UDC 504

# Mercury in Natural Objects of West Siberia

E. E. LYAPINA, E. A. GOLOVATSKAYA, I. I. IPPOLITOV and YU. I. PREIS

Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch of the Russian Academy of Sciences,

Pr. Akademicheskiy 10/3, Tomsk 634055 (Russia)

E-mail: eeldv@mail.ru

(Received June 4, 2008; revised July 6, 2008)

### **Abstract**

In the course of ecological and chemical examination of mercury content in environmental objects, comparative evaluations of the accumulating properties of various natural indicators were made for bog and urban ecosystems as examples. Experimental data on mercury content in urban soil, peat, lichens, mosses, wood and needles are reported.

Key words: mercury, bioaccumulation, ecotoxicity, natural indicators, monitoring

#### INTRODUCTION

Mercury and its compounds are widespread in nature and migrate both on the regional scale and on the global one [1–6]. One of the most important features of mercury is its ability to intense bioaccumulation. The toxicity of mercury and its compounds of natural and anthropogenic origin determines increasing attention of ecotoxicologists to the problem of environmental pollution with mercury [7–9]. However, without evaluation of the level of mercury pollution of air, soil, vegetation, it is impossible to get a general overview of the technogenic load of this element on the environment.

### **OBJECTS AND METHODS OF INVESTIGATION**

The objects of investigation were soil ground of Tomsk and peat deposits of the Tomsk Region and Khanty-Mansi Autonomous District.

To determine mercury content of soil ground from the Tomsk Region, ground samples were collected in the nods (points) of a network uniformly covering the entire territory of the city. Soil sampling and sample preparation for analysis were carried out according to the requirements of State Standard GOST 17.4.4.02-84 [10].

All the studied objects in the Bakchar district of the Tomsk Region are the spurs of the Bolshoye Vasyuganskoye Bog. Expedition works were carried out at the basis of the research ground Vasyuganye of the Institute of Monitoring of Climatic and Ecological Systems (IMKES), SB RAS, situated in Polynyanka village (200 km to north-west from Tomsk). Samples were taken at typical plots of raised and lowland bogs. Characteristics of peat deposits are presented in Table 1.

The peat deposit Bakcharskoye is a natural region, while Vasyuganskoye, Sukhoye-Vavilovskoye deposits had been subjected to anthropogenic action to one extent or another during reclamation works and peat production.

Peat deposit Tagan situated at a distance of 13 km to south-west from the centre of Tomsk may be considered as an ecosystem directly affected by the city, while the peat deposits Ozernoye and Salymo-Yuganskoye are affected by the oil and gas mining complex.

The samples of peat and mineral ground were taken with the help of a peat borer (TBG-1) with testing step of 2–5 cm up to the depth of 1 m and with the testing step of 10 cm over the full depth of the pool. The samples were packed in polyethylene bags, dried at room temperature to the constant mass, and comminuted with the help of a sieve with mesh

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TABLE 1

Characterization of the peat deposits under investigation

Key plot	Thickness of peat pool, m	Characteristics	Location
	Bakchar	oligotrophic bog	
Swampy forest (BSF)	0.2	Natural plot	Bakchar district, Tomsk Region
Raised ryam (BRR)	1.0	« «	The same
Lowland ryam (BLR)	3.0	« «	«
Open sedge-sphagnum bog (BSS)	2.7	« «	«
	Vasyuga	nskoye, oligotrophic bog	
Lowland ryam (VLR)	2.8	Region of forest reclamation	«
	Sukhoye	e-Vavilovskoye, eutrophic bog	
Sukhoye-Vavilovskoye (SV	) 2.6	Worked out plot	«
	Ta	igan, eutrophic bog	
Pasture (TP)	1.4	Worked out plot	Tomsk district, Tomsk Region
	Oz	zernoye, oligotrophic bog	
Hummock-ridge bog (HRB)	3.4	Plot under anthropogenic influence	Kargasok district, Tomsk Region
	Salymo-Y	uganskoye, oligotrophic bog	
The same (SUHRB)	3.1	Natural plot	Khanty-Mansi Autonomous District

diameter 0.25 mm. The choice of room temperature for drying was due to the fact that mercury starts to evaporate from the sample at a temperature above  $30-40\,^{\circ}\text{C}$ .

Mercury was determined in natural objects growing in ecologically pure regions and in the zone of anthropogenic influence:

- in sphagnous moss (Sphagnum sp.);
- in lichens (Cladonia stellaris (Opiz) Pauzor et Vezda, Cladonia arbuscula (Wallv.) Flot. ssp. Mitis Cladonia deformis (L.) Hoffm, Cladonia cornuta (L.) Hoffm, Cladonia stygia (Fr.) Ruoss, Evernia mesomorpha Nyl., Usnea subfloridana Stirt.);
- in wood of annual rings of pine (*Pinus sylvestris* L.) that grew in the region affected by Seversk, and black poplar (*Populus nigra* L.) that grew in the zone directly affected by the urban environments of Tomsk;
- in the needles of different ages from different tree species growing on typical regions of raised bogs.

Mercury content was determined using the mercury gas analyzer RGA-11 by means of atomic absorption spectroscopy. Detection limit is 0.1 ng/g, error of determination 30 % [11].

The procedure of determination of mercury content in soil was developed at IMKES together with the Laboratory of Environmental Control of the Chemical Department of the Tomsk Polytechnical University [12].

# **RESULTS AND DISCUSSION**

The distribution of mercury content in the soil of Tomsk measured in August 2005 is shown in Fig. 1. One can see that the distribution has a clearly focal character. Mercury content in focuses varies from 300 to 2250 ng/g (MPC for mercury in soil is 2100 ng/g). The most intense focus (see Fig. 1) corresponds to the location of the ash dump of electric power station No. 2. It was difficult to identify other less intense sources. However, it may be stressed that increased mercury content in ground is observed at the territories of regions with intense traffic, residential areas with predominant furnace heating and regions with a large number of unofficial dumps.

Additionally, we sampled ground (56 samples) from the territories of 16 industrial en-

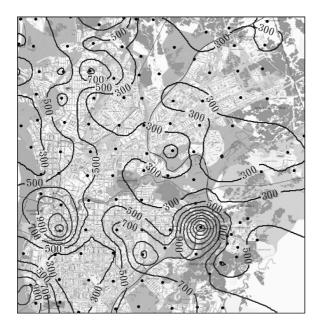


Fig. 1. Distribution of mercury content in soil over the territory of Tomsk, ng/g of dry matter (August 2005).

terprises situated within the boundaries of Tomsk. Analysis showed that mercury content in soil samples collected from the territories of sleeper-dipping plant (2570 ng/g) and yeast plant (5210 ng/g) exceeded the MPC. However, in general, except for the case of electric power station No. 2, no direct connection between the focuses of increased mercury concentration and the positions of industrial enterprises could be established.

It is known that the highest mercury content is characteristic of soil enriched with the organic matter, first of all peat-bog soil [13–15]. Judging from its properties, peat relates to natural sorbents. In view of the high sorption capacity, a peat pool may accumulate industrial aerosol [14]. Layer-by-layer burial of mercury in a peat pool allows us to estimate the dynamics of mercury flux from the atmosphere during the whole period of peat accumulation.

Analysis of mercury distribution over the depth of peat pool in the studied peat bogs revealed the maxima of mercury content in the upper part of the profile (Fig. 2, a), which points to the anthropogenic character of its arrival. The same result was obtained also by other researchers [13, 19, 20]; the age of the upper maxima, according to dating on the ba-

sis of <sup>210</sup>Pb and <sup>137</sup>Cs, is confined with the period of 1989–1991. Mercury content in near-bottom layers and in underlying rocks is approximately identical.

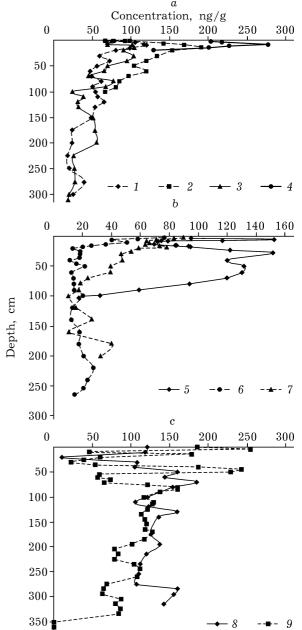


Fig. 2. Mercury content in the peat of native bog systems (a), bog systems under anthropogenic influence (b) and systems situated in oil and gas mining regions (c): 1-4 – Bakcharskoye deposit (1 – open sedge-sphagnum bog; 2, 3 – raised and lowland ryam, respectively; 4 – swampy forest); 5 – lowland ryam of the Vasyuganskoye deposit; 6 – a plot at the Sukhoye-Vavilovskoye deposit; 7 – pasture of the Taganskoye deposit; 8, 9 – hummock-ridge bog of the Ozernoye and Salymo-Yuganskoye deposits, respectively.

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TABLE 2

Data on mercury concentration in peat of bog systems, ng/g

Concentration	Plot	Concentration
209 (277-129)	sv	26 (176-11)
121 (192-67)	TP	94 (153-17)
58 (104-19)	HRB	117 (255-23)
59 (120-19)	CUHRB	132 (185-105)
47 (90-10)		
	209 (277-129) 121 (192-67) 58 (104-19) 59 (120-19)	209 (277-129) SV 121 (192-67) TP 58 (104-19) HRB 59 (120-19) CUHRB

Note. For designations, see Table 1.

The average mercury content in peat from the studied native bog ecosystems (see Table 1) varies substantially. Averaged data on mercury content over the vertical profile and the data on its maximal and minimal concentration in peat of the studied bogs are listed in Table 2.

In the native Bakchar massif, with is a convex raised bog, the highest layer-by-layer values of mercury content are observed in the peat of its edge zone - swampy forest (BSF) and raised ryam (BRR) (see Fig. 2, a). Thus, the average mercury content for a 20-cm thick peat layer from BSF and BRR exceeds the corresponding value for the lowland ryam (BLR) by a factor of 1.8 and 2.3, respectively, while mercury content in the samples from the open sedge-sphagnum bog (BSS) exceeds that value only by a factor of 1.1. This is due to the fact that the edge zone serves as a geochemical barrier due to the features of the surface relief of the massif. From the apical BLR, mercury deposited from the atmosphere is carried away by the surface runoff towards BRR and BSF, and partially towards BSS.

Average mercury content in peat samples from bog systems under anthropogenic action (bog reclamation) varies within the range 24-85 ng/g (see Fig. 2, b).

Eutrophic bog Tagan is situated in the direct vicinity of Tomsk (13 km), so increased mercury content (94 ng/g) in the peat of the upper part of the profile is connected first of all with the anthropogenic effect of the city. The same explanation is for the elevated average mercury concentrations in the peat of this deposit in comparison with the peat deposits Sukhoye-Vavilovskoye and Vasyuganskoye.

The average mercury content in peat pools of Ozernoye and Salymo-Yuganskoye deposits is about twice as high as that for the pools of the southern part of the Tomsk Region (see Fig. 2, c). In this situation, the excess in the pre-anthropogenic layer is 4-10 times, while in the anthropogenic layer additionally affected by the gas-and-oil producing industry the excess is less substantial.

These bogs are situated above oil and gas deposits characterized by substantial mercury content. According to the data reported in [17], the high background mercury content in peat is connected exactly with the presence of oil and gas deposits. The average mercury content in the peat pool of the Ozernoye deposit corresponds to that in the Salymo-Yuganskoye deposit (SYuGMK), however, scattering of the values of layer-by-layer content is much higher and equals 28-255 ng/g.

At the constant rate of peat accumulation and mercury flux from the atmosphere, its content per 1 g of dry peat will depend on the volume mass of peat. To determine the amount of mercury in unit volume, we additionally sampled peat monolith from the BLR site; the monolith was 40 cm thick, we separated it into samples 2–5 cm thick. Peat samples were dried and weighed.

Comparative analysis of the values of layer-by-layer mercury content calculated per unit mass and volume of peat provides evidence of substantial differences in the character of changes in its content over depth (Fig. 3). One can see from the data shown in Fig. 3, a that the curve of mercury content *versus* depth calculated per unit mass is characterized by more substantial variation of layer-by-layer values and only one peak instead of five ones. Therefore, to obtain more reliable data on changes of mercury concentrations in peat pools, it is necessary to take into account their layer-by-layer volume mass.

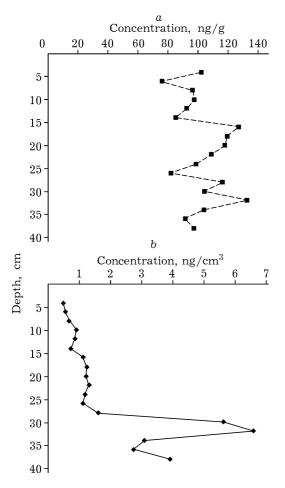


Fig. 3. Changes in mercury content over depth in the upper layer of the pool in the lowland ryam of the Bakcharskoye peat deposit, calculated per unit mass (a) and volume (b).

It is known that mercury spreads mainly due to atmospheric transport. In this connection, such natural components as lichens, mosses, wood, needles that are able to concentrate heavy metals may be used as the indicators of atmospheric emission of mercury.

Investigation of mercury content in sphagnum mosses showed that they contain 28-70 ng/g as an average (Fig. 4, a), which is comparable with that for the mosses in the Altay Territory (50–90 ng/g). Some differences in these data are determined by mercury content in soil and by growing sites. The effect of mercury accumulation in mosses is achieved due to their high sorption surface per unit mass [15].

Accumulation of mercury in lichens depends on atmospheric and geochemical conditions. It was established that the average mercury content in lichens does not depend on sampling sites. At the same time, one can see in the data presented in Fig. 4, b that the epiphytic lichen species (*Evernia mesomorpha* Nyl., *Usnea subfloridana* Stirt.) exhibit high accumulation of mercury with a 3.5-fold excess over other lichen species. This is due to the high sensitivity of these species to the composition of atmospheric precipitation [15].

Analysis of mercury content of wood did not reveal differences in the accumulation of the pollutant depending on wood species. It is accepted that the tree bark accumulates pollutants much more intensively than other organs and tissues of plants [16, 18]. However, we did not detect this dependence in our work. In addition, we made an attempt to reveal the interconnection between mercury content and the width of annual rings (Fig. 5). The results of calculation of the correlation coefficient for the width of annual ring and mercury content provide evidence that any direct correlation between these parameters is almost absent. We also did not detect correlations of mercury content in the wood of studied trees with climatic characteristics (air temperature during the vege-

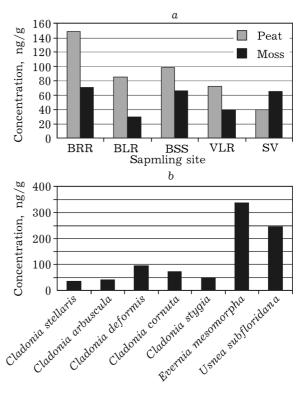


Fig. 4. Mercury content in sphagnum mosses (a) and lichens (b). For designations, see Table 1.

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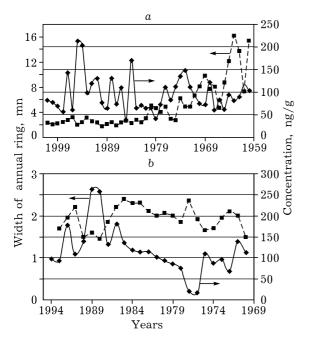


Fig. 5. Distribution of mercury content in annual rings of poplar (a) and pine (b).

tation period since May till September, precipitation).

According to the data of comparative analysis of mercury content in the needles of different wood species (cedar, abies, spruce, pine) the maximal mercury content (165 ng/g) is characteristic of pine needles (BSF), while the minimal one (60 ng/g) occurs in pine needles (BSS) (Fig. 6). The age-related differences in the ability of needles to accumulate mercury are exhibited only weakly, except for cedar (BSF), which agrees with the data reported in [15].

We failed to detect any correlations between the climatic parameters (air temperature during the vegetation period and precipitation) and

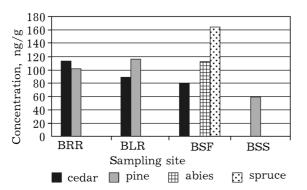


Fig. 6. Mercury content in the needles of different ages from different tree species. For designations, see Table 1.

mercury content in the needles of different ages from different tree species. We also did not establish any dependence between mercury content and needle sampling site. In general; the data obtained correspond to the averaged data for coniferous tree species of the Altay Territory (30–230 ng/g) [15].

### CONCLUSIONS

The following conclusions may be drawn on the basis of the results of investigation.

- 1. In Tomsk, the formation of mercury scattering aureoles is connected with the power engineering facilities, traffic, as well as with the microrelief of the city and predominant wind direction. Due to the inhomogeneity of the distribution of industrial enterprises over the city territory, the presence of unofficial dumps, inhomogeneity of traffic fluxes, the ecological load on the city environment has inhomogeneous character, too. In the future, the dimensions and scales of industry related anomalies fixed in soil with increase in the regions affected by almost all the examined enterprises.
- 2. Monitoring of mercury over the spurs of the Bolshoye Vasyuganskoye Bog was carried out (over the peat deposits in the Bakchar district of the Tomsk Region). The data on mercury distribution over depth obtained for the first time at background sites are comparable with the results obtained previously for other background plots [12, 19, 20].
- 3. The obtained data on mercury content in natural components (lichens, mosses, wood, and needles) correspond to the data reported by other authors [15] but exceed the background values reported in [21].

## REFERENCES

- 1 Zh. A. Dimidenok, S. G. Kharina, *Issledovano v Rossii* (online journal).
  - http://zhurnal.ape.relarn.ru/articles/2005/039.pdf
- 2 Rtut' v Okruzhayushchey Srede Sibiri: Otsenka Vklada Prirodnykh i Antropogennykh Istochnikov (Itogovy doklad vremennogo nauchnogo kollektiva po proektu SKOPE "Otsenka Rasprostraneniya Rtuti i Yeyo Roli v Ekosistemakh"), Novosibirsk, 1995.
- 3 O. F. Vasiliev, A. A. Obolensky, M. A. Yagolnitser, Sci. Total Environ., 213 (1998) 73.

- 4 Regional and Global Mercury Cycles: Sources, Fluxes and Mass Balances, NATO ARW, Novosibirsk, 1995.
- 5 Povedeniye Rtuti i Drugikh Tyazhelykh Metallov v Ekosistemakh (Review), parts 1-3, Novosibirsk, 1989.
- 6 L. V. Tauson, V. F. Geletiy, V. I. Menshikov, Chem. Sust. Dev., 3, 1-2 (1995) 151.
- 7 A. B. Antipov, E. Yu. Genina, Yu. A. Golovatskiy, Opt. Atm. Okeana, 15, 1 (2002) 81.
- 8 T. G. Laperdina, Opredeleniye Rtuti v Prirodnykh Vodakh, Nauka, Novosibirsk, 2000.
- 9 V. V. Ivanov, Ekologicheskaya Geokhimiya Elementov (Handbook), book 5: Ekologiya, Moscow, 1997.
- 10 GOST 17.4.4.02-84. Okhrana Prirody. Pochvy. Metody Otbora i Podgotovki Prob dlya Khimicheskogo, Bakteriologicheskogo i Gelmintologicheskogo Analiza.
- 11 Gazoanalizator Rtutny RGA-11, Tekhnicheskoye Opisaniye i Instruktsiya po Ekspluatatsii, AMYa2.770.001 TO, 1992.
- 12 Svidetelstvo No. 08-48/034 o Metrologicheskoy Attestatsii Metodiki Kolichestvennogo Khimicheskogo Analiza Pochv na Soderzhaniye Mikrokolichestv Rtuti Metodom Atomno-Absorbtsionnoy Spektroskopii, Tomsk, 1992.

- 13 H. Biester, R. Kilian, C. Hertel et al., II Ann. Int. Conf. on Heavy Metals in the Environment, Contribution #1029, University of Michigan, Ann Arbor Sci. Publ., Inc., MI, 2000.
- 14 L. I. Inisheva, T. N. Tsybukova, Geogr. Prirod. Res., 1 (1999) 45.
- 15 G. N. Anoshin, I. N. Malikova, S. I. Kovalev et al., Chem. Sust. Dev., 3, 1-2 (1995) 69.
- 16 A. I. Perelman, N. S. Kasimov, Geokhimiya Landshafta (Textbook), Astreya-2000, Moscow, 1999.
- 17 S. L. Dorozhukova, E. P. Yanin, A. A. Volokh, Vestn. Ekol., Lesoved. Landshaftoved., 1 (2000) 157.
- 18 B. N. Fomin, I. Ya. Nikolishin, G. N. Voronskaya, Problemy Ekologicheskogo Monitoringa i Modelirovaniya Ekosistem, Gidrometeoizdat, St. Petersburg, 1992, vol. XIV, pp. 103-118.
- 19 M. Goodsite, C. Lohse, T. S. Hansen et al., II Ann. Int. Conf. on Heavy Metals in the Environment, Contribution #1029, University of Michigan, Ann Arbor Sci. Publ., Inc., MI, 2000.
- 20 L. D. Lacerda, M. G. Ribeiro, J. J. Abrao, *Ibid*.
- 21 E. P. Yanin, Rtut' v Okruzhayushchey Srede Promyshlennogo Goroda, IMGRE, Moscow, 1992.