primorsky Krai varied from 0.16 to 0.45 mg/kg, on average 0.22 ± 0.04 mg/kg. This value was lower than the mercury concentration in the Amur tiger fur from the inland and coastal areas. The total mercury concentration in the leopard fur collected in the Khasansky District varied from 0.07 to 1.01 mg/kg, on average 0.64 ± 0.05 mg/kg. This value was higher than the mercury concentration in the Amur tiger fur from the inland and coastal areas. The total mercury concentration in the fur of the last predator from the inland areas is unknown. The total mercury content in the Himalayan bear fur collected in the Khasansky District varied from 0.055 to 1.233 mg/kg, on average 0.336 ± 0.056 mg/kg (Poddubnaya et al., 2022). This value was higher than the mercury concentration in the Amur tiger fur from the inland areas and lower than that from the coastal areas. The total mercury concentration in the fur of the last predators from the inland areas is unknown. Further research is needed.

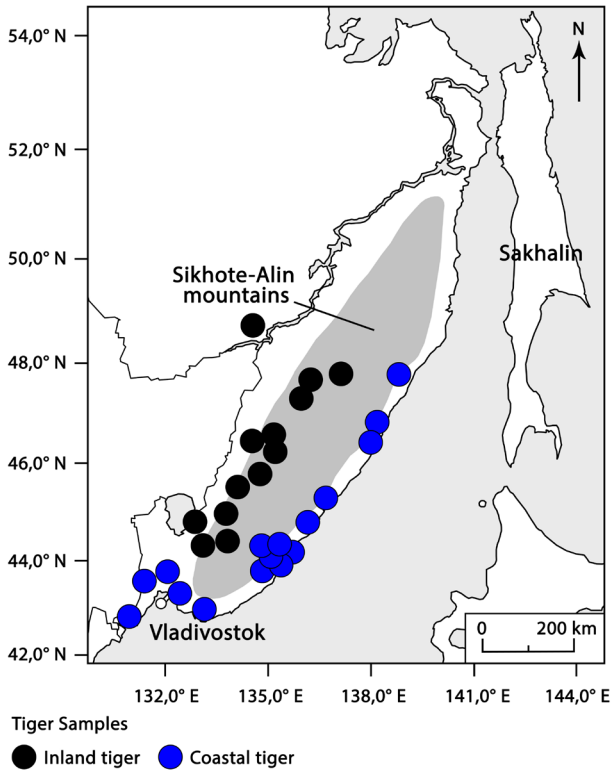

Fig.1. Map of sampling sites and mean values of total Hg in tiger fur. Blue circles represent samples from the coastal subregion, and the black ones – from the inland subregion.

Our data on higher mercury levels in lichens and tigers of the coastal area compared to inland areas were obviously related to the impact of coastal

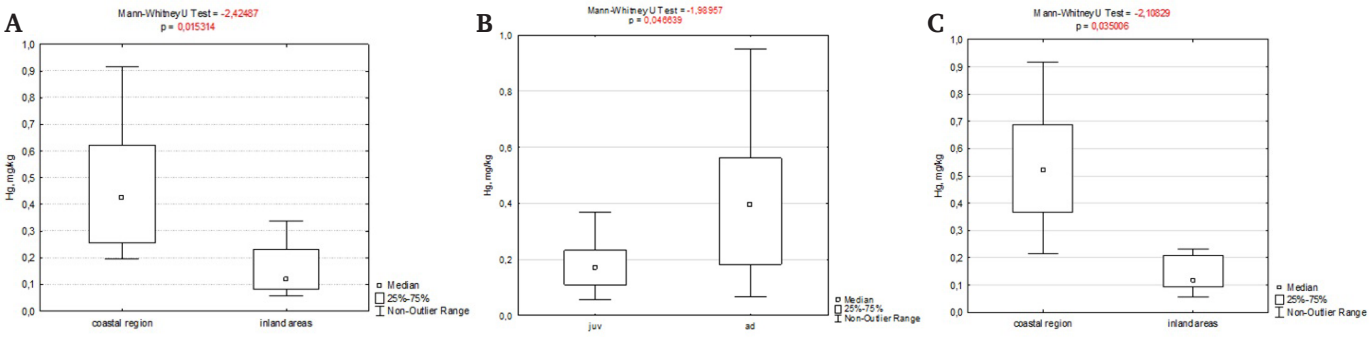

Fig.2. Statistics on the subsets of the concentration data: A – tigers from the coastal and inland areas, B – young and adult tigers and C – female tiger. All concentrations are presented in mg/kg.

marine atmospheric fog, a potential source of monomethylmercury (mmHg) formed in the ocean (Weiss-Penzias et al., 2019). A local elevated mercury concentration in the body of tigers may also be associated with deposits of mercury-containing minerals (southwest of Primorye), but this statement has not yet been confirmed by studies (a high THg concentration in the Himalayan bear of 1.233 mg/kg was recorded only for one individual). The mercury concentration that we detected in Siberian tigers from the Russian Far East was approximately four times lower than the mercury content in the fur of a cougar from California. Apparently, such differences were due to the position of these regions relative to the zones of deep faults of the East Pacific Platform mantle formation. The studies of mercury in pink salmon support this: fish from the Sea of Japan contained much less mercury than fish from the Kuril region closer to the fault zone (from 0.045 to 0.087 mg/kg wet weight) (Khristoforova et al., 2015).

4. Conclusions

Thus, in the south of the Russian Far East, there are risks for predators, which are associated with mercury and, possibly, as a consequence, with changes in behavior and deterioration of the health of animals. Therefore, in the study of rare and endangered animals, it seems to be appropriate to start research on the mercury concentrations in the fur of predators in comparison with their behavior. In this regard, it makes sense to place fur traps next to camera traps.

Acknowledgments

The authors thank Yu.A. Darman, D.S. Matyuchina and V.Kh. Kryukov for the help in collecting the material as well as L.S. Eltsova, E.S. Ivanova, D.D. Pavlov, O.Yu. Rumyantseva, A.A. Smirnova, and V.A. Nikandrova for assistance in the primary processing of the material.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
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Differential diagnosis of sleep disorders in the presence of chronic mercury intoxication

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ABSTRACT. Insomnia is a widespread pathological condition in the general population, which has numerous social and medical consequences. Sleep disorders in patients with chronic mercury intoxications are much more common than in the general population. This study aimed to determine the most significant differential diagnostic criteria for sleep disorders in patients with chronic mercury intoxications for their further effective treatment. In this regard, we examined 30 patients with chronic mercury intoxications, whose age averaged 56 ± 0.71 years, and 30 patients of the control group, whose age averaged 54 ± 0.66. All patients underwent clinical, neurological, polysomnographic, and psychological examinations, and neurotransmitters were determined in the blood. Discriminant analysis based on polysomnography, psychological testing and neurotransmitter metabolism revealed significant differences in the examined groups of patients for the following indicators: total sleep time (decreased in the chronic mercury intoxication group) and wake within sleep (increased in the chronic mercury intoxication group) based on polysomnography, blood dopamine level (increased in the chronic mercury intoxication group) as well as reactive anxiety level according to the Spielberger-Khanin scale (increased in the chronic mercury intoxication group). Taking into account the data obtained, it is possible to improve approaches to the diagnosis and treatment of insomnia in the presence of chronic mercury intoxication.

Keywords: sleep, insomnia, chronic mercury intoxication, dopamine, reactive anxiety

1. Introduction

Metallic mercury is an industrial poison that primarily affects the central nervous system. In the Irkutsk Region, this neurotropic poison was used in the production of caustic soda at chemical enterprises in the cities of Usloye-Sibirskoye (Usolyekhimprom) and Sayansk (Sayanskkhimplast).

According to the previous data, in the case of occupational chronic mercury intoxication (CMI), the following structures of the central nervous system are gradually involved in the pathological process: nonspecific structures of the midbrain, the limbic system and reticular formation, which provide basal emotions and vital functions, maintain a certain level of wakefulness and regulate muscle tone (Lakhman et al., 2014). Therefore, sleep disorders occur already at the early stages of occupational CMI characterised by the presence of functional disorders of the nervous system in the form of asthenic and autonomic defects. Further development of organic disorders in the central nervous system is accompanied by an increase in the severity of mental and sleep disorders (Lipenetskaja et al., 2004).

Insomnia is a widespread pathological condition in the general population, which has numerous social and medical consequences. According to various social surveys, the prevalence of this condition among the adult population reaches 15% (Schutte-Rodin et al., 2008). There is a direct relationship between the severity of sleep disorders and a decrease in physical performance, cognitive functions and life expectancy of an individual (Poluektov, 2016). At the same time, this problem is one of the least studied among various specific diseases.

Currently, insomnia is known to have a high comorbidity with various somatic and neurological diseases (Lichstein et al., 2016). Sleep disorders are much more common among patients with CMI than in the general population. Based on our surveys, 88% of these patients complained of sleep disturbances; 100% had difficulties in maintaining sleep, and 60% – early

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Received: July 6, 2022; A***ccepted:*** July 14, 2022;
A***vailable online:*** July 31, 2022

final awakening. According to the questionnaire data on subjective sleep characteristics, a decrease in the total assessment of sleep quality was observed among 100% of the respondents (Katamanova et al., 2016).

According to the State Service for Medical and Social Expertise, in the Irkutsk Region, over the past five years, occupational neurotoxicosis has been ranked third or fourth in the structure of disability causes associated with occupational diseases, after vibration disease, sensorineural hearing loss and respiratory diseases (Boklazhenko and Bodyenkova, 2019). Therefore, the characterisation of occurrence and development of sleep disorders, as well as methods of their objective diagnosis in patients with occupational neurotoxicosis, are of great clinical and social significance.

Neurotransmitters such as serotonin, acetylcholine, catecholamines, histamine, and dopamine that are involved regulating the above vital functions play an important role in the CMI pathogenesis (Katamanova et al., 2010). At present, the dopaminergic system is known to be associated with strong emotions and stress (Kovalzon, 2012). Previously, we determined that with the predomination of organic personality disorder with psycho-emotional disorders of anxiety and depression nature in the CMI clinical picture, there was a significant increase in the level of reactive anxiety based on the data on the psychological condition of the patients.

Therefore, the aim of the study was to identify the most significant differential diagnosis of sleep disorders in patients with occupational CMI for their further effective treatment.

2. Materials and methods

Two groups were included in the study. The first group consisted of 30 patients (men) with occupational CMI, who worked at Ulsoyekhimprom and were aged on average 56 ± 0.71 years. The second group (control) consisted of 30 male patients aged on average 54 ± 0.66 years, who complained of sleep disorders but had no contact with toxic production factors.

Sleep disorders were diagnosed using a Neiron-Spektr-4 electroencephalograph manufactured by Neirosoft (Ivanovo, Russia), followed by evaluation of the resulting hypnogram.

The concentration of dopamine (DA) was determined in blood plasma obtained with EDTA as anticoagulant by a solid-phase competitive enzyme immunoassay on microplates using the 3Cat ELISA test kits (LDN, Germany) on a BioTek enzyme immunoassay reader (USA). DA was preliminarily extracted from blood samples using an affinity gel specific for cis-diol groups, then acidified to N-acyl-dopamine and subjected to enzymatic conversion to N-acyl-3-methoxytyramine during the detection procedure. The evaluation of the physiological condition of the examined patients included determination of anxiety level, asthenic condition and depression. The levels of reactive and trait anxiety were assessed based on the Spielberger-Khanin scale; the level of asthenic condition – based on the asthenic condition scale (Akhmedzhanov, 1995), and the level of depression – using the V. Zung scale adapted by T.N. Balashova (Krylov, 1990).

Statistical processing of the material was carried out with Statistica for Windows v.6 Ru (license No. AXXR004E642326FA; license holder East-Siberian Institute of Medical and Ecological Research). The median value and the interquartile range (25^{th} and 75^{th} percentiles) were calculated for the indicators. Discriminant analysis was used to determine the differential diagnosis of insomnia. Step-by-step procedures determined the information content of the indicators. The initial installation parameters were made according to the recommendation of V. Borovikov (2001). $F \geq 3.5$ was chosen as the threshold value.

This study does not infringe on the rights or jeopardise the well-being of the examined patients according to the requirements of biomedical ethics imposed by World Medical Association Declaration of Helsinki (2000) and the Order of the Ministry of Health of the Russian Federation No. 266 (dated 19 June 2003).

3. Results

In the first group of patients, for the long-term period of occupational CMI, in 97.7% of cases, we recorded stage II of the disease, and in 2.3% of cases – stage III. The frequency of encephalopathy in this group was 90% [95% CI 78–95]. Asthenic disorder was identified in 30% of cases [95% CI 19–45]; vegetative dysfunction – in 55.6% of cases [95% CI 35–70]. Patients with CMI complained of non-systemic headaches and dizziness, difficulty remembering current events, increased irritability, and fatigue. Complaints about sleep disorders were recorded in 100 % of cases.

Based on the clinical examination of the patients in the control group, the detection frequency of gastrointestinal tract diseases (chronic gastritis) was 36%, diseases of the organs of vision (myopia and hypermetropia) – 40% and vertebrogenic pathology – 36%. Complaints about sleep disorders were recorded in 47% of the patients.

As psycho-emotional disorders of anxiety and depression nature prevailed in the clinic picture of patients with CMI, both groups underwent psychological tests to detect anxiety, asthenic condition and depression. Analysis of the indicators of the psycho-emotional domain in the two groups indicated the presence of astheno-depressive syndrome with an anxious component in the CMI group and its absence in the control group. Comparative analysis of the psychological indicators revealed the statistically significant differences ($p < 0.05$) characterising levels of depression (67.4(59-70) and 37.9(32-45) points, in the first and second group, respectively), trait anxiety (58.7(55-62) and 37.0(31-46) points in the first and second group, respectively), reactive anxiety (54.7(49-60) and 36.4(29-41) points in the first and second group, respectively), and asthenic condition (84.1(78-92) and 23.5(19-28) points in the first and second

group, respectively).

For an objective diagnosis of nocturnal sleep disorders, patients in both groups underwent full in-lab polysomnography (gold standard of sleep studies, Level 1 study). Polygraphic registration of biopotentials with subsequent assessment of the resulting hypnogram revealed in patients with CMI an increase in falling asleep time (35.0 (30.5 to 47.0) min), a decrease in sleep duration (total sleep time 339.5 (305.0 to 374.0) min), an increase in the number of activations (2.9 (1.9 to 3.6) % of total sleep time) and total wake within sleep (11.3 to 23.5) %), a decrease in the number of sleep cycles (3.0 (2.0 to 4.0)) as well as a decrease in the sleep efficiency index, SEI (70.95 (60.7 to 78.2) %) and an integrative sleep quality index, SQI (17.8 (13.4 to 27.5)).

The results of polysomnographic study of the patients in the control group revealed the following changes in quantitative and qualitative indicators of nocturnal sleep structure: an increase in the total wake within sleep (12.2 (8.4 to 18.6) %), an increase in the latent period of REM-stage (93.0 (72.0 to 117.0) min), a decrease in the number of sleep cycles (3.0 (3.0 to 4.0)) as well as a decrease in SEI (78.4 (73.9 to 81.5) %) and SQI (14.1 (10.9 to 20.6)).

For a more detailed study of sleep disorder mechanisms in patients with CMI, we studied the concentration of the DA transmitter in the blood. In the CMI group, the DA concentration was elevated in the blood of the patients. In the control group, the DA concentrations in the blood of the patients were within the reference values.

To determine the differential diagnosis of insomnia in patients with occupational CMI, we carried out a discriminant analysis for 26 indicators of polysomnography, psychological testing and neurotransmitter metabolism in both groups. As a result of statistical analysis, we obtained four most significant diagnostic criteria, in which F inclusions and confidence level were statistically significant (Table).

Table. Results of the analysis of discriminant functions in the examined groups

No	Indicator	F inclusions	p
a1	total sleep time (min)	4.7	0.03
a2	wake (%)	5.3	0.02
a3	DA level (pg/mL)	3.6	0.04
a4	reactive anxiety level, (points)	142.2	0.000000

4. Discussion

Based on an objective technique for studying sleep disorders, we identified that patients with occupational CMI had more manifested qualitative and quantitative changes in the indicators of nocturnal sleep structure than in the control group.

The results of psychological testing that revealed significant changes in the emotional domain (increase in depression level, reactive and trait anxiety, and asthenic condition compared to the control group) confirmed the presence of a more manifested form of insomnia in patients with occupational CMI.

The limbic-hypothalamic-reticular complex maintains the level of attention and muscle activity, regulation of the sleep-wake cycle, basal emotions and autonomic reactions. These processes occur in the body during the normal functioning of transmitter metabolism (Andreeva et al., 2002). In the presence of CMI, the transmitter system showed elevated DA concentrations in the blood. The identified changes corresponded to the currently existing theory of chronic neurotoxicosis pathogenesis as well as to the disorders detected in the psycho-emotional domain and from polysomnography of patients with CMI.

The discriminant analysis based on the polysomnography, psychological testing and transmitter metabolism revealed significant differences in the examined groups of patients for the following indicators: total sleep time (decreased in the CMI group) and wake within sleep (increased in the CMI group) based on polysomnography, blood DA level (increased in the CMI group) as well as reactive anxiety level according to the Spielberger-Khanin scale (increased in the CMI group). Taking into account the data obtained, it is possible to improve approaches to the diagnosis and treatment of insomnia in the presence of CMI.

5. Conclusions

1. The resulting set of diagnostic indicators is specific for sleep disorders in the presence of occupational CMI.
2. A certain set of diagnostic criteria can be used for differential diagnosis of insomnia in the presence of occupational CMI.

Conflict of interest

The authors (Korchuganova E.N., Katamanova E.V., Slivnitsyna N.V., Kudaeva I.V., and Kazakova P.V.) are the inventors of the patent “Method for diagnosing dyssomnia associated with chronic mercury intoxication”.

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Participation of water deer (Hydropotes inermis argyropus) in mercury transport in the ecosystem of Southern Primorye

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ABSTRACT. We present the first opportunity to study mercury in the fur of a water deer that recently entered Russia.13 samples from 7 animals (fur was taken from the back and belly) were collected similarly to the World Health Organization recommendations for humans. The mean concentration of total mercury in the fur of water deer was 0.01 ± 0.003 mg/kg, which roughly coincides with the mercury in the fur of other herbivorous animals. For a more accurate assessment, it is necessary to obtain data for other deers in the study region.

Keywords: aquatic and terrestrial ecosystems, total mercury concentration, *Hydropotes inermis argyropus*

1. Introduction

Mercury problems are important in themselves (Minamata Convention ..., 2013), but research related to rare and dispersing species is particularly intriguing. The latter includes the water deer. The water deer was once widespread around the Yellow Sea, from the west coast of the Korean Peninsula to the lower reaches of the Yangtze River. By the mid-20th century, only two locations of the species survived: the Chinese water deer (*Hydropotes inermis inermis*) in southern China and the Korean water deer (*H. i. argyropus*) on the border of South and North Korea. The number of Korean subspecies has increased many times in recent decades due to its high fertility, and the population exceeds half a million individuals (Kim et al., 2011; Eom et al., 2018). Annual population growth can be more than 50% (Eom et al., 2018). Since 2015, this deer has been recorded on the territory of the Land of the Leopard National Park (Darman et al., 2019), and in 2019 it was recognized as a new, 327th, mammal species in the fauna of Russia (Darman et al., 2019). Increasingly frequent encounters with water deer and the remains of dead animals, victims of predators, indicate that this deer can become a common food for the Far Eastern leopard (Darman and Sedash, 2020).

The water deer or marsh musk deer, as it is called by Russian border guards (Darman et al., 2019) lives in grassy thickets along the banks of rivers and lakes and in swamps. Its food objects are mainly grass, as well as leaves, mushrooms and young shoots. It was important to assess the mercury levels in the samples of water deer fur collected at the protected area "Land of the Leopard" to understand its significance for the specially protected wild cats of the Southern Primorye.

2. Materials and methods

The material for the study was collected by the staff of the protected areas on the territory of the national park "Land of the Leopard" (Fig. 1). The fur of water deer was collected from animals found dead due to natural causes or as a result of poaching from 2010 to 2021.

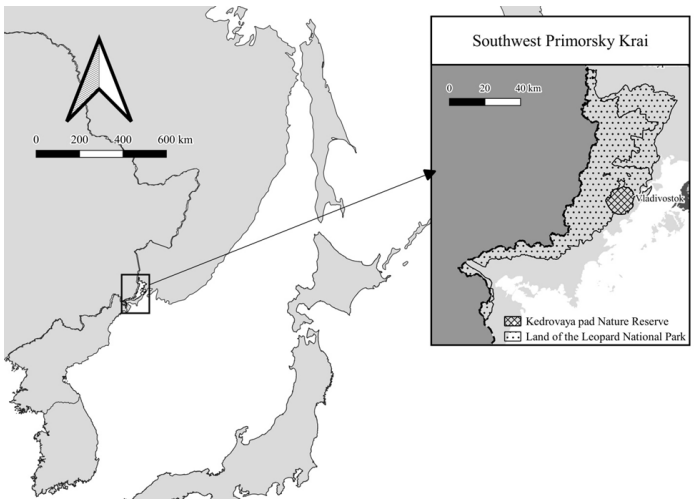

Fig.1. Map of the research area.

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Received: June 17, 2022; ***Accepted:*** July 15, 2022;
Available online: July 31, 2022

The material included 13 samples from 7 animals (fur was taken from the back and belly). The samples were collected similarly to the World Health Organization recommendations for humans. They were dried and stored in self-sealing plastic bags. For one month, they were kept in the freezer (to destroy possibly trapped eggs of skin worms or moths). Thereafter, for several months, the wool samples were stored at room temperature in sealed plastic boxes. The material was processed in the ecological and analytical laboratory of Cherepovets State University. Fur analysis was performed on a RA-915M+ mercury analyzer with the PYRO-915+ attachment by the atomic adsorption method of cold vapor. To verify the accuracy of the device, mercury concentrations were determined in reference samples (DORM-4, DOT-5) with a known mercury concentration (mg/kg).

3. Results and discussion

The distribution of values in the sample was checked for normality using the Shapiro–Wilk test and the Kolmogorov–Smirnov test. Due to the lack of normality in the distribution of values, nonparametric statistical methods were used. The Mann–Whitney U–test was used to compare two independent samples.

The study revealed that the mean total mercury concentration in a water deer the fur was 0.008 ± 0.003 mg/kg, from 0.001 mg/kg to 0.026 mg/kg (Table).

The Mann—Whitney U–test used to evaluate the differences between two independent samples (Fig. 2) turned out to be $p = 0.26$, which indicates that there were no significant differences between the samples. Possibly, this was due to a small sample size. The mean mercury content, median and quartiles in the fur of a water deer from the back and belly are shown in Fig. 2.

The data on the mercury concentration in the fur of water deer corresponded to the mercury level in other herbivorous mammals. Thus, THg in beaver fur was 0.06 mg/kg, elk – 0.009 mg/kg (Ivanova et al., 2014), muskrats, hares and artiodactyls fur – about 0.2 mg/kg (Ivanova et al., 2014; Scheuhammer et al., 2007), and THg in red vole fur varied from 0.001 to 0.147 mg/kg (Ivanova et al., 2014).

4. Conclusions

Thus, the mean concentration of total mercury in the fur of water deer was 0.01 ± 0.003 mg/kg, which roughly coincides with the mercury levels in the fur of other herbivorous animals. For a more accurate assessment, it is necessary to obtain data for other deer in the study region.

Acknowledgments

The authors thank Yu.A. Darman and V.B. Storozhuk for the help in collecting the material.

Conflict of interest

The authors declare no conflict of interest.

Table. Statistical characteristics of the sample.

Mean	Median	Min	Max	First Quartile	Third Quartile	SD	Standard Error
0.01	0.008	0.001	0.026	0.003	0.015	0.007	0.003

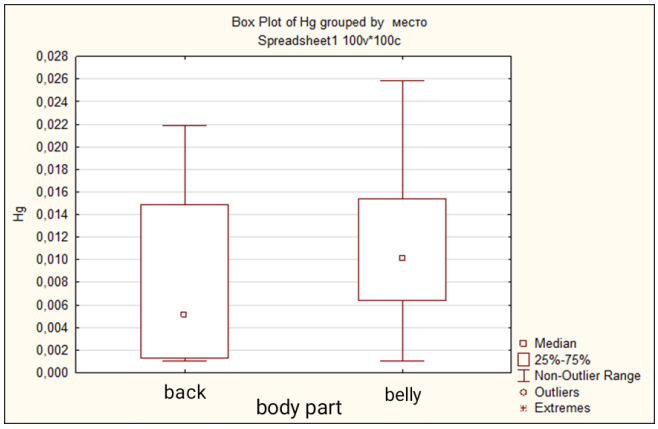

Fig.2. Mercury concentrations of water deer depending on body part.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Mercury hazard of earthquakes in the Baikal seismic zone

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ABSTRACT. On the west coast of Lake Baikal, we defined long-term and short-term variations in Hg concentrations of groundwater in 2017 to 2019 and from 2019 to the present, respectively; the latter variations were associated with the 2020–2021 Baikal-Khubsugul seismic reactivation of active faults. We inferred that increasing Hg concentration in groundwater was due to crustal extension with the highest Hg enrichment related to aftershocks. We argue that a Hg flux depends on the nature of fault activities and elevated Hg concentrations in sedimentary layers may designate the release of Hg_{gas} and Hg_{ow} from seismically active faults in the past 14.4 Ka.

Keywords: mercury, groundwater, earthquake, Lake Baikal, monitoring

1. Introduction

It is widely accepted that half of the mercury emissions into the atmosphere are due to volcanic activities; another half are due to the human industrial revolution. An increase in both contributions was inferred from the content of about 4 ng of mercury in 1 cubic decimeter of ice before 1850 with the later increase in mercury concentration. Concerining the volcanic contribution, it is reasonable to connect Hg concentration with the intensity of eruptions of the Earth's volcanoes. In fact, volcanic activities intensified before 1850. The strongest historical eruption of the Tambora volcano occurred in 1815. Volcanic ejects were estimated throughout the global aerosol optical depth (AOD). This parameter is characteristic of the transparency of the stratosphere for solar radiation expressed in terms of the rate of sulfate accumulation (10.5 kg/km^3). There is a good agreement between 16 eruptions and cooling events in the time interval of 1630–1850 years. Thereafter, a relative decrease in AOD indicated a decreasing intensity of volcanic activities (Crowley et al., 2008). Consequently, these data did not support the current opinion about the increase in mercury influx due to increased volcanic activity since 1850.

In addition to volcanism, there is another sufficient natural source that contributes mercury to the atmosphere. Mercury is extracted from rocks during earthquakes. For example, 1.2 days before the main shock of the Dushanbe earthquake on 29 September 1981, the concentration of gaseous mercury (Hg_{gas}) increased by 400 % at a distance of 20 km from the epicenter (Varshal et al., 1984). Therefore, a release of Hg_{gas} was considered an earthquake precursor (Cicerone et al., 2009). The recorded mercury emission showed anomalous behavior of this metal in seismogenic faults. Elevated mercury concentrations related to earthquakes were also detected in groundwater (Koval et al., 2003; 2006).

The aim of this paper is to show anomalously high Hg concentrations in groundwater, which were recorded in the Kultuk area on the west coast of Lake Baikal before and during the Baikal-Khubsugul seismic reactivation in 2020 and 2021.

2. Materials and methods

The Kultuk polygon was arranged for hydrogeochemical monitoring in 2012 within the frame of the Irkutsk State University project funded by the Federal Target Program "Scientific and scientific and pedagogical personnel of innovative Russia" for 2009–2013 to substantiate the forecast of strong earthquakes in the southern Baikal basin. Six groundwater stations were selected from 45 ones for regular measurements of concentrations for 72 chemical elements (including Hg), as well as uranium isotope ratios, by ICP-MS technique using an Agilent 7500ce mass spectrometer. The water was sampled on average every two weeks.

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Received: June 13, 2022; ***Accepted:*** July 18, 2022;
Available online: July 31, 2022

During the Baikal-Khubsugul seismic reactivation in 2020 and 2021, samples were taken more frequently (every three or four days). A 2 ml water sample was passed through a 0.45 μm filter, fixed with a drop of nitric acid and used for element measurement. The activity ratio of the uranium isotopes ($^{234}U/^{238}U$) (*AR4/8*) and the activity of ^{234}U (*A4*) were measured after uranium separation on an ion exchange column. The method used for water analysis and the stations of the Kultuk area were described elsewhere (Chebykin et al., 2015; Rasskazov et al., 2015).

3. Results

Preparation of strong earthquakes was traced through variations of *AR4/8* and *A4*. Both parameters increased when active faults were affected by extension and decreased when those experienced compression (Rasskazov et al., 2020). In addition to uranium isotopes, mercury showed variations that can be used for the prediction of strong earthquakes (Chebykin et al., 2022) (Fig.). Other chemical elements and hydrochemical parameters (Eh and pH) varied in different ways. Their predictive value was uneven because causes of their temporal variations remained unclear, even if they changed before and during an earthquake. Such parameters could change during one earthquake but remained unchangeable during another one.

From a series of observations of uranium isotopes, we recorded a complete seismogeodynamic cycle from crustal compression to extension in the southern Baikal basin, suggesting the pulsating development of seismogenic deformations in the Baikal seismic zone as a time-ordered process. Due to gravitational forces, the upper crust experiences all-round compression, against which additional compressional and extensional impulses occur.

In groundwater from the Kultuk area, a range of mercury concentrations was measured from values below the detection limit (about 0.01 μg/dm^3) to 0.12 μg/dm^3. In a comparative analysis of the time series of Hg and ^{234}U, the behavior of gaseous and dissolved mercury in water was presented in terms of compression and extension in the crust.

4. Discussion

Based on observations during the preparation and implementation of the 1999 earthquake in the southern Baikal basin, we inferred that mercury concentration bursts in the area of the Listvyanka settlement, which 20–30 or more times exceeded background values, were associated with seismicity and that the maximum emission of mercury from faults was produced before seismic events (Koval et al., 2003; 2006). Subsequent observations in this area showed discrete mercury emissions that continued after the earthquake in the southern Baikal basin until 2004. The latest growth of Hg concentration was detected in 2006. Until 2013, mercury concentrations remained at the level of the

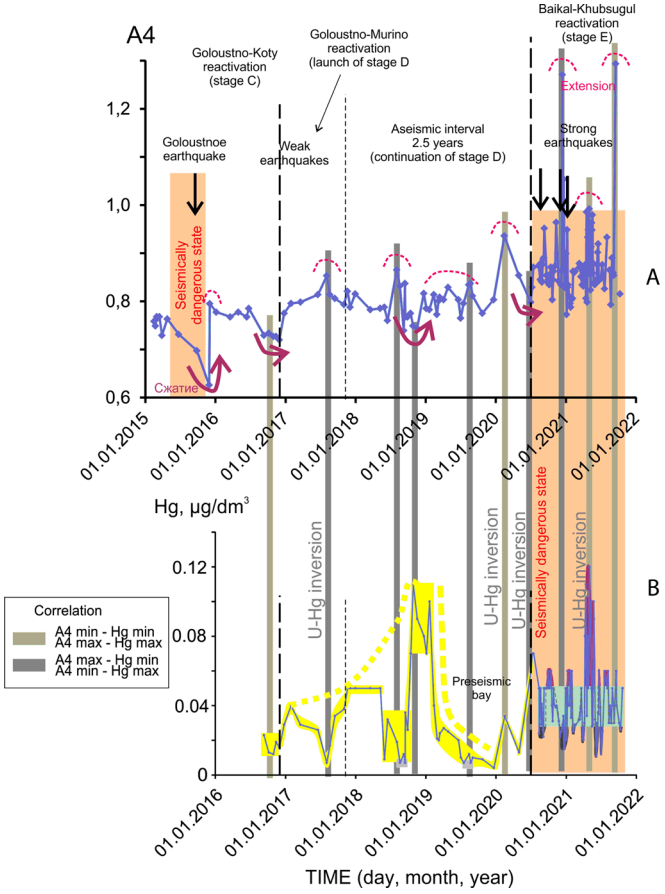

Fig. Transition from crustal compression of 2015 to extension of 2020–2021 in terms of maxima and minima of *A4* (A) and maxima and minima of Hg_{gw} (B) in the groundwater time series of station 27 (Kultuk area).

background value. During the 2008 Kultuk earthquake and later, no mercury anomalies were recorded in the Listvyanka area (Grebenshchikova et al., 2020).

Listvyanka observation series from 1997 to 2013 indicated an increase in the Hg concentrations caused by the 1999 strong earthquake, but there was no increase related to the 2008 strong earthquake in the southern Baikal basin. This selectivity was due to specific reactions to seismogenic deformations in the Angara fault of the Listvyanka area. The fault was reactivated during the 1999 seismic event in the southern Baikal basin but did not show any reactivation during the 2008 Kultuk earthquake. A series of the Hg_{gw} observations in the Kultuk area, which were obtained during the preparation and implementation of the Baikal-Khubsugul reactivation, exhibited data on the most sensitive site for recording reactivated faults in the southern Baikal basin.

Mercury concentrations were also studied in the bottom sediments from a shallow Lake Okunevoe in the Selenga delta where an increase in mercury concentrations from 20 ng/g to 40 ng/g and more was determined around 1870 and in the second half of the 20th century (Roberts et al., 2020). To match the title of the journal “Environmental Pollution”, the authors interpreted the increase in mercury concentrations as a consequence of the industrial development in Siberia

and Mongolia: water pollution associated with gold mining. However, the authors did not provide specific information about gold mining activities in this area, so the proposed explanation for the increase in mercury concentrations has no grounds. Mercury, indeed, concentrates in bedrock, soils, bottom sediments, and surface waters in the industrial zone of the Irkutsk Region (on the left bank of the Angara River from the Baikal to Zima railway station) and along the northwest coast of Lake Baikal (Kitaev et al., 2008).

The Selenga delta is an area of high seismic activity. A series of strong seismic shocks occurred here in 1769 to 1779 (three events in 10 years) and in 1839 to 1885 (5 events in 46 years). A new (currently ongoing) seismic series in the area was marked by the earthquake in the central Baikal basin on 29 August 1959, although strong earthquakes (Mondy and Gobi) occurred somewhat earlier, in 1950 and 1957, respectively (Melnikova et al., 2012). Consequently, the recorded increase in the mercury concentrations in the sedimentary layers of Lake Okunevoe around 1870 and in the second half of the 20th century was likely not related to human activities but reflected the natural process of mercury entering the sediment due to the flux of Hg_{gas} and Hg_{gw} during earthquakes.

Paleoearthquakes accompanied by volcanism in the Baikal seismic zone date back to the past 14.4 Ka with shortening quasi-periods from 5600 to 3100 years or less (Rasskazov and Makarov, 1997). Similar to mercury-elevated sedimentation marking seismicity in the 19th to 21st centuries, mercury marking earlier seismic episodes can be expected.

5. Conclusions

Based on groundwater monitoring in the Kultuk area, we determined long-term increase and decrease in the Hg concentrations in 2017 to 2019 and short-term ones in 2019 to the present, which were definitely related to seismicity of active faults. We recorded increasing Hg concentration in groundwater resulted from an increase in the extension and detected the highest values during aftershocks. We indicated that a Hg flux depended on character of fault activities, and elevated Hg concentrations in sedimentary layers might designate release of Hg_{gas} and Hg_{gw} from seismically active faults in the past 14.4 Ka. Therefore, the elevated Hg concentrations in sedimentary layers of the second half of the 18th century to the present in the Selenga delta may originate from fault activities.

Acknowledgments

Analytical work was carried out using an Agilent 7500ce mass spectrometer at the Center for Collective Use “Microanalysis” (LIN SB RAS).

Conflict of interest

Authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Influence of environmental and social factors on mercury accumulation in the hair of residents of the Northwest Russia

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ABSTRACT. Mercury is a global pollutant. The main source of mercury in the human body is seafood and freshwater fish. More than 90% of methylmercury from total mercury is found in fish muscles. The main aim of this study was to investigate the mercury levels in the hair of the population of the Vologda Oblast, Northwest Russia, where the heterogeneous distribution of rivers and lakes is the resource base of fishing. The mean mercury concentration in the hair of residents of the Vologda Oblast was 0.445 ± 0.018 mg/kg. 10.7% of the samples studied had mercury concentrations exceeding 1 mg/kg. The minimum mercury concentrations were detected in residents of Cherepovets and the eastern districts of the Vologda Oblast. Residents of western districts, where local reservoirs are the main sources of commercial fish, had the maximum concentrations. There were no differences in the amount of this metal between men and women. At the same time, mercury concentrations in men and women from the western districts of the Vologda Oblast had a higher percentage of exceeding the recommended standards.

Keywords: mercury, human hair, recommended levels of mercury, consumption of wild fish

1. Introduction

Mercury is a neurotoxin for a living organism. Even low doses of mercury compounds can cause brain dysfunction (WHO, 2015). Fish is the most important source of mercury in Russia for the population. More than 90% of methylmercury (MeHg) from total mercury (T-Hg) is found in fish muscles (US EPA, 2010). The methylmercury contained in the muscles of fish during digestion is absorbed in the human intestinal tract by 95%. The determination of mercury in hair is widely used in assessing the level of metal intake into the human body (UNEP, 2008). The concentration of methylmercury in hair usually reaches 90% of the total amount of THg.

In different countries, the rationing of the mercury concentrations in the hair differs. According to the World Health Organization (WHO, 2015), the recommended mercury concentration in hair is 2 mg/kg. The US Environmental Protection Agency (US EPA, 2010) established recommended levels of mercury in hair < 1 mg/kg (NRC, 2000). At the same time, a recommended value of 0.58 mg/kg was established for women of reproductive age (Bellanger et al., 2013).

The mercury accumulation in the biotic and abiotic components of biosystems has been studied in the Vologda Oblast over the past 25 years (Komov et al., 2016; Ivanova et al., 2020). Few studies have been conducted on the analysis of mercury concentration in human hair (Rumiantseva et al., 2018).

The aim of this study was to investigate mercury levels in the hair of the population of the Vologda Oblast, Northwest Russia, where the heterogeneous distribution of rivers and lakes are the resource base of fishing. There is traditionally a high level of consumption of wild fish by residents. Rather often, there are high concentrations of mercury in the muscles of fish in local water bodies, whereas the issue of mercury entering the bodies of the residents has not been sufficiently investigated.

2. Materials and methods

This study involved 1,643 residents of the Vologda Oblast for the period from 2016 to 2020. Samples of human hair in the form of a strand from the occipital part of the head, several mm thick, were sampled according to the recommendations of the World Health Organization. The mercury concentration was determined in the hair from the root with a length of about 2 cm (UNEP, 2008) using a RA-915M mercury analyzer (Lumex LLC, St. Petersburg, Russia).

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Received: July 4, 2022; A***ccepted:*** July 18, 2022;
A***vailable online:*** July 31, 2022

Each person signed an agreement to participate in the study. This study was carried out in accordance with the Helsinki Declaration of the World Medical Association (WMA) – Ethical Principles of Medical Research involving People (WMA, 2008). The program of this study was discussed and approved by the Bioethics Commission of Cherepovets State University and the Territorial Department of Health of the Vologda Oblast (No. 2-1/55).

Based on the results of the normality test, nonparametric methods were used, with a significance level (p) of less than 0.05.

3. Results and discussion

The mean mercury concentration in the hair of Vologda Oblast residents was 0.445 mg/kg. The main part of the sample had mercury levels in the hair less than 1 mg/kg. In 10.7% of the studied material, mercury concentrations exceeding 1 mg/kg were detected.

In different localities of the Vologda Oblast, there were different mean concentrations of mercury in the hair. Residents living in the western part of the Volga Oblast had significantly high mean concentrations: Kirillovsky District – 1.226 ± 0.235 mg/kg, Vytegorsky District – 0.954 ± 0.125 mg/kg and Babaevsky District - 0.916 ± 0.141 mg/kg. Also, high values were detected in residents of the Belozersky District (0.739 ± 0.182 mg/kg) and Sokolsky District (0.679 ± 0.138 mg/kg). The mercury concentrations in the hair of people from the western districts of the Vologda Oblast were comparable with those in the hair of residents from areas where gold mining is developed (1.21 mg/kg and 1.61 mg/kg) (Harada et al., 2001).

The minimum mean concentrations of mercury were detected in residents of the Sheksninsky District(0.184 ± 0.029 mg/kg) and Cherepovets (0.327 ± 0.017 mg/kg), and also in residents of the Verkhovazhsky District (0.063 ± 0.023 mg/kg). Residents of the following eastern districts had intermediate values of mercury concentrations in their hair: Babushkinsky - 0.398 ± 0.053 mg/kg, Kich-Gorodetsky - 0.513 ± 0.144 mg/kg and Tarnogsky - 0.540 ± 0.083 mg/kg.

Mercury concentrations were are higher in the western part of the region due to natural and climatic conditions. Mercury methylation occurs in water bodies with the formation of a compound toxic to organisms (methylmercury) that accumulates in the tissues and organs of aquatic animals and is transmitted along the food chain. Thus, we can assume that people living in the western districts are more exposed to mercury because lakes have favorable conditions for the conversion of mercury into organic form. The dimension value for the entire region is 1.98%, but for the western districts it exceeds 4%, and in the eastern districts it is a fraction of a percent.

There were no differences in the amount of mercury between men and women. Notably, mercury concentrations in the hair of men living in the eastern part of the region and in Cherepovets were less than 1 mg/kg , i.e. in 92% and 91% of cases, respectively. 33% of men living in the western regions of the region had metal concentrations exceeding 1 mg/kg (Fig. 1).

Mercury concentrations in the hair of women living in the eastern part of the region and in Cherepovets were also less than 0.58 mg/kg (the threshold, at which there is a risk of disruption of the nervous system in the fetus), i.e. in 87% and 89% of cases, respectively. At the same time, the concentrations exceeding 1 mg /kg (the threshold, above which mental retardation may occur in children in the future) were detected in 13 and 11% of women from these areas. At the same time, 35% of women living in the western districts of the Vologda Oblast were at risk (Fig. 2).

4. Conclusions

The mean mercury concentration in the hair of residents from the Vologda Oblast was 0.445 ± 0.018 mg/kg, ranging from less than 0.002 to 7.64 mg/ kg. 10.7% of the samples studied had mercury concentration more than 1 mg / kg. The minimum concentrations of mercury were detected in residents of Cherepovets and the eastern districts of the Vologda Oblast, and the maximum cocnetrations were observed in residents of western districts where local reservoirs are the main sources of commercial fish. There were no differences in the amount of this metal between men and women. At the same time, mercury concentrations in the hair of men and women from the western districts of the Vologda Oblast had a higher percentage of exceeding the recommended standards.

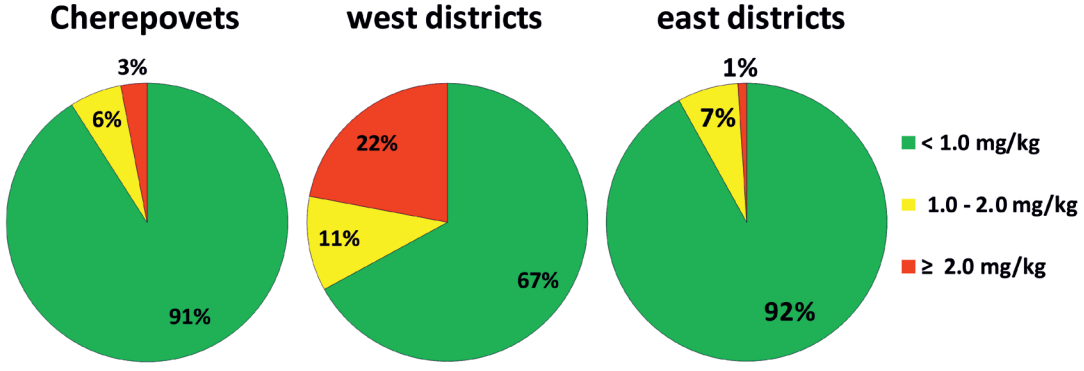

Fig.1. Percentage of mercury concentrations in the hair of men from different districts.

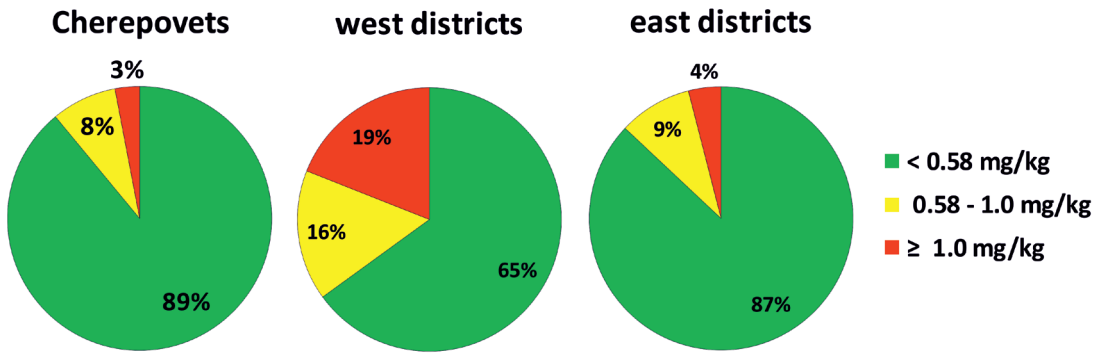

Fig.2. Percentage of mercury concentrations in the hair of women of childbearing age from different districts.

Conflict of interest

Authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Mercury in bottom sediments of Russian Arctic lakes

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ABSTRACT. This article presents the results of studying the distribution of mercury in the cores of bottom sediments of both background and technogenic Arctic lakes in three regions: the Kola North, Malozemelskaya tundra and northwest Siberia. For all cores, the elemental composition, granulometry, and loss on ignition (LOI) were determined layer by layer. Mercury showed a significant excess of the local background in the near-surface sedimentary layers of most lakes. Fluxes of mercury from the pre-industrial period to the present were calculated. We discuss the possibility of technogenic pollution due to transboundary transfer.

Keywords: Arctic lakes, bottom sediments, mercury, sedimentation rate

1. Introduction

Studies of dated cores from Arctic lakes have been carried out since the early 1990s to determine the fluxes and history of heavy metal sedimentation. This is largely driven by the need to understand the spatial and temporal pollution trends in the Arctic and the impact pathways for wildlife and humans. Arctic lakes are sensitive indicators of global environmental and climate change as well as of the impact of regional and transboundary transport of pollutants. A huge number of lakes are concentrated in the Arctic regions of the continental tundra. In the Russian part of the Arctic, there are over 2.5 million of them. However, only about 19 thousand lakes have an area of more than 1 km^2. Nevertheless, the total area of the entire water surface of the Arctic lakes reaches 160,000 km^2, which is slightly less than half the area of all natural water bodies in Russia.

Mercury in the Arctic is a subject of particular interest. Mercury, as a global pollutant, is a cause for concern due to its potential toxicity and increased bioaccumulation in the Arctic food chain, including humans.

In recent decades, significant advances have been made in describing the cycle and behavior of mercury in freshwater environments. A large amount of new data on Hg concentrations, forms, and fluxes has been provided and summarized for water and sediments, but all this applies mainly to the Canadian Arctic and Alaska (Chételat et al., 2015; Douglas et al., 2012). Only a few studies were devoted to the behavior of mercury in lake sediments in the Russian Arctic (for example, Dauvalter and Kashulin, 2018; Tatsii and Baranov, 2022).

Biogeochemical processes that control the accumulation of mercury in sediments are not well understood. Additionally, the Arctic is undergoing profound environmental changes associated with climate warming, and preliminary evidence suggests that this may affect the cycle and bioaccumulation of mercury.

The aim of the work was to study the distribution of mercury in lake sediment cores from various regions of the Russian Arctic, both background and subject to technogenic influence, to assess the dynamics of mercury sedimentation and to identify the anthropogenic contribution.

2. Materials and methods

2.1. Study area and sample collection

Samples of bottom sediments were taken in several regions:

- in the lakes of northwest Siberia (Langtibeito Lake and Goltsovoye Lake) by colleagues from Tyumen State University in 2011;
- in the lakes of the Malozemelskaya tundra by the British expedition in 2017, and
- in the Kola North by the author and colleagues from Vernadsky Institute of Geochemistry in 2018.

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Received: June 16, 2022; ***Accepted:*** July 19, 2022;
Available online: July 31, 2022

Table. Basic data of the studied lakes

Lake	Coordinates		Area, km²		Height a.s.l., m	Average depth, m	pH	Core lengths, cm
	Latitude	Longitude	Lake	Watershed				
Langtibeito	71.063917	70.321806	10.3	8.2	43.4	3.0	7.71	57 and 10
Goltsovoye	71.423333	78.849444	3.87	8.1	9.6	3.5	7.39	48 and 23
NARY 1_2	68.53787	53.71337	1.5	-		0.6	5.9	8
NARY 4_2	68.35489	53.96419	0.07	-		0.7	7.3	9
NARY 9_1	68.3535	53.9571	0.04	-		1.1	8.6	10
Dolgoe	69.454966	31.902271	0.56	12.7	210.0		6.53	25
Keinojärvi	69.45152778	30.65202778	0.14	4.75	131.1		7.12	40

All lakes are located in the Arctic tundra subzone that is characterized by a long duration of snow cover (about 10 months) and a short summer with low temperatures (1-5°C). The main source of income for tundra lakes is atmospheric precipitation and water formed during the seasonal thawing of permafrost. All lakes, except for the Kola lakes, are thermokarst.

For the sampling of the bottom sediments, different types of core samplers with tubes of different diameters were used. Under field conditions, all cores were cut into slices 1 and 0.5 cm thick.

Lakes vary in both size and position. Langtibeito and Goltsovoye are located far from the sea coast; NARY 1-2 is located about 5 km from the coast, and NARY 4-2 and NARY 9-1 are located on Lovetsky Island at a distance of 300 m from each other and about 1.5 km off the coast. The Kola lakes are located far from the coast and are subject to technogenic influence, as they are located in the zone of influence of large metallurgical smelter.

Langtibeito Lake and Goltsove Lake are located far from the sea coast, NARY 1-2 is about 5 km off the coast, and NARY 4-2 and NARY 9-1 are located on Lovetsky Island at a distance of 300 m from each other and about 1.5 km off the coast. Kola Lakes are located far from the coast and are subject to technogenic influence, as they are in the zone of influence of large metallurgical complex (settlements of Nikel and Zapolyarny).

2.2. Core dating and mercury determination

All cores were radiometrically dated by measuring the activity of isotopes ^{210}Pb and ^{137}Cs. Loss on ignition (LOI) was determined by keeping in a furnace at 550°C for at least 2 hours (to constant weight). For individual layers, granulometric analysis by dry sieving for five fractions was performed.

Mercury was determined in all samples from a sample of 20 to 100 mg (n = 3) by pyrolysis of a solid sample with a preliminary accumulation on a gold collector and recording on an AA spectrometer. Calibration was carried out by saturated mercury vapor. The elemental analysis (63 elements) after acid decomposition was performed using ICP-MS at Vernadsky Institute of Geochemistry.

3. Results and discussion

Based on the dating results, we estimated sedimentation rates, background concentrations and enrichment factors relative to the pre-industrial period (before ~1850). The enrichment factors were calculated relative to the local background levels of mercury (and some other elements), which were determined as the average value of those measured in several lower slices of the cores.

Mercury background levels were 5.2, 4.3, and 7.0 ng/g for lakes Goltsovoye, Langtibeito, and NARY 1-2, respectively. For lakes subjected to technogenic influence, Dolgoe and Keinojärvi, background concentrations were 103 and 78 ng/g, respectively. The higher background levels of mercury in these lakes appear to be related to the underlying geology.

The concentration profiles of Hg in the bottom sediments themselves only indirectly reflected the nature of the metal entering the sediments and its source. The flows of elements in the sediments are more informational and complementary. The overall sedimentation rates (black curves in the figure) in all lakes, except for Langtibeito, gradually decrease to the surface layers, while Hg concentrations increase. The average mercury fluxes calculated from deposition rate, slice volume and weight, and mercury concentration in each layer (red curves) show gradual increases in the Langtibaito and Goltsovoe cores and decreases in all NARY cores.

The background fluxes of the total Hg (before 1850) in the studied background lakes were similar and as accounted for 5.1, 2.5, and 1.6 μg/m²year for Goltsovoe, Langtibeito, and NARY 1-2, respectively. Compared to the preindustrial period, the Hg flux had a 3.9-fold increasein Goltsovoye and a 7.9-fold one in NARY 1–2. In Langtibeito, there was a 16.4-fold increase, which is unusually large for polar lakes and may indicate a possible strong anthropogenic influence. In technogenic lakes, the background fluxes were significantly higher: 11.2 μg/m²year in Dolgoe and 9.9 μg/m²year in Keinojärvi. In Keinojärvi, this flow increased by a factor of 5, while in Dolgoe it did not change. It should be noted that the present values of Hg fluxes exceed the atmospheric deposition estimated for the Canadian Arctic as 6-12 μg/m² per year (Chételat et al., 2015).

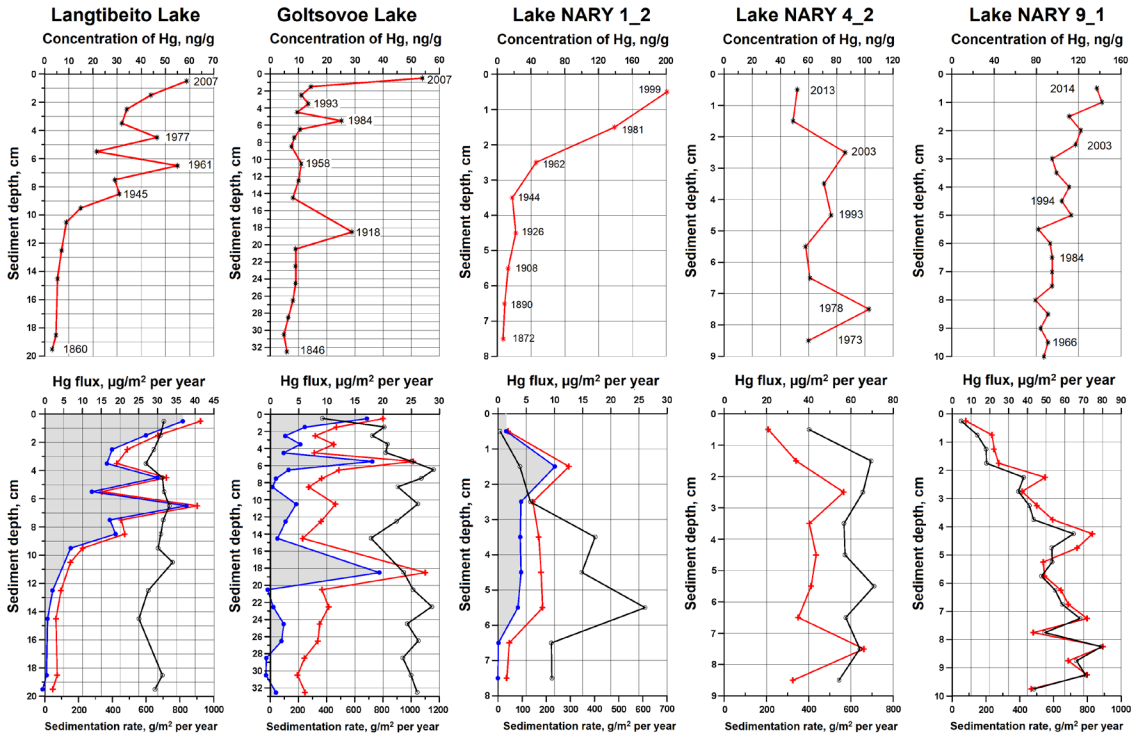

Fig. Features of the Hg distribution in Arctic lakes. Top – concentration distribution of Hg and dating; bottom – curves of deposition flux (black), mercury fluxes (red), and mercury fluxes corrected for Sc and Fe (blue).

To identify the conditionally "anthropogenic" flux in background lakes, the formula proposed by Norton and Kahl (1987) was used to isolate anthropogenic concentrations. We used it to isolate Hg fluxes of non-lithogenic origin. The results are reflected in the blue curve at the bottom of the figure. Fe, Ti, Mg, and Sc were used as reference elements, which gave almost identical curves. The shaded region can be represented as a "conditionally anthropogenic" Hg flux, i.e. non-lithogenic. This flux, in addition to direct atmospheric deposition, may include watershed inputs as well as those from permafrost thawing.

The change in conditionally lithogenic fluxes according to the core data from the studied lakes ranged from 3 to 7 μg/m^2 year during the post-industrial period. The insignificance of the lithogenic contribution was also reported by Lindqvist et al. (1991) and Swain et al. (1992).

In Langtibaito, the total Hg influx increased approximately since the 1940s, reaching 41.5 μg/m^{2}year now, which is rather high for an Arctic thermokarst lake. Two episodic increases around the early 1960s and late 1970s were not accompanied by changes in sedimentation rate but correlated with LOI and particle size distribution.

In Goltsovoe Lake, the anthropogenic Hg flux began to gradually increase approximately since 1970, with an episodic sharp increase around 1980. Sharp increases in Hg flux in both lakes occurred approximately at the same time (late 1970s and early 1980s).

In NARY 1-2, some increase in Hg flux occurred approximately in the same period, around the 1980s. However, all this took place with a gradual decrease in deposition, which became minimal in the upper layer. At the same time, the concentration in the upper layer reached its maximum values.

For NARY 4-2 and 9-1, background fluxes, as well as adjusted fluxes, could not be determined because the depth of the cores did not reach the pre-industrial levels.

4. Conclusions

A layer-by-layer analysis of two cores of bottom sediments showed that the Hg distribution differs significantly from the distribution of other elements by much more intensive enrichment of surface layers.

Studies have revealed that the concentration distribution along the cores does not always unambiguously characterize the entry of mercury into the bottom sediments of Arctic lakes. Analysis of Hg fluxes indicates a non-lithogenic mercury flux. The problem of identifying a purely anthropogenic flux remains unresolved.

Based on the results of the distribution of elements in sediments, all lakes for all studied elements (except for Hg) are background. For Hg, the lakes are not background but remain unpolluted.

Acknowledgements

The research was supported by the RSF grant 22-17-00061

Conflict of interest

The authors declare no conflicts of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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The study of mercury accumulation by plants depending on the chemical form of the element in the growing media

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ABSTRACT. The ability of plants to accumulate pollutants from natural and technogenic environments has found a wide application for cleaning up polluted areas. Most of the works published on this topic are related to the study of the plants efficiency to extract pollutants from polluted areas, including the intensification this process. However, much less attention is paid to the influence of chemical factors on the intensity of the elements accumulation as a function of their speciation. However, the chemical form of the element determines its migration pathways (mobility), bioavailability and toxicity. This issue is in the focus of the present work where the results of the study of mercury accumulation are discussed on the example of white mustard (*Sinápis álba*) depending on the chemical form of the element initially introduced into the growing matter. We have indicated that methylmercury is the most intensively accumulated species in comparison with mercury chloride and mercury sulfide.

***Keywords*:** mercury accumulation, elemental speciation, thermal evaporation technique.

1. Introduction

Intensive economic activity of mankind has led to the formation of many isolated storage zones of man-made materials that are dispersed and transformed in migration processes. The modern technologies allow using only a small part of mining rocks that are processed annually in the world, while the rest is accumulated as the waste, polluting the natural environment. Such areas represent a serious danger, which can be viewed as a challenge to modern humanity, in fact a 'chemical temporary bomb'. The problem of industrial waste disposal is especially important for the areas where mining industries previously functioned. When traditional technologies are used, a large amount of chemical reagents (acids, alkalis, solvents, etc.) will be required, and it is hardly possible to speak about the preservation of the natural environment. In contrast, phytotechnologies can be considered the most nature-friendly approaches (Yan et al., 2020). Some plants are known to accumulate one or more compounds and elements at a concentration level of 0.1-1% dry biomass, which makes this approach promising for the removal of toxic elements from polluted areas. In the articles published on this topic, the plants ability to extract pollutants is at the forefront, but the chemical aspect issues are very limited. The key question about the effect of the chemical form of an element in the growing medium on its accumulation by plant is insufficiently studied; however, this knowledge elucidates the essence of bioaccumulation phenomenon. As mercury refers to the most hazardous elements, the development of new approaches for mercury removal from polluted areas using bioaccumulation remains an actual issue of phytoremediation. The concept of the chemical form of an element is often substituted by a form of existence characterized by the binding of the element to the solid matter of the habitat, which usually specified using stepwise leaching, i.e. through the release of water-soluble compounds by the destruction of the material with the associated element (Hass and Fine, 2010; Chai et al., 2020; Huang et al., 2020). In one of the latest works, in a certain degree associated with the influence of the chemical form of mercury on the accumulation by plants the relationship between the extraction efficiency dependently on the form of its presence in technogenic environments, but the form the element existence does not allow to judge its toxicity, bioavailability and migration routes in nature. Although, frankly, it is worth noting in a few published

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Received: June 17, 2022; ***Accepted:*** July 19, 2022;
Available online: July 31, 2022

works (Godbold, 1991; Ribeyre and Boudou, 1994; Wang, 2004), the authors of which assessed the effect of organic and inorganic mercury on the viability of macrophytes in laboratory experiments. It was shown that methylmercury had higher accumulation efficiency than Hg^{2+} reducing plant viability. Unfortunately, these studies did not receive further development. Currently, there are no data in the literature on the study of mercury accumulation from media containing various species of elements, especially considering their possible transformation during the growth process.

The scientific issue, at which this article is aimed, includes the study of relationship between the chemical forms of the element on the example of mercury and the efficiency of its accumulation by plants in relation to the mercury species typical of a real man-made object, Urskoe sulfide tailing dump (Kemerovo Region).

2. Materials and methods

2.1. Plant material

White mustard (*Sinápis álba*), annual plant, effective mercury accumulator, a green manure that improves the soil structure, changes acidity and enriches it in nitrogen, quickly sprout and bloom.

2.2. Planting medium

The lowland peat of the Siberian region with neutral acidity (pH 6.8) was used as a model medium for growing plants: this was due to the further perspective research on the phytoextraction of mercury from the materials of mining waste, the composition of which is represented by peat-bearing material that is in fact an organic-mineral mixture referred to as natural organic matter (Lazareva et al., 2019).

2.3. Reactants and materials

All chemicals used in research were not lower than analytical grade: mercury chloride, methylmercury chloride and mercury sulfide from Sigma-Aldrich (Australia), nitric acid, hydrochloric acid, oxygen peroxide, aluminum oxide, and sodium hydroxide from Reachem (Russia). Multi-elemental standard solutions for ICP-AES analysis were purchased from SKAT (Russia). Lowland peat of Charodey LLC (Russian Federation) was used as a growing medium.

2.4. Instrumentation

A RA-915+ mercury analyzer with Zeeman correction of nonselective absorption equipped with the RP-91C attachment (Lumex Instruments, Russia) and the RAPID data acquisition software (Lumex Instruments, Russia) was applied for the direct mercury determination in growing substrate and plants under study. For mercury speciation, a sample introduction system was modified with a thermocouple to control the temperature in the dosing unit and with a home-made adjustment to move the dosing unit inside the atomizer. LED lamps “Green power” LWL-2014-01CL ultraviolet lamp (Russia) was used to provide optimal conditions for the plants growth. An iCAP 6500 Duo atomic emission spectrometer with inductively coupled plasma (Thermo Fisher Scientific, USA) equipped with a special attachment for mercury cold vapor generation. A MARS 5 microwave system (CEM Corporation, USA) was used for mineralization of solid samples (peat and plants) before analysis.

2.5. Experiment description

2.5.1. Preparation of the media for planting

The peat sample was divided into four portions (2.5 kg each). Solutions (suspensions) of the studied mercury species were introduced into the peat as follows: spraying a certain volume of mercury chloride ($HgCl_2$) solution (C = 310 ppb) and methylmercury chloride CH_3HgCl (C = 330 ppb), constantly stirring in a volume until the concentration of mercury in the peat was at the level of ~2 ppm (as mercury). In the case of mercury sulfide, HgS (C = 310 ppb), a suspension of mercury sulfide was also introduced into the peat with constant stirring. Then the peat samples were analyzed for the total mercury concentration using a RA-915+ direct analyzer to clarify an exact concentration of the element.

2.5.2. Planting

The peat samples weighing 0.50 kg with a layer thickness of 10 cm were placed in containers. Overall, five containers were prepared with various forms of mercury, and five containers were not seeded.

After 30, 60 and 90 days of the start of experiment, the total mercury concentrations and its species contents were determined in growing media. The accumulation abilities of the plant relative to their species were evaluated using bioaccumulation factor: $BCF = C_{pl}/C_{med}$, where C_{pl} and C_{med} are mercury concentrations in plant and peat, respectively (Arnot and Gobas, 2006). Mercury speciation in the peat material was performed according to our approach proposed previously based on the dilution of the samples with aluminum oxide to unify the analysis procedure and prevent the matrix effect (Shuvaeva et al., 2008).

3. Results and discussion

To study the efficiency of mercury accumulation by plants, we refined the total concentration of the element in the peat samples after introducing various species using the TR-ETA-AAS technique. Obviously, after the completion of the mercury species introduction into the peat substance, the results differed slightly from the calculated ones, which was due to their uneven distribution in the sample.

The results of mercury distribution in the studied plant and bioaccumulation factors (BCF) for each chemical form of mercury in temporal dynamics are presented in Table and in Fig. 1*A*.

Table. Mercury concentrations in parts of white mustard and BCF values for the plants grown in various substrates, n = 3

Experiment duration, days	Mercury concentration			BCF
	Roots	Upper part	The whole plant	
Mercury chloride, $HgCl_2$, 1.9 ± 0.2 ppm				
30	N/d	N/d	0.7 ± 0.3	**0.4**
60	3.9 ± 1.1	0.5 ± 0.2	2.2 ± 0.8	**1.2**
90	11.4 ± 5.5	7.4 ± 2.1	9.4 ± 2.3	**4.9**
Methylmercury chloride, CH3HgCl, 1.2 ±0.1 ppm				
30	N/d	N/d	1.9 ± 0.3	**1.6**
60	11.8 ± 6.0	4.2 ± 1.1	8 ± 2	**6.7**
90	30.2 ± 9.1	11.6 ± 0.4	20.9 ± 5.1	**17.4**
Mercury sulfide, HgS, 1. 4±0.3 ppm				
30	N/d	N/d	1.4 ± 0.7	**1**
60	4.3 ± 0.5	0.6 ± 0.1	2.5 ± 0.2	**1.8**
90	13 ± 7.1	3.4 ±1.8	9.9 ± 2.5	**7.1**

It was obvious that the plants extracted mercury most intensively from the environment containing methylmercury chloride: BCF values within 90 days of the experiment increased from 1.6 to 17.4.

However, it was surprising that the element was extracted more intensively from a medium containing insoluble mercury sulfide compared to that containing mercury chloride. As an explanation for this effect, we can assume that mercury sulfide was oxidized to sulfate in the growing medium, which was confirmed by the data on translocation factor (TF) for mercury sulfide in the plant (Fig. 1*B*) assessed as the ratio of element concentrations in the upper (green) part of the plant to that in the root. In evaluating the efficiency of element accumulation by plants, the value of the translocation factor (TF) is often taken into account: the more TF, the more the plant is able to accumulate the element and, hence, the higher its accumulation capacity. A plant is considered an effective accumulator if TF > 1.

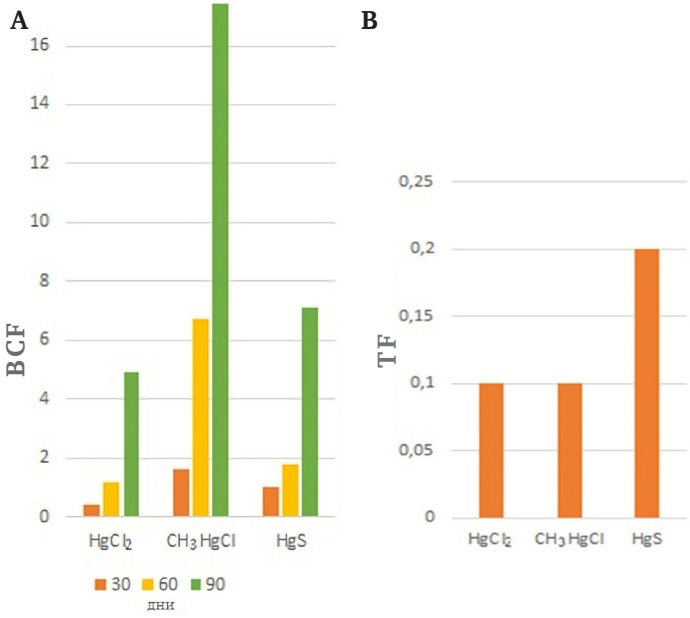

Fig.1. Factors of bioconcentration (*A*) and translocation (*B*) of the studied plant depending on mercury speciation in growing media.

4. Conclusions

In summary, the study indicates that in the process of growth in media containing various forms of mercury, namely, mercury chloride, etc. white mustard extracts accumulate methylmercury chloride most efficiently. At the same time, the translocation factor for mercury sulfide is higher than for other forms, which suggests the transformation of mercury forms in the media during plant growth. This issue is important for a deeper understanding of the essence of the bioaccumulation phenomenon.

Acknowledgments

This work was supported by Russian Science Foundation (grant number 22-27-00684).

Conflict of interest

Authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
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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 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

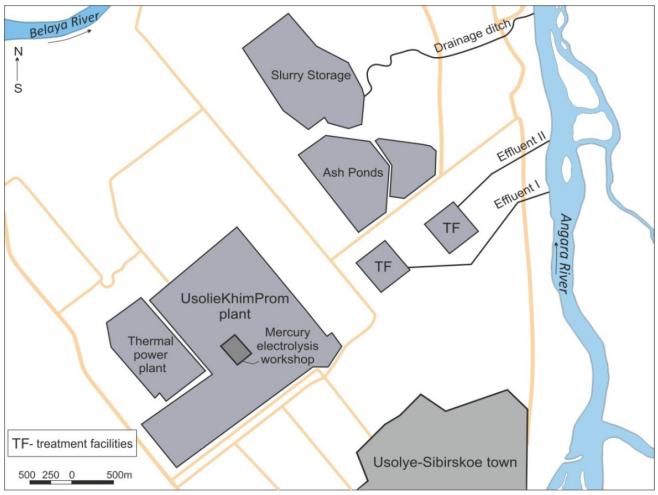

Fig.1. Schematic map of Usolye-Sibirskoye industrial zone.

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Received: June 17, 2022; ***Accepted:*** July 19, 2022;
Available online: July 31, 2022

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 μg/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 μg/l (Rush and Khitskiy, 2003). In 2006 to 2008, mercury concentrations were also very high: up to 9.0 μg/l in effluent I, up to 8.1 μg/l in effluent II and up to 2.5 μg/l in the drainage ditch (Alieva et al., 2011). In 2010, they were 2.39 μg/l in effluent I –, 0.40 μg/l in effluent II, and 1.99 μg/l 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 μg/l. According to (Rush and Khitskiy, 2003), the variability of mercury

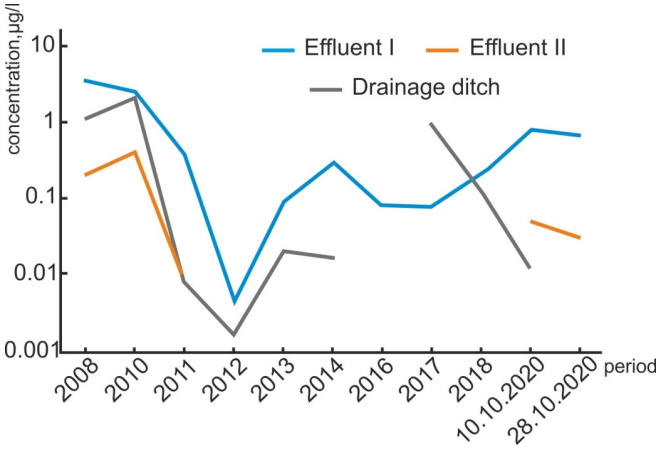

Fig.2. Mercury concentrations in wastewater from the Usolye-Sibirskoye industrial zone.

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 years 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 μg/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 μg/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 μg/l in effluent II, while in the drainage ditch it was 0.013 μg/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.

Acknowledgements

The study was carried out within the framework of the State Project No 0284-2021-0003.

Conflict of interest

Authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
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Automatic monitors for direct continuous mercury measurement in ambient air, hydrocarbon, and industrial gases

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ABSTRACT. Mercury (Hg) has various sources of natural and anthropogenic emissions, can be transferred for a long distance in the atmosphere, and accumulate in deponent media and food chains. Due to its toxicity, mercury is considered a global pollutant. The Minamata Convention on Mercury (Articles 19 and 22) stipulates mercury monitoring to obtain information on the environmental cycle, transport, deposition, transformation, and fate of mercury and mercury compounds in various ecosystems. The developed monitors based on Zeeman atomic absorption spectrometry allow the fully automatic real-time determination of mercury in such different media as ambient air, industrial, and process gases.

Keywords: Zeeman atomic absorption spectrometry, mercury monitoring, ambient air, hydrocarbon and process gases

1. Introduction

The use of atomic absorption spectrometry with Zeeman correction of background absorption (ZAAS) enables us to avoid the Hg accumulation on sorbent traps and to design a family of real-time RA-915AM monitors that are intended for monitoring of ambient air, natural, process, and stack gases.

2. Materials and methods

The RA-915AM mercury monitor (Fig. 1) is based on ZAAS (Sholupov and Ganeyev, 1995; Sholupov et al., 2004) and is designed for the long-term non-attended Hg measurement; it has a built-in PC for data acquisition and processing, self-diagnostics, and data transfer.

Analysed air or gas is continuously pumped at the flow rate of ca. 8 L/min through the multipath analytical cell having an effective optical length of 9.6 m. The readings are collected continuously each 1 sec and are averaged for reporting at any chosen time interval, e.g. 5 min. The combination of the multipath cell with the ZAAS ensures direct continuous real-time measurement of the background mercury concentration in ambient air, as well as the mercury concentration in a wide range of natural and industrial gases. An activated carbon filter is used for zero drift control to detect Hg in ambient air and industrial gases; a special zero filter is used for natural hydrocarbon gases to eliminate an effect of non-selective absorbance of BTEX (benzene, toluene, ethylbenzene, and xylene). Automatic zero drift correction and autocalibration functions provide stable analytical parameters, operational reliability, and safety. For multiple sampling at 2 to 16 sites, the MLT-915 multiplexer is applied.

Fig.1. The automated mercury RA-915AM monitor.

The limit of detection (LoD) was determined three times exceeding the standard deviation of the blank measurement, as 0.3 to 0.5 ng/m^3. Further reduction of the LoD can be achieved by increasing the averaging interval, e.g. for 30-min averaging, the LoD is 0.1 – 0.2 ng/m^3.

Unique features of the monitor, which provided direct real-time measurement with frequency of 15 times per second readings, were used for the specific mercury surface to air mercury flux calculation (Osterwalder et al., 2020).The monitor can also be used

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Received: June 30, 2022; ***Accepted:*** July 18, 2022;
Available online: July 31, 2022

in applications when the analysed ambient air has a reduced pressure, down to 40 kPa (at an altitude up to 5300 m or in the plane measurements (Weigelt et al., 2016)). Since the monitor does not require consumables, including gas cylinders, the use of RA-915AM monitors makes it possible to simplify maintenance at high-altitude and remote monitoring stations.

3. Results and discussion

Most required application for automatic RA-915AM monitors are: the background air monitoring, the indoor measurement at industrial facilities, and mercury determination in hydrocarbon and process gases.

3.1. Air monitoring

Examples of the RA-915AM application for long-term background air mercury measurement at two monitoring stations during a year are shown in Fig. 2. The Listvyanka monitoring station run by Limnological Institute SB RAS (LIN) is located in a rural area on the coast of Lake Baikal. The nearest major anthropogenic source of atmospheric pollution is the city of Irkutsk located at a 70 km distance to the northwest of Lake Baikal (Mashyanov et al., 2021). The South African Weather Service (SAWS) monitoring station is located at the southernmost tip of the Cape Point; the nearest city, Cape Town, is located 60 km to the north. The mean background mercury concentration for the year is 1.50 ng/m^3 (Listvyanka) and 1.53 ng/m^3 (Cape Point).

An example of indoor mercury monitoring at two sampling sites of a mercury storage facility during one year is shown in Fig. 3. The maximum mercury concentration of about 14 ng/m^3 that does not exceed the threshold limit value (TLV = 0.025 mg/m^3) averaged over an 8-hour work shift. The differences in mercury concentrations at different levels are rather small, which indicates good ventilation in the storage facility.

3.2. Hydrocarbon gases

Mercury concentration in hydrocarbon gases varies in a wide range, covering six orders of magnitude (Ozerova et al., 1999). A high Hg concentration in hydrocarbon gases poses some technological and environmental problems (contamination of equipment and products, poisoning of catalysts) and initiates intense corrosion of technological equipment, thereby enhancing accident risk. An example of the mercury monitoring in natural gas is shown in Fig. 4. A special concern is mercury in gas used for liquefaction when the volume of liquefied gas has a 600-fold decrease, and liquid mercury can precipitate even from a gas with a low Hg concentration. Therefore, for liquefaction, the Hg concentration must be brought down to a value below 10 ng/m^3.

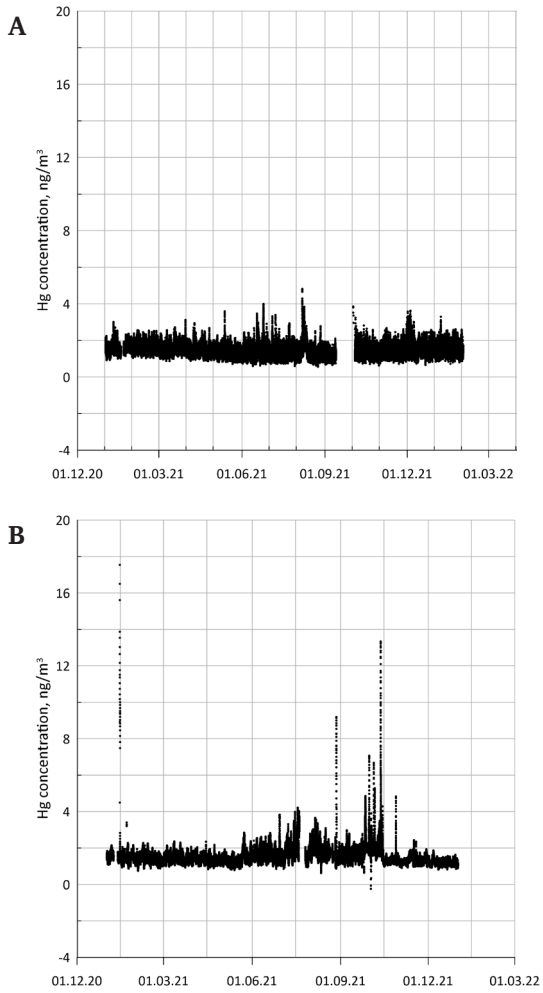

Fig.2. Background mercury monitoring of ambient air during a year at the Listvyanka (A) and SAWS Cape Point (B) monitoring stations. Courtesy of LIN and SAWS.

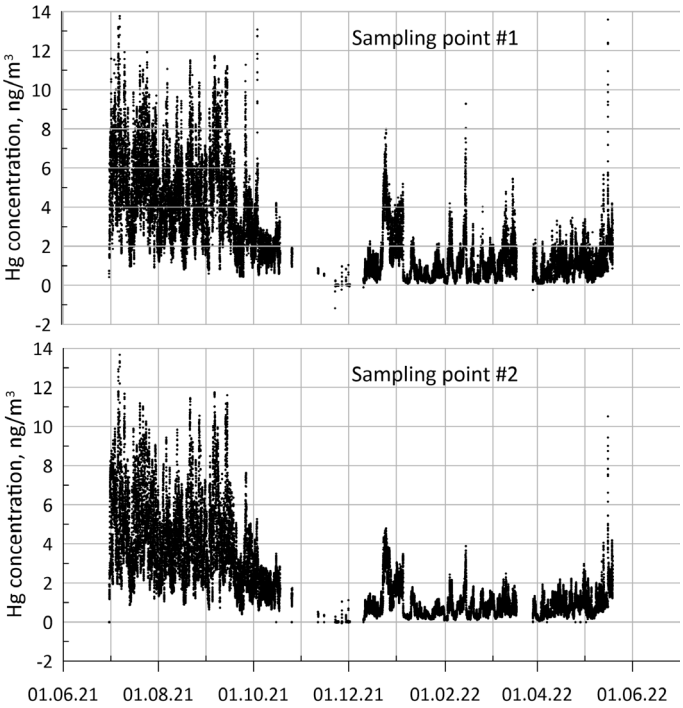

Fig.3. Two-channel mercury air monitoring in the storage for mercury containers at the sampling site #1 (at the level of the upper airways) and at the sampling site #2 (20 cm above the ground). Courtesy of Lumex Analytics.

3.3. Industrial gases

Industrial and process gases are the most complicated objects for mercury monitoring. Nevertheless, high selectivity of ZAAS enables direct online measurement under extremely complex gas composition (Fig. 5).

4. Conclusions

ZAAS technology ensures the development of mercury monitors with outstanding analytical features, combining low LoD, the highest selectivity, and a wide dynamic range. The monitors are used for direct continuous measurement of mercury concentration in ambient air and gases of complex composition. Fully automated data acquisition and processing, built-in self-diagnostics, as well as absence of consumables, enables long-term not attended operation at the remote monitoring sites.

Acknowledgements

The authors are thankful to Prof. T. Khodzher and Dr. V. Obolkin (LIN) and Dr. L. Martin (SAWS) for air monitoring data as well as to Lumex Instruments group of companies for support in the research.

Conflict of interest

Authors declare no conflict of interest.

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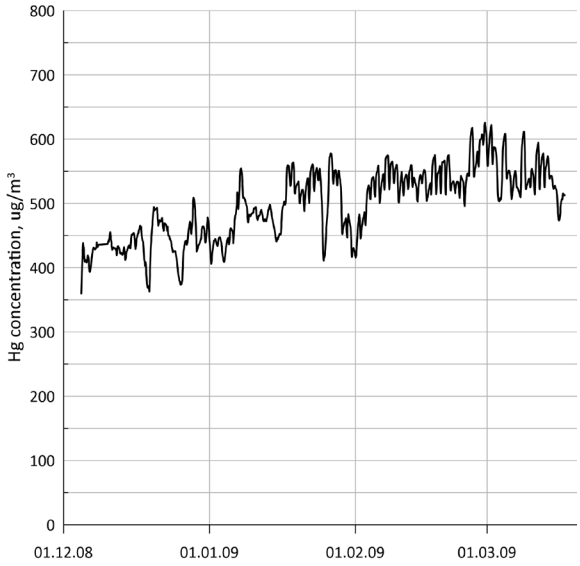

Fig.4. Mercury monitoring in natural gas. Courtesy of Petronas.

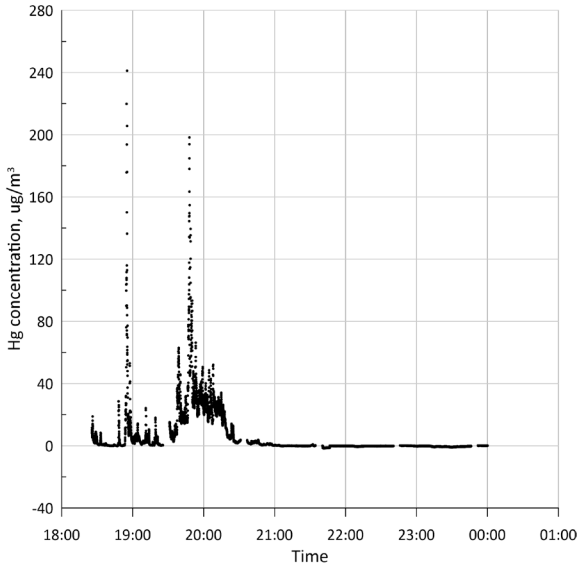

Fig.5. Mercury ambient air monitoring near the medical waste incineration plant. Courtesy of Lumex Analytics.

Short communication

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Mercury concentrations in the surface bottom sediments and cores of the East Siberian and Laptev seas and the adjacent area of the Arctic Ocean

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ABSTRACT. The mercury content in the bottom sediments of the East Siberian, Laptev, Chukchi seas and the adjacent part of the Arctic Ocean was studied. The dependence of its contents on the granulometric composition of sediments and redox conditions of bottom waters is established, which generally manifests itself as the bathymetric zonality of the distribution.

Keywords: geochemistry, geoecology, ecology, mercury, heavy metals, anthropogenic pollution, natural sources, Arctic and Far Eastern seas

1. Introduction

Bottom sediments are the most informative part of aquatic ecosystems in terms of assessing the degree of their permanent pollution. They are undoubtedly associated with all other components and can accumulate contributions from different sources. Typical mercury concentrations in bottom sediments are three or four orders of magnitude higher than in the water. This removes many analytical difficulties and, as a rule, makes the bottom sediment-based assessment of the pollution pattern in the basin much more reliable than the water-based one.

2. Materials and methods

Mercury concentrations were detected in 79 surface bottom sediments and 15 cores (multi-cores) with undisturbed surface (Fig. 1). To determine mercury, an RA-915M+ mercury analyzer with a PYRO-915 pyrolytic attachment was used. The lower detection limit was 0.5 ng/g. The analysis error was 2-3%. GSO 7183-95, SPDS-1,2,3, HISS-1, MESS-4, and PACS-3 served as reference materials for mercury. External control was carried out annually in the manufacturer's laboratory (Lumex LLC, St. Petersburg). Statistical distribution parameters were determined with the GeoStat programme.

3. Results and discussion

The data processing revealed that the mercury concentration changed with bathymetric level (Fig. 2). The study area was characterised by a selection of 79 samples of surface bottom sediments (0 to 5 cm), which were divided into two groups: i) to a depth of 100 m (n = 67) and ii) within the depth range from 100 to

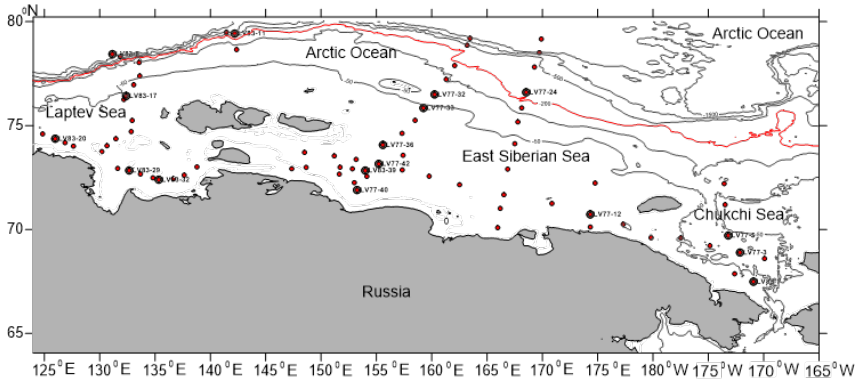

Fig.1. Map of stations in the Chukchi, East Siberian and Laptev seas and the adjacent area of the Arctic Ocean. The dots highlight sampling stations. Isolines indicate bottom topography (m). The labeled stations mark the cores where mercury was detected vertically.

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Received: July 4, 2022; ***Accepted:*** July 20, 2022;
Available online: July 31, 2022

260 m (n = 12). Mercury concentrations for this area varied from 3 to 92 ppb, with mean and median concentrations of 31 and 29 ppb, respectively. The median value served as the background concentration, which was well correlated with the previously determined background of 28 ppb for the bottom sediments of the Chukchi Sea and the adjacent area of the Arctic Ocean (Ivanov, 2014).

The presence of oxidized or reduced sediments is the main factor that determines the variability of mercury concentrations in the bottom sediments. The twofold excess over the background is typical of the deep part (depth 100 to 2600 m) where oxidized sediments are widespread. In the shallow part (0 to 50 m) of the Laptev Sea, where reduced sediments with various compositions are widespread, the mercury concentrations were much lower, but there was also the influence of the Lena River. It is necessary to take into account that the products of thermal and wave abrasion of the material from the nearshore ice complex determine the influx of terrigenous organic matter to the sea. Samples of the surface bottom sediments taken at the estuary of the Lena River in 2008 to 2009 had the same mercury concentrations (Ivanov, 2011). Also, elevated concentrations at stations LV77-30, 31 and 32 were associated with the presence of ferromanganese nodules at the bottom.

A similar pattern of mercury distribution in the surface bottom sediments was typical of other Arctic areas with its natural sources. In the central part of the Arctic Ocean, where oxidized sediments are widespread, mercury concentrations were 80 to 100 ppb; in the surface sediments of the coastal area of the Beaufort Sea – 20 to 100 ppb; in the coastal part of the East-Siberian and Laptev seas – 20 to 40 ppb, and near the estuaries of large rivers – about 60 to 80 ppb (Table).

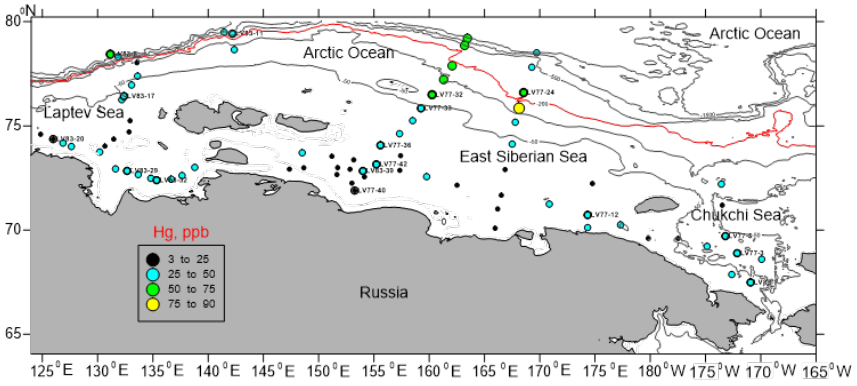

Fig.2. Mercury concentrations in the surface bottom sediments of the Chukchi, East Siberian and Laptev seas and the adjacent area of the Arctic Ocean. The dots highlight sampling stations. Isolines indicate bottom topography (m).

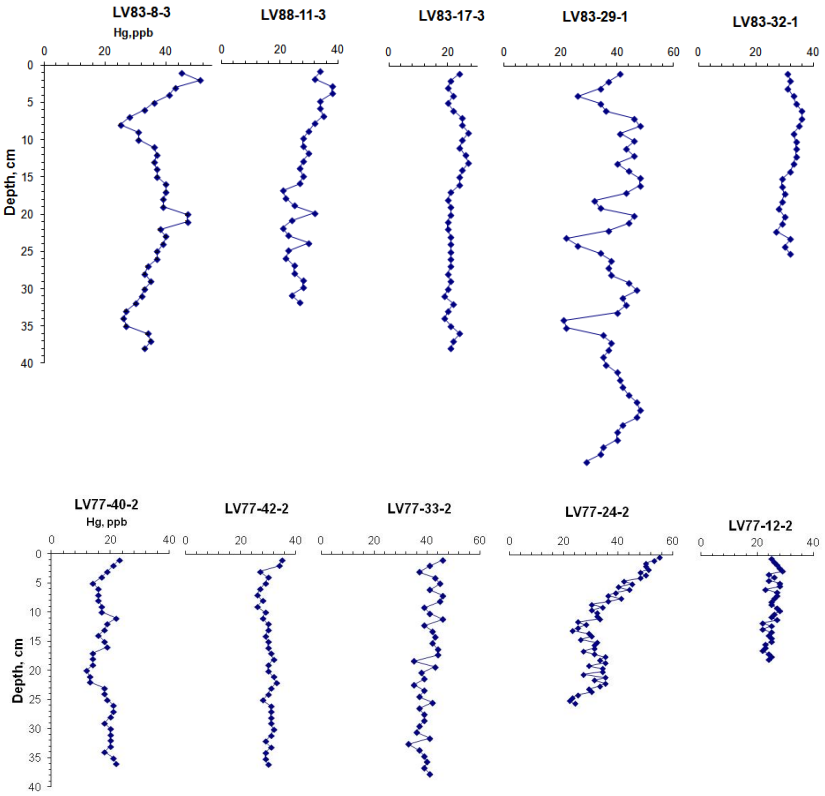

Fig.3. Mercury concentration (ppb) in some multi-cores.

Table. Mercury concentrations (ppb) in the surface bottom sediments of the Arctic and Far Eastern seas.

Object	Number of samples	Hg, mean	Background	Background variation limits	Abnormally high concentrations	Reference
Chukchi Sea and adjacent area of the Arctic Ocean	263	36	28	7-92	146	Ivanov, 2014
Deryugin Basin of the Sea of Okhotsk	51	61	29	6-197	371	Ivanov, 2014
Amur Bay of the Sea of Japan	119	50	13	12-198	550	Ivanov, 2014
East-Siberian Sea and Laptev Sea	79	31	29	3-92	-	This study, 2017-2018
Kara Sea	-	28	-	-	-	Fedorov, 2018
Beaufort Sea	-	-	-	17-74	-	Fedorov, 2018

Analysis of the mercury distribution in multi-cores of bottom sediments indicated that in the deep part it was characterised by a rather high vertical variability that was associated with the alternating oxidized and reduced sediments in the section, which accumulated, respectively, during the warming and cooling periods. Mercury concentrations in multi-core LV83-8-3 sampled in the deep area ranged from 25 to 51 ppb (Fig. 3). In multi-cores LV83-1-2 and LV83-17-3 located on the shelf (Figure), mercury concentrations were much lower, about 25 μg/kg.

4. Conclusions

The study results revealed that the presence of oxidized or reduced sediments was the main factor determining the variability of mercury concentrations in surface bottom sediments. As in other Arctic seas, mercury concentrations depended on the granulometric composition of the bottom sediments.

There was no anthropogenic mercury pollution of the sediments, but it is likely that some part of it entering together with the water of the Lena River and accumulating in the shallow part of the Laptev Sea may be of anthropogenic origin.

Acknowledgements

This study was supported by RSF grant No 21-17-00081; analytical work was supported by RSF grant No 18-77-10017-P. Expeditionary work was partially funded by the State Project No 121021700342-9.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Mercury in paleoarchives as a proxy of environmental and climate changes

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ABSTRACT. The paper presents a case study of mercury in two types of paleoarchives: ice cores and prehistoric animal hair, to assess the potential of Hg using as a proxy for environmental and climate changes. Belukha ice core is well-suitable for reconstruction short-term and long-term Hg deposition, recording global and regional, natural and anthropogenic emissions as well as regional climate changes during 320 years. Hg concentrations in hair of mammoth fauna mammals reflect the variation in Hg level in the environment during period from 45 to 10 ka yr BP. Hg concentrations changes following climatic changes are in a good agreement with other paleoarchive data (Hg fluxes of the EPICA Dome C ice core and Lake Baikal sediments).

Keywords: mercury, paleoarchives, ice cores, animal hair, climate changes, proxy

1. Introduction

Proxy Data represent preserved physical characteristics of the environment that can be used for direct measurements. Proxy data from natural archives such as ice cores and ice caps, lake, marine and ocean sediments, peat bogs, tree rings, caves, and corals record information about climate variability and environmental changes. There are 3 main criteria for the suitability of an archive for paleoreconstructions: 1) Correlation between climatic and ecological changes in the environment and the concentration of marker in the corresponding layers (samples) of the natural archive; 2) Stability (or controlled change in concentration) of substances-markers throughout the lifetime of the archive; 3) Possibility to separate and identify layers (samples) with ensuring their reliable dating. Layers or rings store information about the climate and the state of the environment at the time of their formation, differing in temporal resolution (it can be a decade, a year, or growing season). Each type of archive has its own advantage and disadvantage. Ice cores from high altitude glacier are well-suited for studying anthropogenic influence and rapid climate changes, since they provide continuous records having high temporal resolution, but have rather short time interval. The oldest continuous ice core records date back 123,000 years in Greenland and 800,000 years in Antarctica. Antarctic ice cores are used to reconstruct past climate changes, while Greenland ice-core records are ideal for studying fast climate variations in the North Atlantic region (Steffensen et al., 2008) due to their well-constrained chronologies. The main limitations for ice cores are their location in remote sites (at high latitudes or high elevation hard to reach), the complexity of the work (cold and high mountain condition, climbing skills, expensive expedition), and special requirements for storage and analysis (ultra-clean protocol, low temperatures (bellow -20°C), expensive equipment, well-trained staff). Lake and marine sediments having a wide time interval are widely used to reconstruct past trends of climate and anthropogenic pollution, although there is delay of response and multifactor influence on it. Lake sediments accumulate Hg deposited directly on the lake surface itself and exported from the watershed to the lake. This is confirmed by the Hg isotopes analysis demonstrated that lake sediments contain a mix of both precipitation-derived Hg and vegetation-bound Hg (Chen et al., 2016). So small remote lakes with little watershed can reveal variability in the global atmospheric Hg cycle, while lakes located near industrial, or urban centers, mining, etc. will record local Hg emissions and its change through time. Most of marine sediments' researches are based on the sampling of surface sediments in bays and estuaries, identified Hg contamination from plants, waste discharges, shipyard activity, etc. Complexation by organic matter, binding to Fe-Mn oxides, hydrothermal emissions, river discharge, point pollution sources, competition with sulfides and methylation may play a significant role

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Received: August 03, 2022; ***Accepted***: August 04, 2022***;***
Available online: August 17, 2022

on the accumulation of Hg (Cooke et al., 2020). Peat bogs are the most widely used archive for researches of atmospheric Hg deposition, since in comparison with other environmental archives peatlands cover a broader spatial distribution (from the tropics to the high latitudes), have relatively high time-resolution and record atmospheric input (both dry and wet deposition). Although there are some problems such as fires influence, mobility/release of mercury after deposition, peat decomposition, and mire vegetation. Biester et al. (2007) stated that the lower background mercury accumulation rates in peat as compared to lake sediments is the result of nonquantitative retention and loss of mercury during peat diagenesis. Tree rings are active samplers of atmospheric Hg recording regional gradients in GEM concentrations; also they contain annual records of climate for centuries to millennia. Temporal consistency may vary within a geographic location due to differing biotic and abiotic factors influencing ring growth (Peckham et al., 2019). It should be noted that in addition to continuous natural archives, there are such "keepers of history" as hair which help to assess the level of environmental pollution by its impact on the body (Thompson et al., 2014). Hair presents the cumulative average exposure, so museum samples of animal and human hair, bird feathers were used for assessment environmental Hg pollution and anthropogenic impact on the environment. Thus, all considered environmental archives make it possible to reconstruct spatial and temporal patterns in atmospheric Hg deposition at different timescales, but their using requires an understanding of how each archive accumulates and retains Hg (Cooke et al., 2020).

2. Materials and methods

Whereas for the ice core analysis ultra-clean conditions and ultra-sensitive method of determination are decisive, for the hair analysis the most important points are optimization of pretreatment and digestion.

2.1. Ice core

In July 2001 a 139 m ice core was recovered at the Belukha glacier (49°48'26"N, 86°34'43"E, 4062 m a.s.l.), the highest mountain in the Altai region. Ice-core sections were transported frozen to the Paul Scherrer Institute (PSI, Switzerland) for glaciochemical analyses. 671 samples of ice and firn were prepared for Hg analyses in the cold room of the PSI at -20°C. Details of ice core cutting and decontamination procedure were described in the paper (Eyrikh et al., 2017). All field and analytical works were carried out in accordance with the "ultra-clean protocol". Possible contamination of an ice core samples during sample preparation was tested using radial experiments using both artificial and real ice. Total Hg concentrations were determined by Mercur Duo Plus Analyzer (Analytik Jena, Germany) in accordance with the US EPA 1631 method. A certified reference material (ORMS-2, Natural Research Council Canada) and standard addition method were used to prove analytical accuracy. The recovery was 98-102% and the reproducibility 1-6%. The average limit of detection (LoD) was 0.04 ng/L.

2.2. Mammoth fauna mammals hear

Mercury was determined in seven specimens of mammoth fauna mammals: 4 woolly mammoths, 2 steppe bisons and 1 woolly rhino. Hair samples were obtained from the Geological Museum of DPMGI (Yakutsk). All the studied fossil mammals inhabited in Yakutia region in the period from 45 to 10 ka yr BP. Detailed description of fossil mammals (location and time of the discovery, estimation of the geological age by radiocarbon dating, calibrated age, sex and physiological age of the animal) and method of Hg analysis were presented in the paper (Eyrikh et al., 2020). It was necessary to select the optimal parameters at which there are no losses of volatile components and complete decomposition is achieved. Procedure of sample preparation (washing, cutting and microwave digestion) and Hg determination were developed and tested using hair samples of modern yak and Certified Reference Material of human hair (Hair DC 73347, China). Total Hg concentrations were determined by Mercur Duo Plus Analyzer (Analytik Jena, Germany). Method Detection Limit was 0.003 μg/g. The average uncertainty on duplicate sample analysis did not exceed 5%.

3. Results and discussion

3.1. Hg in the Belukha ice core

A high resolution paleoreconstruction from the Belukha ice core reflected the history of atmospheric deposition of Hg over a 320-year period. The concentration profile represents both prolonged mercury emission and short-term events (such as volcanic eruptions, dust storms, and anthropogenic accidents). The obtained results showed that the part of the core related to the period 1700-1900 mainly reflected the history of the regional mining and metallurgical industry of Rudny Altai in the 18-19 centuries (Fig. 1). Hg concentrations increased from 1740 to 1850 due to the contribution of the regional component, then from 1850 the regional contribution decreased and the global one increased, and after 1880 mercury concentrations mainly reflect the global atmospheric background. In the 20th century, trends in Hg concentrations and deposition fluxes are in a good agreement with other glaciers in the world, with the exception of the last 10 years, when an increase in Hg concentrations in the Belukha core revealed growing mercury emissions from Asian countries due to coal burning and small-scale gold mining (Eyrikh et al., 2017). Regional climate response following the Little Ice Age (LIA) is amplified as compared to the Northern Hemisphere average, most probably caused by the strong continentality of the Siberian Altai region (Henderson et al., 2006). Thus, the ice core reflects both regional and global environmental changes, as well as regional climate changes.

3.2. Hg in hairs of prehistorical animals

Such archives as wool and hair give a screening assessment in a certain period of time recording the cumulative mid- to long-term average exposure (depending on the length of the hair sample). The hair of mammoth fauna mammals is a screening material reflecting the environmental situation in the last year of their life, since the animal's hair is replaced by new one across 1-1.5 year. All prehistoric animals have low Hg level in their hair below concentrations associated with toxicity in wildlife and do not exceed background levels of mercury in hair of non-seafood consumers (0.5 μg/g). Most of Hg concentrations were within the reference range for modern cattle (Eyrikh et al., 2020). Hg concentrations in hair reflect the variation in Hg level in the environment following climatic changes. Increase of Hg concentration in hair during the coldest climatic stages (such as LGM) coincided rise of Hg deposition on the surface associated the highest atmospheric dust loads. Also mercury can release to the atmosphere because of permafrost thawing during interstadial warming, highest Hg concentration belongs to Karginian interstadial of the Late Pleistocene, the period when maximum insolation and warming was observed. Hg concentrations in mammoth fauna mammals related to different climatic periods are in a good agreement with Hg fluxes recorded in the EPICA Dome C ice core (Fig. 2A) and bottom sediments from Baikal (Fig. 2B) demonstrated the response of Hg cycle on the climate oscillates between cold and warm periods.

4. Conclusions

Mercury record from the Belukha ice core reflected both short-term and long-term Hg deposition preserved both global and regional impacts which contributions have varied considerably over time. Short-term climatic changes also were recorded in the studied ice core. Hg in hairs of prehistorical animals is new and promising proxy of environmental and climatic changes. It is prehistoric animals that can be the key to understanding the relationship of Hg level changes associated with climate changes. This is a big deal, especially since the extent of climate fluctuations across the Earth and regional differences in climate shifts are still unclear. At this point, there are a lot of Hg records recovered from natural archives for many regions of the world (such as Canada, USA, Europe), but for such huge regions as Russia more data are needed. Russia has a great potential for research of almost all kinds of natural archives. Reconstructed data on wide spatial-temporal scale will allow assessing past trends in atmospheric Hg deposition and distribution, identifying natural and anthropogenic sources involved in Hg cycling. Joint consideration of different records taking into account the strengths and weaknesses of each archive is a way to get better understanding of the processes and patterns influencing on Hg cycling and the response of Hg cycling on environmental and climate changes.

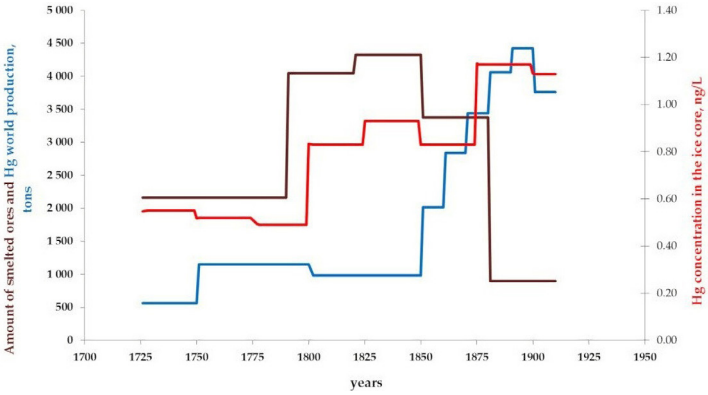

Fig.1. The amount of smelted ore (tons*10) in Altai mining district, world mercury production and average 25-year Hg concentrations record in the Belukha ice core.

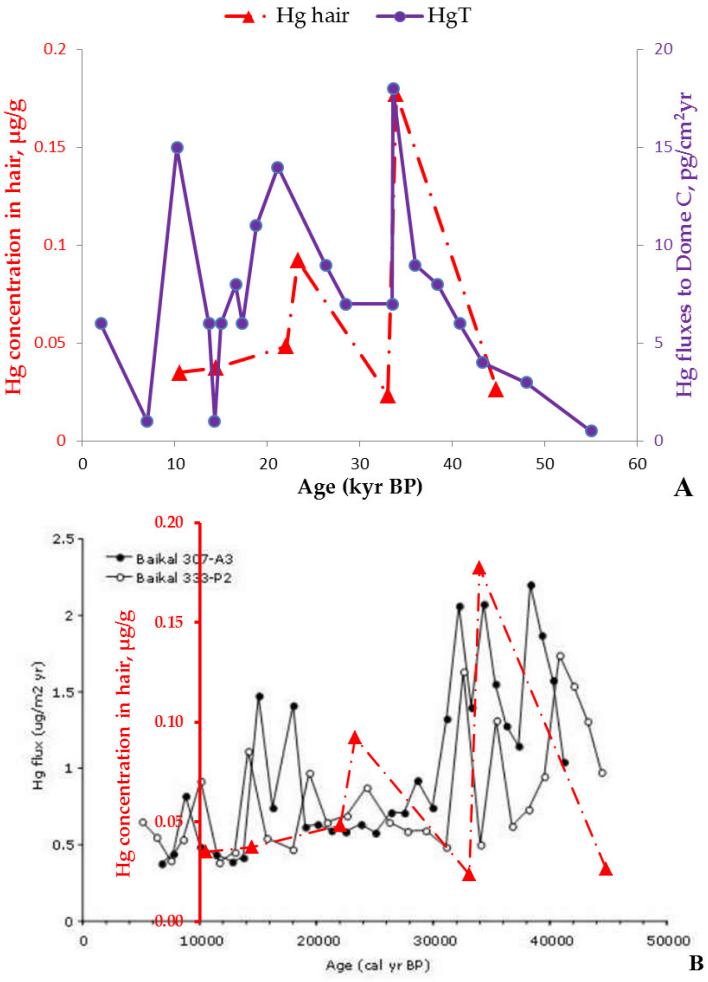

Fig.2. Total Hg concentrations in mammoth fauna mammals' hair and fluxes of total mercury (HgT) in the EPICA Dome C ice core (A) (data taken from Jitaru, 2009_SI) and Hg accumulation in Lake Baikal (B) (Lamborg, 2011).

Acknowledgments

Author is thankful to Margit Schwikowski (PSI, Switzerland) for exciting long-term collaboration in ice core projects, Gennady Boeskorov (DPMGI SB RAS, Yakutsk) for fascinating joint mammoth researches, and Tatyana Papina as an intelligent leader for giving me the opportunity to engage in these researches.

The study was carried out under a state assignment of the IWEP SB RAS by the Ministry of Science and Higher Education of the Russian Federation.

Conflict of interest

The authors declare no conflict of interest.

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ISSN 2658-3518
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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)

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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

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Received: July 06, 2022; A***ccepted:*** July 15, 2022;
A***vailable online:*** August 17, 2022

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, $HgCl_4^{2-}$ ≈ 92-96%, $HgCl_3^-$ ≈ 2.7-5.9% and $HgCl_2^0$ ≈ 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).

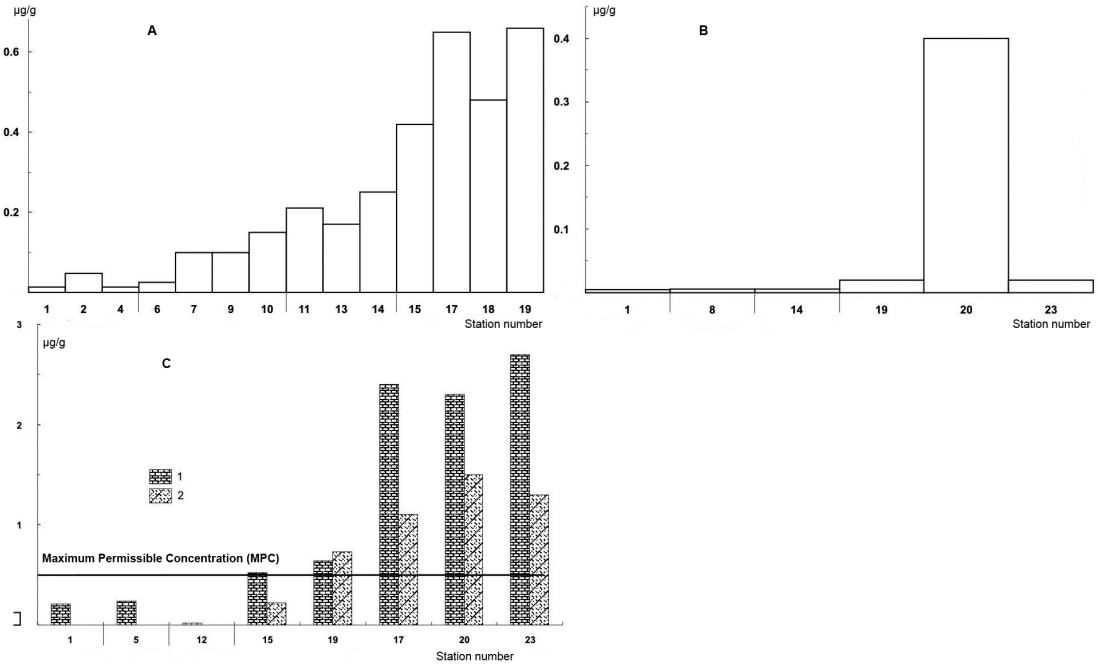

Fig.1. Mercury concentrations in the aquatic organisms of the Bratsk Reservoir: A) in plankton, B) in aquatic plants and C) in the muscle tissue of fish. 1 – perch and 2 – roach. The abscissa shows sampling stations.

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).

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.

Acknowledgements

This study was carried out within the framework of the IGM SB RAS and IGC SB RAS state projects. The results were obtained at the Analytical Centre for Multi-Element and Isotope Research of IGM SB RAS and the Analytical Centre of IGC SB RAS.

Conflict of interest

The authors declare no conflict of interest.

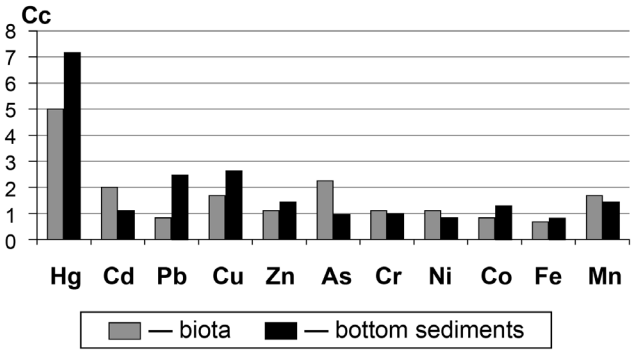

Fig.2. Elemental concentration coefficients (C_c) in the biota (*Artemia salina*) and bottom sediments of Lake Bolshoye Yarovoye in the influence zone of the Altaikhimprom plant.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Distribution of the total and dissolved mercury concentrations at the Irkutsk city snow sampling during winter 2021-2022

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ABSTRACT. We took 41 samples for a quantitative assessment of the total and dissolved mercury concentrations in the snow of the city of Irkutsk during winter 2021-2022. The maximum concentration of total mercury was recorded near the Eternal Flame memorial (248 ng/dm^3); the minimum concentration was 6 ng/dm^3 at the Jewish cemetery. The maximum concentration of dissolved mercury was recorded near the Aviation Plant (11.5 ng/dm^3), and the minimum – near the Maratovskoye traffic circle and Secondary School No. 66 (0.1 ng/dm^3). In four samples, we did not detect dissolved mercury. Determining the mass concentration of mercury revealed that the concentrations of mercury compounds in the snow from Irkutsk were much lower than the MPC. Based on the results of the analysed samples, we created a cartographic material.

Keywords: total and dissolved mercury, concentration, snow, winter, Irkutsk

1. Introduction

Mercury is a low-active metal that is liquid under normal conditions. Metallic mercury itself is less hazardous, but it easily evaporates, and its vapor is extremely toxic. In nature, mercury is found in all components of the environment: soil, water and air. The organic mercury compounds are the most toxic.

The unique geochemical and toxicological properties of mercury determine the specifics of its concentration and redistribution in various components of the environment. A characteristic feature of metallic mercury is low heat of vaporization, causing high volatility of its vapor and not only possible evaporation from the surface of metallic mercury but also diffusion through water layers (Antipov et al., 1999). Mercury evaporation occurs even at the temperature below its freezing point (-390°C), due to which a 'mercury atmosphere' is created, elucidating the mercury dispersion in various spheres of the Earth (Grebenshchikova et al., 2008). This explains the ability of mercury to accumulate in food chains, the diversity of migration forms and specifics of their transformation under natural and technogenic conditions as well as a wide and varied range of negative impacts on humans and other living organisms, their populations and ecosystems as a whole. Combined with the comparatively easy reduction of mercury to the metallic state under ambient conditions, this feature may lead to the global atmospheric transport of mercury. Mercury and its compounds are highly toxic and disrupt protein metabolism and the enzymatic activity of living organisms (Efimova et al., 2016).

Of great interest is the supply of mercury in the cold continental regions during winter where snow, being a specific accumulator of air pollutants, represents one of the intermediate stages in the general mercury cycle. A stable snow cover is formed in most of Russia. The duration of snow periods differs for different regions. Snow in winter is an effective sink for air pollutants from fuel combustion, industrial emissions, vehicle exhaust, and transboundary transport (Davidson et al., 1996). Therefore, snow is a subject of many studies as a reliable indicator of air pollution, which can provide information about pollutant sources.

This study aims at quantitative assessment of mercury concentrations in the snow from the city of Irkutsk.

2. Materials and methods

During winter 2021-2022, 41 snow samples were taken in the city of Irkutsk. Mercury concentration in snow was studied in Laboratory of Hydrochemstry and Atmosphere Chemistry at Limnological Institute SB RAS. Sample preparation for chemical analysis was carried out according to PND F 14.1:2:4.271-2012 "Method

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Received: August 08, 2022***; Accepte***d: August 08, 2022;
Available online: August 17, 2022

for measuring the mass concentrations of mercury in samples of natural, drinking, mineral, and waste water by the atomic absorption with Zeeman correction of non-selective absorption on an RA-915M (M 01-51-2012) mercury analyzer" with the RP-92 attachment. The snow samples were analysed for dissolved and total mercury by permanganate mineralization (Method A).

3. Results and discussion

Data on mercury concentrations at different sampling sites are presented in the form of cartographic material that was created in QGIS 3.10 using the QuickMapServices OSM Standard module. Figure 1 shows the distribution of total mercury concentrations in the snow samples from different areas of Irkutsk in winter 2021-2022.

As seen in Fig. 1, three samples were taken near the thermal power plant, and with distance from the pollution source, the mercury concentration decreased in the snow, from 178 ng/dm^3 to 121 ng/dm^3. In the samples collected near boiler houses located in Rabochee District, the mercury concentrations were 146 ng/dm^3, which is higher than the city average of 95 ng/dm^3. The maximum concentration of total mercury was recorded near the Eternal Flame memorial, 248 ng/dm^3. The minimum concentration of total mercury was 6 ng/dm^3 at the Jewish cemetery. Notably, maximum permissible concentration (MPC) of mercury in drinking water is 500 ng/dm^3.

Figure 2 shows the distribution of dissolved mercury in the Irkutsk snow at the same time.

In four samples, we did not detect dissolved mercury, which indicates extremely low concentrations of dissolved mercury in the snow. Like in Fig. 1, there was a trend to elevated concentrations of dissolved mercury at sites near the thermal power plant and its decrease with distance from the pollution source, from 4.1 to 2.2 ng/dm^3. In Rabochee District, the concentration of dissolved mercury was minimum compared to the concentration of total mercury. The maximum concentration of dissolved mercury was recorded near the Aviation Plant, one of the strategic industrial enterprises in Irkutsk, and accounted for 11.5 ng/dm^3. In all analysed samples, the concentration of dissolved mercury was below the lower detection limit of the PND F 14.1:2:4.271-2012 method.

4. Conclusions

Determining the mass concentration of mercury revealed that concentrations of mercury compounds in the snow sampling during winter 2021-2022 from Irkutsk were lower than the MPC of mercury in drinking water (500 ng/dm^3). The maximum concentration of total mercury was recorded near the Eternal Flame memorial (248 ng/dm^3); the minimum concentration was 6 ng/dm^3 at the Jewish cemetery. The maximum concentration of dissolved mercury was recorded near the Aviation Plant (11,5 ng/dm^3), and the minimum – near the Maratovskoye traffic circle and Secondary School No. 66 (0.1 ng/dm^3). In four samples, we did not detect dissolved mercury. Taking into account that snowfall contributes to the precipitation of pollutants from the atmosphere, we can state the minimum content of mercury compounds in the atmosphere of Irkutsk during winter 2021-2022.

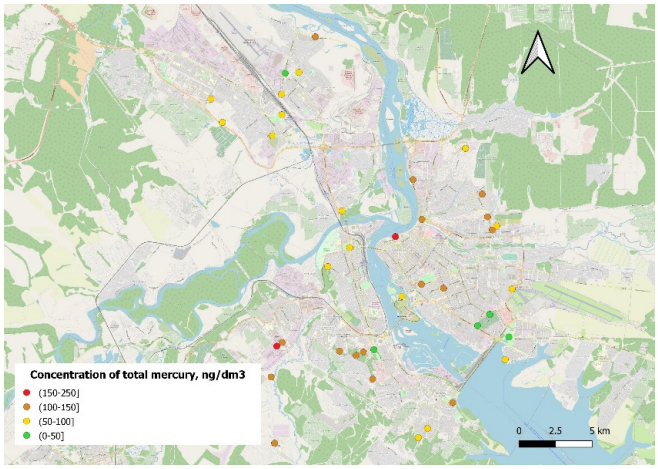

Fig.1. Schematic map of total mercury concentrations at snow sampling sites in Irkutsk.

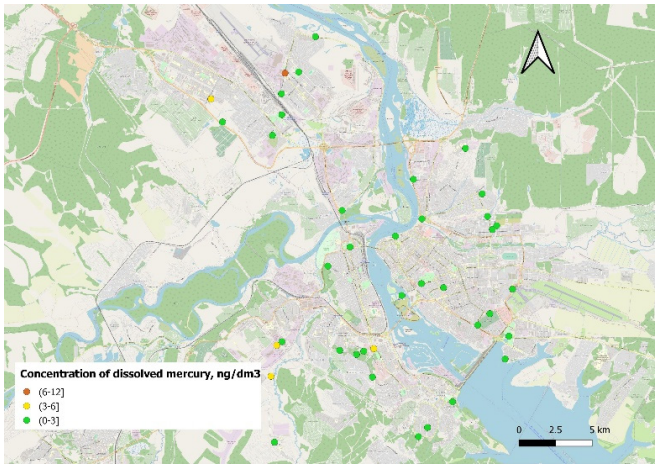

Fig.2. Schematic map of dissolved mercury concentrations at snow sampling sites in Irkutsk.

Acknowledgements

This study was supported by the State Project No. 0279-2021-0014.

Conflict of interest

The authors declare no conflict of interest.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Migration of mercury at different stages of the existence of the Nizhne-Koshelevskoe Novoe thermal field (Kamchatka)

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ABSTRACT. This article presents data on the behaviour of mercury in near-surface layers of the Nizhne-Koshelevskoe thermal field that appeared in 2008 and existed until 2016. The observation of the new heated area revealed two periods of the field existence. Monitoring of mercury concentrations in the soil-pyroclastic strata on the surface of the field elucidated the characteristics of mercury accumulation and migration at different stages of the existence of thermal fields.

Keywords: mercury, hydrothermal systems, Kamchatka

1. Introduction

The studies were carried out in the south of the Kamchatka Peninsula, near the Koshelevsky volcanic massif. The Quaternary volcanic massif consists of five volcanic structures (Vakin et al., 1976). Two large thermal fields are confined to the Koshelevsky volcanic massif: Nizhne-Koshelevskoe and Verkhne-Koshelevskoe. Here, the Koshelevskoe steam-hydrothermal deposit was discovered (Pozdeev and Nazhalova, 2008). In the thermal fields of the Koshelevsky volcanic massif, the composition of the discharged solutions is ammonium sulfate, while that of the condensate of the steam from deep exploration wells is bicarbonate-sulfate and sulfate-bicarbonate. All condensates have high concentrations of chlorine and ammonium ions, which may indicate its deep origin (Pozdeev and Nazhalova, 2008).

2. Materials and methods

In 2008, on the western slope of the Koshelevsky volcanic massif, near the Nizhne-Koshelevskoe thermal field (300 m to the south), there was a rare natural phenomenon, a formation of the new thermal field that was called Nizhne-Koshelevsloe Novoe (Rychagov et al., 2014). Heating of this site lasted about two years, and then cooling followed. The formation of this thermal field was associated with widespread hydrothermal processes in this area and the closely located Nizhne-Koshelevskoe thermal field (Fig. 1), which the geophysical research conducted here confirmed (Nuzhdaev and Feofilaktov, 2013). The study of mercury concentration in the strata of soil-pyroclastic deposits in the Nizhne-Koshelevskoe Novoe field allowed us to examine in detail the behaviour of mercury under near-surface conditions during the formation and decay of a thermal anomaly. For this purpose, in the 2010, 2011 and 2013 fieldwork seasons, the wells were traversed in the central and marginal parts of the field area. Each stage was characterised by the individual distribution of mercury in the section.

3. Results and discussion

The first stage was the heating of the field, which was accompanied by an intensive supply of mercury and its accumulation. This stage was characterised by high temperatures throughout the field area. In 2009, the temperature reached 90 ºC at some sites. Previously, there were no signs of hydrothermal activity in the field area. Apparently, before the formation of the field, mercury concentrations were at the background level. Based on the 2010 survey, the maximum mercury concentrations in the field area were 27.25 mg/kg, whereas the background concentrations were at the level of 0.08 mg/kg. During the disclosure of the section by the well traversed through the entire thickness of the soil-pyroclastic cover in the central part of the field, at the most heated site, high mercury concentrations were observed throughout the section as well as a sharp increase in the temperature with depth (Fig. 2).

The second stage was the decay, cooling and disappearance of the thermal field. Since 2011, there

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Received: August 16, 2022; ***Accepted:*** August 17, 2022;
Available online: August 22, 2022

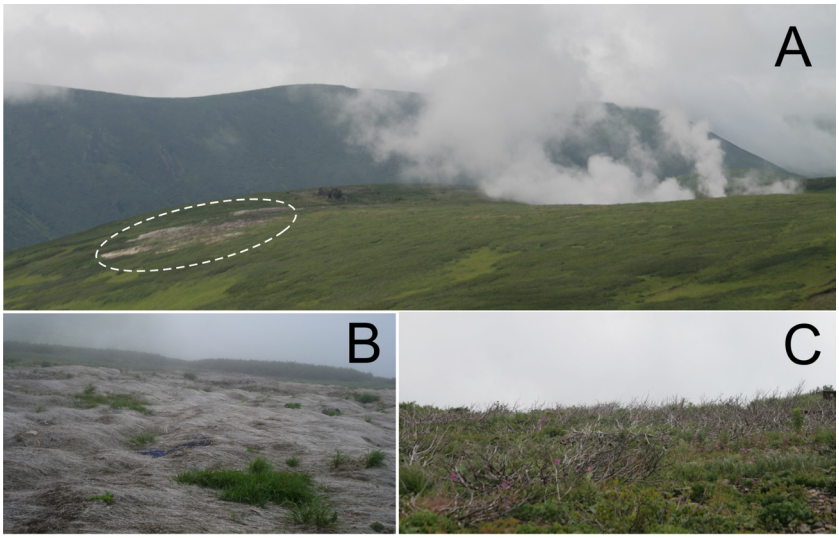

Fig.1. Nizhne-Koshelevskoe Novoe thermal field: A – general view (marked by a dotted line); B – grass burnout in the field area; C – bush burnout in the field area.

was a gradual decrease in the temperature and reduction of the area of the thermal field (measured by isolines of 15 ºC and 20 ºC) and, at the same time, some increase in the area of the mercury anomaly, with a decrease in its intensity. In the section of the central part of the field, there was a decrease in mercury concentrations in the lower layers and an increase in its concentrations in the upper near-surface layers. In other words, there could be the redistribution of mercury that previously entered and accumulated in the section as well as its migration to the upper layers (Fig. 2).

4. Conclusions

This study allowed us to observe the behaviour of mercury in the entire cycle of the existence of the thermal field: from the appearance to complete decay. During the heating of the thermal field, mercury entered the near-surface layers and accumulated in the section of the soil-pyroclastic strata at the sites of the maximum heating. As the thermal field cooled, the mercury accumulated in the section redistributed: decreased in the lower layers and concentrated in the upper layers of the soil-pyroclastic section. Also, mercury migrated throughout the field area. At the early stages of the existence of the thermal field, mercury concentrations increased at the sites associated with the most heated zones. With the cooling of the thermal field, the area of the anomaly increased, and its intensity decreased. Furthermore, a change (increase) in mercury concentration was observed in the section of the soil-pyroclastic cover outside the thermal field, as it cooled. In other words, mercury accumulated at the early stages of the existence of the field could migrate intensively as the field cooled, spreading beyond the thermal field.

Conflict of interest

The authors declare no conflict of interest.

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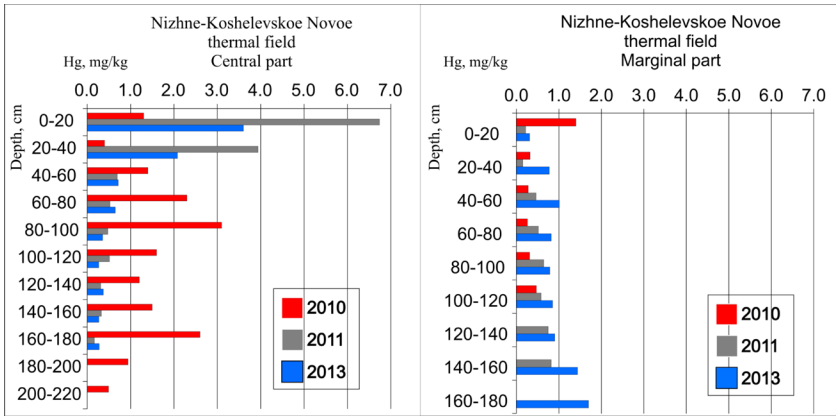

Fig.2. Diagrams showing the distribution of mercury concentrations in the sections of soil-pyroclastic cover in the central and marginal parts of the Nizhne-Koshelevskoe Novoe field (2010 to 2013).

Rychagov S.N., Nuzhdaev A.A., Stepanov I.I. 2014. Mercury as an indicator of modern ore-forming gas-hydrothermal systems, Kamchatka. Geochemistry International 52: 131-143. DOI: 10.1134/S0016702913120082

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Gender differences in blood parameters (ALT, AST) in people with cardiovascular diseases and their relationship to the level of total mercury in the hair

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ABSTRACT. Large industrial enterprises are located on the territory of the city of Cherepovets, which are potential sources of mercury entering the environment. The study involved residents of the Vologda Oblast without cardiovascular diseases (men n = 82; women n = 266) and with cardiovascular diseases (men n = 192; women n = 309). The average mercury content in the hair of the study participants was 0.572 ± 0.686 mg/kg. In healthy men and men with cardiovascular diseases, the indicators of alanine aminotransferase, aspartate aminotransferase are statistically significantly (on average 1.2-1.5 times) higher than in women. A significant correlation was established between the concentration of ALT, AST from the amount of mercury in the hair of the study participants: in men ALT - RS = 0.168, p ≤ 0.008 and AST- RS = 0.183, p ≤ 0.004, respectively; in women ALT: RS = 0.121, p ≤ 0.007, AST is not statistically significant RS = 0.035 p ≤ 0.442. The increase in mercury affects the human body with cardiovascular diseases, increasing the enzymatic activity of alanine aminotransferase, aspartate aminotransferase. The causes of gender differences in CVD are: different reproductive function; different prevalence of autonomous regulation of vascular functions and stress; different features of the development and prevalence of coronary atherosclerosis.

Keywords: mercury, ALT, AST, cardiovascular system, Vologda region

1. Introduction

Large industrial enterprises are located on the territory of the city of Cherepovets, which are potential sources of mercury entering the environment.

It is known that fish consumption is the main source of mercury intake into the human body. Fish from reservoirs of the Vologda region, from remote industrial centers, may contain high concentrations of mercury in muscles that exceed regulatory levels (Komov et al., 2004).

Increased mercury content in the body increases the risk of developing cardiometabolic syndrome (Ivanova et al., 2021). It can be assumed that in the Vologda region there is an alarming situation with the health of the population.

Alanine aminotransferase (ALT) and aspartate aminotransferase (AST) are used as markers of cardiovascular diseases (CVD). Due to the fact that the degree of changes in general metabolism differs in individuals of different sexes, it can be assumed that blood counts (ALT and AST) differ.

Thus, this work is aimed at identifying gender differences in blood parameters (ALT, AST) in people with cardiovascular diseases and their relationship with the level of total mercury in the hair.

2. Materials and methods

The study involved residents of the Vologda Oblast without cardiovascular diseases (men n = 82; women n = 266) and with cardiovascular diseases (men n = 192; women n = 309).

Hair samples from the study participants were collected from the back of the head in the form of strands several millimeters thick. The mercury content in the hair was determined without preliminary sample preparation using the mercury analyzer RA-915M with the prefix PYRO-915 + (LLC "Lumex", St. Petersburg, Russia). The blood test was carried out on an automatic biochemical device BioSystems A-15 (Spain) using standard test kits from BioSystems, Vector-Best.

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Received: August 16, 2022; ***Accepted:*** August 17, 2022;
Available online: August 22, 2022

3. Results

The average mercury content in the hair of the study participants was 0.572 ± 0.686 mg/kg. There were no statistically significant differences between the amount of metal in the hair of men (0.615 ± 0.731 mg/kg) and women (0.552 ± 0.662 mg/kg).

It was found that the mercury content in the hair of study participants with CVD (0.646 ± 0.727 mg/kg) was significantly higher, on average 1.5 times higher than in conditionally healthy (0.459 ± 0.589 mg/kg).

It was found that the mercury content in the hair of people (correlation coefficient $R_S = 0.336$, $p \leq 0.000$) who consume fish up to 1000 g per month, the amount of metal in the hair is 2-3 times lower than in the study participants whose fish in the diet is more than 2000 g per month.

In men and women with cardiovascular diseases, the concentration of liver enzymes (ALT, AST) in the blood is more than 2.5 times higher than in healthy people. In healthy men and with CVD, ALT and AST indicators are statistically significantly (on average 1.2-1.5 times) higher than in women.

A significant correlation was established between the concentration of ALT, AST from the amount of mercury in the hair of the study participants: in men ALT - $R_S = 0.168$, $p \leq 0.008$ and AST- $R_S = 0.183$, $p \leq 0.004$, respectively; in women ALT: $R_S = 0.121$, $p \leq 0.007$, AST is not statistically significant $R_S = 0.035$ $p \leq 0.442$.

It was noted that the average values of mercury content in human hair are higher in study participants with increased aminotransferase activity. At the same time, such differences are statically significant for ALT (Table).

4. Discussion

The mercury content in people's hair depends on the amount of fish in their diet. Frequent consumption of fish from local reservoirs can create a risk of mercury accumulation in the body of the population with negative health consequences.

The mechanism of mercury's effect on the cardiovascular system is associated with increased oxidative stress, decreased oxidative protection, endothelial dysfunction and thrombosis (Genchi et al., 2017). Chronic exposure to mercury affects heart rate variability, parasympathetic activity of the heart (Choi et al., 2009) and intima thickness of the carotid arteries (Choi et al., 2009). Exposure to mercury is associated with an increased risk of hypertension.

It was found that per 100 thousand of the population from cardiovascular diseases, the mortality rate of men is higher than among women. The causes of gender differences in CVD are: conditions inherent in only one sex (reproductive function): erectile dysfunction, preeclampsia/hypertension of pregnant women; different prevalence of autonomous regulation of vascular functions and stress: pulmonary hypertension, migraine; associated with the peculiarities of development and prevalence of coronary atherosclerosis: local – in men and diffuse – in women with the involvement of microcirculation (Oganov and Maslennikova, 2012).

It is known that cardiovascular diseases lead to an increase in the concentration of aminotransferases in the blood. Men smoke, drink alcohol more and more often than women. Women are characterized by a greater tendency to a sedentary lifestyle and obesity, but have healthy eating habits. The presence of a sexual gradient of dyslipidemia, hyperuricemia in different age groups also makes a significant contribution to increased cardiovascular risk. The development of primary and repeated cases of CVD in men is surpassed more often. Differences in psychosomatic regulation in men and women under stress cause a difference in the response of the regulatory systems of the body and in the levels of cardiovascular morbidity (Shapovalova et al., 2019).

The established relationship between the amount of mercury in the body and the concentration of aminotransferases in the blood is consistent with the results obtained in South Korea. Low levels of mercury in the blood may pose a risk of mild liver dysfunction (Lee et al., 2014).

5. Conclusions

Thus, the increase in mercury affects the human body with CVD, increasing the enzymatic activity of ALT, AST. Blood enzymes (ALT, AST) are an important factor in the long-term prognosis and prevention of vascular diseases. These indicators can be used as a predictor in predicting the risk of vascular diseases from the toxic effects of mercury.

Conflict of interest

The authors declare no conflict of interest.

Table. The average mercury content in the hair of people with different concentrations of aminotransferases

Blood indicator	Hg, mg/kg Q blood indicator				R_S, p
	1st Q	2nd Q	3rd Q	4th Q	
ALT	0.418[a] 2-13.1	0.49[ab] 13.2-19.6	0.584[b] 19.7-29	0.67[b] 29.1-1837	$R_S = 0.142$; $p = 0.000$
AST	0.473 7-17.6	0.454 17.7-21.9	0.631 22-31	0.615 31.1-1876	$R_S = 0.084$; $p = 0.023$

H-test (a, b) – values of mercury content in human hair differ statistically significantly at $p \leq 0.05$ (Kruskal-Wallis test)

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Determination of mercury content in coal dust collected from coals

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ABSTRACT. The problems of coal dust emission are relevant in the coal industry. The greatest danger is represented by coal dust with particle sizes of less than 10 and 2.5 microns. Such fine airborne dust can have a negative impact to human health, susceptibility to weathering, tendency to long-term environment damage, settling on the soils and transferring into waters. The contents of coal dust must be controlled, therefore coal dust was included in the list of pollutants regulated by Hygenic standards GN 1.2.3685-21. It is well known that coal dust may contain potentially hazardous elements, the concentration of which is determined by the form of their occurrence in coal. Among these potentially hazardous elements, mercury compounds are the most dangerous. In this regard, works aimed at assessing the distribution of mercury in coals and airborne dust are relevant. The current paper presents the results on the determination of mercury contents in coals and airborne dust that was collected from them. Also, the granulometric composition of dust particles was shown.

Keywords: coal dust, airborne dust particles PM10 and PM2.5, potentially hazardous elements, sieve analysis, mercury content

1. Introduction

The emission of coal dust is today an urgent problem in the coal industry. The airborne coal dust with sizes less than 10 and 2.5 μm is of the greatest interest, as it can be suspended in air for a long time and be transported over considerable distances. This has a negative impact on the atmospheric air, soils and water bodies, and can also leads to various diseases of the human pulmonary system, such as fluorosis and selenosis (Dai et al., 2012; Liu and Liu, 2020). Coal dust is included in the list of pollutants in accordance with Hygenic Standards GN 1.2.3685-21 “Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans” (GN 1.2.3685-21, 2021), therefore, issues related to the control of the content of coal dust are an important task in the coal industry.

The composition of coal dust may include various potentially hazardous elements (PHE), one of which is mercury and its compounds. Mercury, as the most toxic element, has always been of great interest (Zharov et al., 1996). An important feature of mercury compounds is the volatility. The authors note that, as a rule, mercury in coals is present in two forms: mercury associated with inorganic and/or organic matter (Yudovich et al., 2005). Currently, there is no reliable information on the mercury content in coal dust. Therefore, in order to control mercury in coal dust and its emission into the environment, it is necessary to carry out a number of measures aimed at studying the content of suspended dust in coals, its composition, as well as the content and forms of PHE in it.

The current work is dedicated to the determination of the mercury content in samples of coal and fine airborne dust, as well as to the determination of the granulometric composition of airborne dust.

2. Materials and methods

The samples of coals from the Kuznetsk basin were used. Sieve analysis of samples was performed in accordance with standard method (GOST 2093-82, 2001). Size class of less than 3 mm was used to collect the airborne coal dust using a specialized laboratory installation (Krasilova et al., 2022a). Table 1 shows the results of proximate analysis of coal samples and dust collected at the laboratory installation.

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Received: August 17, 2022***; Accepted:*** August 17, 2022;
Available online: August 22, 2022

3. Results and discussion

3.1. Determination of the particle size distribution of coal dust by laser diffraction

Granulometric composition of the collected coal dust samples was determined by laser diffraction in accordance with procedure described in (Krasilova et al., 2022b). To determine the particle size distribution, an Analysette 22 Next Nano particle size analyzer (FRITSCH, Germany) was used. The results of determining the granulometric composition are given (Krasilova et al., 2022a). It was shown that the content of particles with sizes up to 10 microns varies between 25.3% and 35.3%, and particles less than 2.5 microns is in the range of 4.7-7.4%.

3.2. Determination of mercury content in coals and coal dust

To determine the mercury content in coal dust, a RA-915M mercury analyzer with thermal decomposition of the sample (Lumex) was used. Measurements were carried out in accordance with standard method (GOST R 59176, 2020). The results are given in Table 2 and Fig. 1.

Mercury is found in all samples of coal dust, in amounts not exceeding Clarke values in the earth's crust according to A.P. Vinogradov (Kasimov and Vlasov, 2015). The highest mercury content was noted in dust of coal № 2 - 0.078 g/t, and the minimum - in dust of coal (0.036 g/t). The results of mercury content determination showed that the mercury content in dust samples slightly exceeds its content in coal.

4. Conclusions

A proximate analysis of coals and airborne dust collected from them was carried out. It was shown that the dust is characterized by a higher ash content, and the sulfur content in the dust practically does not change relative to coals.

The content of mercury in coals and airborne dust collected from them was determined. It was shown that the contents of mercury in dust samples slightly exceeds its contents in coal.

Acknowledgements

The work was carried out within the framework of the Strategic Academic Leadership Program "Priority 2030".

Conflict of interest

The authors declare no conflict of interest.

Table 1. Results of proximate analysis of coals and dust samples.

Sample №	Proximate analysis			
	W^t, %	W^a, %	A^d, %	S_t^d, %
Coal №1	12.1	1.1	11.2	0.33
Dust of coal №1	-	0.8	14.0	0.31
Coal №2	11.4	1.4	9.1	0.28
Dust of coal №2	-	1.0	10.1	0.25
Coal №3	11.4	1.1	8.9	0.30
Dust of coal №3	-	0.8	9.7	0.34

Note: W^t - total moisture; W^a – analytical moisture; A^d - ash contents (on dry basis); S_t^d - total sulfur (on dry basis).

Table 2. Mercury content in coals and dust samples.

Sample №	Hg (on dry basis), g/t
Уголь №1	0.049
Coal №1	0.050
Dust of coal №1	0.074
Coal №2	0.078
Dust of coal №2	0.036
Coal №3	0.040

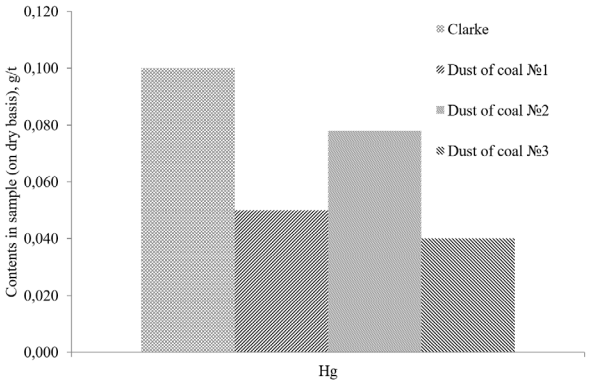

Fig.1. Mercury contents in airborne dust.

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Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
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Standard test method for mercury content evaluation in solid mineral fuels

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ABSTRACT. In addition to carbon, oxygen, hydrogen and nitrogen, fossil fuels contain other chemical elements, some of which may be hazardous to human health and the environment. Mercury and its compounds are one of the most dangerous among them. Therefore, information about mercury contents in coals and products of their processing is extremely important for both mining and processing enterprises and consumers. Mercury compounds may be accumulated in coal mining and processing wastes, and if they transfer into water-soluble forms, may lead to damaging of the environment. In the view of above, a standard method for the determination of mercury content has been developed, which is applicable not only to coals and products of their processing, but also to coal mining and combustion wastes. Also, to control the correctness of measurements by the developed method, reference samples with a certified mercury contents were developed.

Keywords: coal, mercury contents, wastes of coal mining and processing, instrumental methods

1. Introduction

Fossil coals are characterized by various quality indicators. These include ones allowing characterization of coals applicability for energy and coke production; their behavior during processing. Also, there exist indicators allowing for evaluation of environmental safety of coals extraction and utilization.

Mercury contents in coals is one of the indicators of their processing safety. Mercury is one of the most dangerous elements in coals. In this regard, the mercury content in coals is regulated in many countries, including the People's Republic of China. The latter determines the assessment of the mercury content during export of Russian coals.

Mercury can be found in coals in various forms: mineral (silicate and pyrite) and organic (Duan et al., 2017). The form of mercury in coal determines its redistribution during processing (sorting, benefication, combustion, cokemaking, etc.). When coal is burned, mercury compounds can either escape into the atmosphere with flue gases, or concentrate in slags (Boron and Wan, 1990; Streets et al., 2018).

When mercury is concentrated in waste products from combustion and coal mining, there is a risk of its emission into the environment in water-soluble forms. This increases the risks of adverse effects of mercury compounds due to bioaccumulation (Koval et al., 2000).

2. Materials and methods

In the Russian Federation, the determination of mercury content in fossil coals is regulated by the standard method GOST 32980-2014 "Solid mineral fuel. Determination of total mercury content". The essence of this method consists of burning a sample of solid fuel in a calorimetric bomb in an oxygen atmosphere in the presence of a solution of nitric acid. The mercury compounds formed during combustion are absorbed by the nitric acid solution. The bomb is thoroughly washed with water, after which the nitric acid solution from the bomb and the washings are combined and then filtered. The mercury compounds that have been recovered from the sample of fuel are reduced with tin chloride. Mercury is determined by cold vapour atomic absorption spectrometry with a mercury lamp (wavelength of 253.7 nm).

However, the practical implementation of this standard has shown a rather low reproducibility of results when testing high-ash fuels, which is due to the lack of completeness of mercury extraction. Also, the scope of this standard does not include solid waste from the mining and processing of fossil coals. In this regard, a method was developed for determining the mercury content in coal mining and processing wastes, subsequently approved in the form of a national

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Received: August 18, 2022; ***Accepted:*** August 18, 2022;
Available online: August 22, 2022

standard GOST R 59176-2020 “Solid mineral fuels. Determination of mercury by direct combustion”.

3. Results and discussion

The method is based on the thermal decomposition of the sample. This decomposition is accompanied by atomization of mercury, the transfer of atomic mercury into the analytical cuvette of the analyzer by air flow and the measurement of atomic absorption of mercury at a resonant wavelength of 253.7 nm. The mass fraction of mercury in the sample is determined automatically by the peak area (analytical signal) on the basis of a pre-set calibration characteristic using the apparatus software.

This standard method was developed taking into account the main provisions of the standard ASTM D6722-11 “Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis”. The key advantage of the method is the possibility of its implementation on modern domestic equipment - an atomic absorption spectrometer with a module for generating “cold vapor”. When testing the method, an analyzer of the mass concentration of mercury vapor RA-915M (LUMEX-AHK, St. Petersburg, Russia) was used. This device provides high performance analysis and allows analyzing up to 20 samples per hour (when including parallel samples - up to 10 ones). The use of the PA-915M analyzer and similar devices makes it possible to introduce an instrumental express method for determining the mass fraction of mercury into the practice of testing laboratories. Its implementation minimizes the influence of the operator on the testing process, and, as a result, the magnitude of the operator’s error. The high throughput of the equipment makes it possible to apply the method at those stages of the life cycle of coal products, where the speed of results is extremely important. E.g., in the operational management of the flow of mined coal or when coal products pass through the borders of states.

To ensure the quality control of measurements in the implementation of this method, work was also initiated to create reference samples of mercury content in coal and rocks. At the moment, the reference samples are undergoing the certification procedure. Table shows their preliminary characteristics.

The implementation of the standard makes it possible to determine the mercury content in coal, overburden rocks, tailings and coal combustion wastes in the range from 0.010 to 4.000 g/t, which fully covers the ranges of mercury content in these objects. E.g., the average content of mercury in coals varies in the range of 0.05-0.3 g/t (Krylov, 2016), and in solid fuel combustion wastes it can reach 3.5 g/t (Yudovich and Zolotova, 1994).

Table. Characteristics of reference samples of fossil coals, rocks and wastes from coal mining and processing.

RS	Material for the manufacturing of a reference sample	Hg^d, ng/g average
IRS-1	Hard coal	8.4
IRS-2	Hard coal concentrate	265.0
IRS-3	Hard coal	1834.3
IRS-4	Waste of brown coal combustion	2.0
IRS-5	Waste of coal concentrate combustion	287.9
IRS-6	Sandstone	9.3
IRS-7	Claystone roof of coal seam	26.4

4. Conclusions

Standard method was developed for determination (by direct combustion) of mercury contents in solid fossil fuels and wastes of their mining and combustion. The materials have been proposed for manufacturing of the reference samples of mercury contents in coals and wastes from coal mining and combustion.

Acknowledgements

The work was carried out within the framework of the Strategic Academic Leadership Program “Priority 2030”.

Conflict of interest

Authors declare no conflict of interest.

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