Chemistry for Sustainable Development **20** (2012) 89–95

UDC 550.4+553.061.15

Distribution of Mercury in the Environmental Components of Siberia

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Abstract

Data on mercury concentration in various environmental components of Siberia are presented: for bottom sediments of continental lakes and in the soil of their water-collecting areas, in plants (moss, lichens, medicinal herbs, berries, mushrooms, needles) and in the litter of conifers. An increase in mercury content in the upper horizons of averaged sections of bottom sediments starting from the depth of about 15 cm was detected, which corresponds to the years 1960–1970. The dependence of mercury content on the degree of water mineralization and its mineral composition was not revealed. It was established that the concentrations of mercury in bottom sediments are determined by its concentration in the soil of water-collecting areas. The obtained results generally provide evidence of the favourable ecological status of the studied territories, while pollution with mercury has a local character. Coniferous litter, lichens and mushrooms can be used as indicators of pollution with mercury.

Key words: mercury, Siberia, continental lakes, bottom sediments, geochemical background, plants

INTRODUCTION

Bottom sediments of lakes are the final link of landscape geochemical conjunctions; their composition depicts the geochemical features of the soils of catchment areas. The diversity and complicacy of the processes occurring in natural landscapes, differences in the composition of soil-forming rocks and in the contribution from the industry-related component provide the spatial nonuniformity of the geochemical background of mercury [1]. This nonuniformity manifests itself not only in different natural zones but also within the limits of geochemical landscapes.

The high mobility of mercury in the environment is determined by its chemical and physical features, the diversity of its forms (Hg^0, Hg^{2+}, $HgCl_4^{2-}$, HgS_2^{2-}, $HgOH^+$, $Hg(OH)_2$ *etc.*) and their interconversions depending on pH and E_h. Mercury takes an active part in global and local migration cycles. Four forms of mercury in soil are known, differing from each other by bonding with soil particles: ion exchange, bound in complex, sorbed and chemically bound with mineral components. Mercury that enters the soil is held mainly in the form of low-mobile complexes with humic acids. The presence of fulvic acids promotes its migration and enhancement of volatility [2]. Mercury retention on the catchment area reaches 80–90 % [3, 4]. It was revealed that clay fractions are enriched with mercury in comparison with coarse-grained fractions. The aqueous medium contains colloid and soluble forms in addition to suspended forms.

The background mercury concentrations in different regions of Siberia correspond to its content in the upper continental crust and are substantially lower than the MPC for soil (2.1 mg/kg) (Table 1). Increased mercury content was detected in the soils of natural ore anomalies in general; in some samples mercury concentration was 1–2 mg/kg and more. The differences in the distribution of mercury over

TABLE 1

Mercury concentrations in bottom sediments and in soil in different regions of Siberia, mg/kg

Regions	Bottom mud			Soil		
	n	Average	Range	*n*	Average	Range
Yamal-Nenets Autonomous District	135	0.09±0.01	0.01–0.66	62	0.05±0.01	0.002–0.3
Tomsk Region	138	0.04±0.002	0.01–0.19	52	0.02±0.003	0.004–0.04
Altai Territory	740	0.06±0.01	0.01–0.18	1063	0.11±0.04	0.01–0.78
Altai Republic	98	0.07±0.005	0.01–0.18	505	0.10±0.03	0.01–0.95
Novosibirsk Region	54	0.04±0.002	0.01–0.12	137	0.06±0.002	0.02–0.13
Tyva Republic	57	0.05±0.005	0.02–0.08	312	0.06±0.005	0.01–0.36
Irkutsk Region	77	0.04±0.002	0.01–0.10	586	0.06±0.003	0.01–0.22
Republic of Buryatia	198	0.06±0.005	0.001–0.29	76	0.06±0.005	0.001–0.29
Transbaikalia (Aginskoye Buryatia Autonomous District)	80	0.04±0.006	0.02–0.12	101	0.04±0.003	0.01–0.06
Republic of Sakha (Yakutia)	75	0.05±0.002	0.02–0.11	80	0.05±0.005	0.02–0.38
Average for Siberia*		0.07			0.06	
Average for the upper part of the continental crust**					0.06	
Average for world soils***		0.09			0.05	

Notes. 1. *n* is the number of samples. 2. Average value±standard error.

*Our data.

**Data of [17].

***Data of [18].

soil profiles are observed: total mercury content is higher in the humus and humus-accumulative horizons in background regions due to the global supply, accumulation by plants and humus substance; increased mercury concentrations were detected in the lower horizons of natural anomalies. Approximate estimation of mercury income on the soil cover in the Altay region, obtained on the basis of mercury concentration in the upper layer of the carpet of needles is 19–42 g/km^2 [5, 6]. This allows correct evaluation of additional mercury contribution from local sources.

The amount of mercury passing into aqueous and ammonium acetate extracts from the soils of urban territories exceeds the degree of its extraction from the soils of natural landscapes (even in the case of their insignificant pollution). The boundary values for the studied landscape complexes in the south of West Siberia were 0.07–0.10 μg/L, which is the evidence of anthropogenic action at its initial stage. The results obtained are important for monitoring and forecasts [7].

The concentration of mobile mercury forms in soil determines its intake by plants and then along the food chain. Mercury is extracted from the chernozem soil into the aqueous and ammonium acetate extracts only in very small amounts (0.05–0.27 %), while from the rocks of natural anomalies it is extracted in the amount of 0.10–0.27 % (of total mercury). The maximal degree of mercury extraction into the hydrochloric extract reaches 75–100 %.

Substantial alarm is caused by lake ecosystems in industrially developed regions situated in the vicinity of the sources of pollution with mercury. Studies of these objects became especially important in connection with the use of fish contaminated with methyl mercury for food purposes. At present, enormous data on mercury content in the components of polluted lake ecosystems are accumulated [8–11]. At the same time, the ecosystems of remote regions are studied substantially poorer. The majority of researchers agree that at present the anthropogenic emission of mercury is comparable with the natural one [12, 13]. Because of this, evaluation of concentrating, scattering and redistribution of mercury in the bottom sediments of lakes in different regions of Siberia will allow us to present a general view of the global pollution.

There are about 20 thousand lakes at the territory of Siberia. With the generally plain relief, the major role in lake distribution is played by the climatic factor that determines their most essential features. In the northern hemisphere, in the direction from north to south the mineralization of lake waters increases, and its composition changes. We studied the geochemical features of more than 100 lake systems at the territory of Siberia. In the regions of tundra and northern taiga, lakes with fresh and ultra fresh water are developed (Yamal-Nenes Autonomous District (YaNAD) – 14 lakes). In the regions of southern taiga, lake water is fresh but salt content increases (Novosibirsk Region – 8 lakes, Tomsk Region – 5, Altai Territory – 68 lakes). The lakes of the central part of Yakutia are situated in the taiga zone but due to a more arid climate they relate to the brackish water group (10 lakes). Among the lakes of the Baikal region, fresh lakes prevail but saline ones also occur (Irkutsk Region – 10 lakes, Buryatia – 6, Chita Region – 8). The lakes of different types occur in the south of West Siberia: fresh, salty and brackish-water (the Altai Territory – 42 lakes, Tyva – 17) [14].

EXPERIMENTAL

Bottom sediments were sampled with the help of two types of sampling devices: a cylindrical sampler (110 mm in diameter, 100 cm long) with the leaf shutter and a cylindrical sampler with vacuum shutter designed at the RPA "Typhoon" (82 mm in diameter, 50 cm long) which allows one to sample silt strongly watered and sandy sediments. The sediment core was tested to the depth of 90 cm at each 3 cm.

The instrumental determination of mercury by means of atomic absorption was performed with a mercury hydride attachment MHS-20 to the PerkinElmer instrument. Analytical works were carried out at the IGM of the SB RAS (Novosibirsk). The laboratory has been accredited by the Association of analytical centres Analitika and registered in the State Register (No. ROSS RU 0001.510590).

RESULTS AND DISCUSSION

According to the data obtained, the average level of mercury content in bottom sediments and the soil of the catchment areas of continental lakes in Siberia is close to the background level established for soils in the world and for bottom sediments (see Table 1). The geochemical data obtained provide evidence that mercury content in bottom mud is determined by its content in the soil of the catchment areas.

Increased mercury concentration was revealed in the bottom sediments of YaNAD, in the soils of the Altai Territory and the Altai Republic. Increased mercury content in the soil of the Altai is detected within the boundaries of ore anomalies [5]. An increase in mercury content in the bottom sediments of northern lakes is connected, first of all, with acidification of lake-bog systems that are distinguished by their ability to accumulate mercury, second, with the technogenic load from the oil and gas producing complex [15].

According to the data of X-ray spectral and silicate analysis, four groups of bottom sediments were revealed in continental lakes: quartz-feldspar, carbonate, X-ray amorphous (organogenic) and mixed. The Q type cluster analysis split the set of chemical analyses of bottom sediment samples into five groups and revealed connections between them. Comparing with the data of X-ray phase analysis, one may define them as quartz-feldspar, carbonate (calcite-dolomite), X-ray amorphous (organogenic), quartz-feldspar-calcite and organogenic-quartz-feldspar. The R type cluster analysis with the same set gives a direct correlation between chemical elements under study. In the dendrogram of the cluster, mercury together with cadmium is bound with the organogenic part of the sediment (Fig. 1).

It was established (Table 2) that different mineral types of bottom sediments in the continental lakes of Siberia are characterized by almost the same mercury content. In addition, it was discovered that the degree of mineralization of lake water has almost no effect on

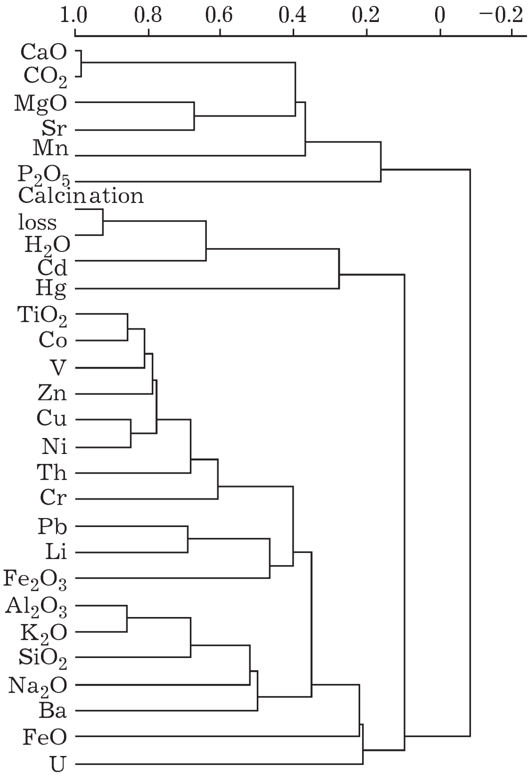

Fig. 1. Dendrogram of the R type cluster analysis of macro- and microelements in bottom sediments and in the soil of their catchment areas of the continental lakes of Siberia.

mercury concentration in bottom sediments. Thus, mercury content in the bottom sediments of fresh-water lakes is (0.051±0.003) mg/kg, brackish water – (0.048±0.005), saline – (0.046±0.003) mg/kg.

To reveal the general character of mercury distribution in the time interval, analysis of its layer-by-layer concentrations was carried out for more than 100 lakes (a step of 3 cm corresponds to the interval of 10–15 years). The set included all the sections of lakes tested to the depth of 50–60 cm, for each region the sections were averaged over sampling depth. Taking into account the rate of sediment accumulation, this allows one to estimate the dynamics of changes of the geochemical composition of bottom sediments in the time interval (150 years). Two types are revealed on the basis of the character of mercury distribution in sections over the depth of bottom sediment (time of formation): in the first case mercury concentration does not change along the section, in the second case mercury content increases in the upper part of the section, sometimes greatly. In this situation, the second type of mercury distribution in the bottom sediments of lakes prevails. A specific feature of mercury distribution in averaged vertical sections of bottom sediments of the lakes in different regions of Siberia is an increase in mercury concentration to upper horizons, especially starting from the depth of 15 cm, which corresponds to the years 1960–1970 when compared with the conjugated plots for radioactive caesium (technogenic element).

TABLE 2

Mercury content in the mineral types of bottom sediments (BS) and soil of the catchment areas of the continental lakes of Siberia

Mineral composition of BS	Mercury content, mg/kg
Terrigenic	0.069±0.006
Terrigenic-organogenic	0.069±0.009
Organogenic	0.058±0.003
Carbonate	0.055±0.006
Terrigenic-carbonate	0.045±0.005
Soil	0.059±0.008

No dependence of mercury distribution in bottom sediments over core depth on the mineral composition of the sediment was revealed.

An example of active industry-related pollution with mercury is the Bolshoye Yarovoye Lake; there is a chemical plant at the lakeside. Near the plant, the average mercury content in bottom sediments is 0.7 g/t, reaching 2.0–2.3 g/t in some intervals. At the opposite side of the lake, bottom sediments contain mercury 0.05 g/t as an average (Fig. 2). To map the isolines of chemical elements in soil and in bottom sediments, we used the GIS ArcMap 9.3 in combination with the Geostatistical Analyst unit (the map was built by D. A. Chupina). The information on the distribution of element concentrations was placed in the vector layer (shape-file) of ArcMap. Isolines were generated using the IDW interpolation method (inverse distance weighed). As a result, the isoline maps of the distribution of chemical elements in soil and in bottom sediments were obtained.

The data on average mercury content in medicinal herbs, mosses, lichens, needles, coniferous forest litter, mushrooms and other products sampled in different regions of Siberia are presented in Table 3. As a rule, mercu-

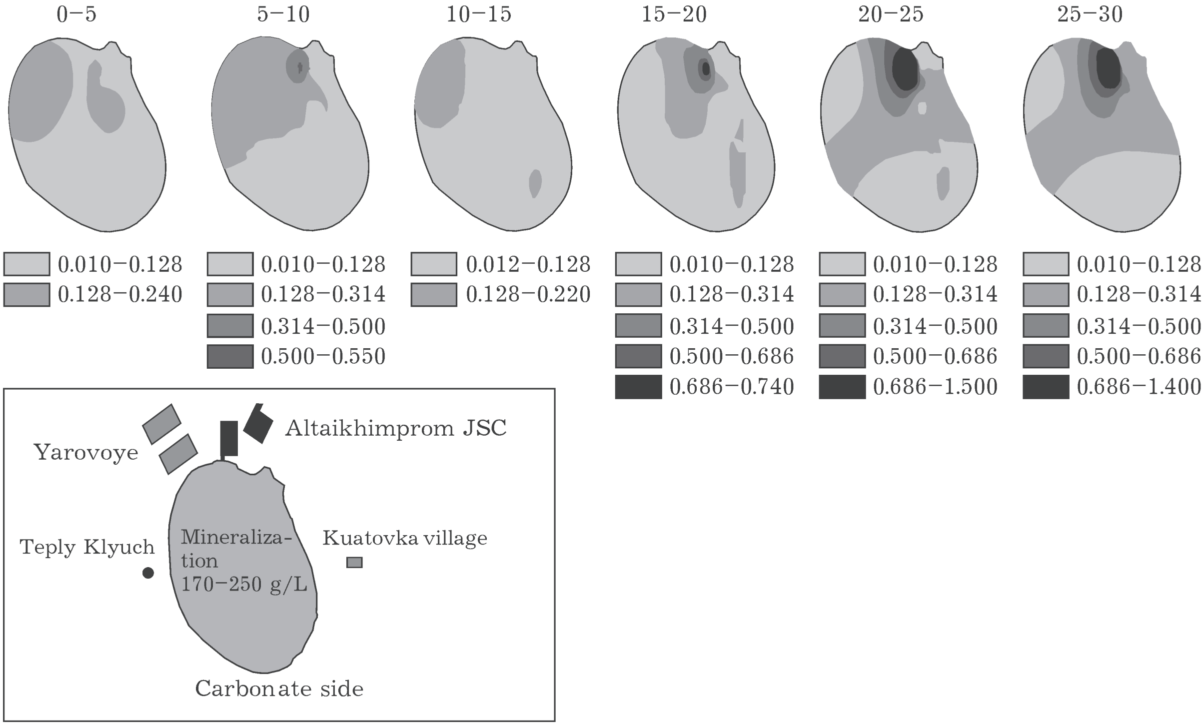

Fig. 2. Vertical distribution of mercury (mg/kg) in bottom sediments over some separated horizons of the Bolshoye Yarovoye Lake.

TABLE 3

Mercury concentrations in natural environmental components in different regions of Siberia

Regions	Mosses	Lichens		Medicinal herbs	Berries	Mushrooms	Needles	Coniferous forest litter
		Epigene	Epiphytic					
Pur district (YaNAD)	0.09 0.02–0.32 (246)	0.056 0.01–0.31 (210)	n/d	n/d	0.004 0.003–0.005 (5)	0.956 0.001–5.500 (7)	0.02 0.01–0.022 (10)	n/d
Altai Territory	0.10 0.05–0.19 (32)	0.063 0.0–0.38 (159)	n/d	0.023 0.004–0.063 (101)	0.08 0.05–0.17 (9)	0.98 0.04–2.3 (31)	0.022 0.01–0.072 (51)	0.146 0.054–0.29 (71)
Altai Republic	0.11 0.04–0.09 (16)	0.052 0.00–0.16 (41)	0.23 0.14–0.32 (10)	0.024 0.004–0.20 (179)	n/d	n/d	0.022 0–0.043 (39)	0.469 0.020–6.100 (66)
Novosibirsk Region	0.16 0.04–0.4 (18)	0.064 0.03–0.16 (72)	0.38 0.16–0.42 (7)	n/d	n/d	n/d	0.029 0.01–0.04 (32)	0.125 80.037–0.220 (40)
Tyva Republic	0.057 0.024–0.13 (84)	n/d	n/d	n/d	n/d	n/d	n/d	0.25 0.032–0.390 (80)
Irkutsk Region (UOBAD)	0.12 0.06–0.24 (44)	0.06 0.02–0.20 (76)	0.13 0.03–0.50 (44)	0.04 0.01–0.11 (42)	0.006 0.003–0.01 (14)	1.18 0.06–4.4 (9)	0.06 0.01–0.44 (67)	0.06 0.017–0.130 (13)
Chita Region (ABAD)	0.08 0.02–0.25 (51)	0.057 0.024–0.13 (23)	0.20 0.08–0.89 (9)*	0.03 0.02–0.04 (5)	n/d	n/d	0.035 0.01–0.13 (56)	0.125 0.024–0.190 (25)
Republic of Sakha (Yakutia)	0.09 0.028–0.20 (58)	0.06 0.01–0.17 (37)	0.56 0.1–1.48 (4)	n/d (3)	0.012 0.011–0.014	0.74 (1)	0.27 0.01–0.44 (8)	0.12 0.11–0.14 (16)

Notes. 1. The average value stands in the numerator, the minimal and maximal values, respectively, are in denominator; the number of samples is indicated in parentheses. 2. n/d – not determined.

* Epigene scale.

ry concentration in medicinal herbs (per dry mass) is smaller than its concentration in soil, which is also characteristic of the total sample over the species of herbaceous plants. Mercury concentrations in herbs are within the permissible level for non-polluted territories [16]. The specific feature of different species is only weakly pronounced, except for the roots of some perennial plants. For the set of one of the through species – artemisia (n = 80) – the differences in the degree of mercury accumulation in the Altai region for background areas and natural mercury anomalies were demonstrated: this average index for the top parts is 0.030 and 0.093 mg/kg, respectively, for roots it is 0.023 and 0.045 mg/kg, respectively.

The maximal accumulation of mercury is characteristic of mushrooms, which is to be stressed because mushrooms serve both as a food product and as an indicator of the state of environment. According to the data for the Altai region, mercury content is minimal in gill fungi (the average value is 0.04 mg/kg of air-dry mass), in spongy fungi it is 0.30 mg/kg of air-dry mass. The high mercury content was detected in puffballs: in the background regions on the rocks of different composition it reaches 0.78–1.29 mg/kg, in the regions with ore mineralization it is 1.7 mg/kg, in mercury zones 4.5 mg/kg, which depicts local differences in the atmospheric emissions of mercury.

Coniferous forest litter and lichens are natural pads that hold atmospheric precipitation, and they can be used as the indicators of pollution, too. The upper layers of forest litter in the background regions of the south of West Siberia contain mercury at the average level of 0.085 mg/kg, to the depth the concentration of mercury in over rotten and disintegrated mass increases to 0.18 mg/kg; passing to soil, a gradual decrease to 0.08 mg/kg is observed. In addition to the features of mercury migration, this is connected with an increase in the admixture of melkozem in the lower layers of forest litter. A noticeable contribution into an increase in mercury content in forest litter is made by fresh needles, as well as by bark, branches and cones that get into it. According to the data of sole determinations, the maximal mercury concentrations are detected in the bark (0.075 mg/kg).

CONCLUSIONS

The following conclusions may be drawn on the basis of the data obtained:

1. In general, the results of mercury determination in different environmental components in Siberia provide evidence that the ecological situation is safe. Local pollution cases are confined with the regions of natural anomalies, as well as with the centres of industrial production and the development of oil and gas complex. The data on the background mercury content in soil and in bottom sediments, its mobile forms and bioindicators can be used to reveal anomalies.

2. Mercury content in the bottom sediments of lakes in Siberia depicts its concentrations in the soil of catchment areas. The average level of mercury in bottom sediments and in the soil of catchment areas of the continental lakes of Siberia is close to the background value established for soil in the world and for bottom sediments. Pollution with mercury in the studied lake ecosystems has the local character.

3. According to the data of cluster analysis, a direct correlation was established between mercury concentration and the organogenic part of bottom mud in the lakes.

4. No dependence of mercury content in bottom sediments of the studied lakes on the degree of water mineralization was revealed; no dependence of mercury distribution over depth in bottom sediments on the mineral composition of the sediment was revealed.

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