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Forms of Occurrence and Migration of Mercury in Components of Ecosystems of Gorny Altai

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Abstract

Natural and technogenic sources of mercury ingress to into ecosystems of Gorny Altai were characterised. The content of mobile Hg forms in polluted soils was determined and its inverse dependence on the gross content of mercury in the soil was revealed. The limited nature of migration of mobile forms of mercury from polluted soils was demonstrated. The main thermoforms of mercury in conditionally background and anthropogenically polluted soils were preliminarily found. Data on levels and forms of its occurrence in components of water ecosystems are presented. Peculiarities of their changes in different hydrological periods, and also during the water transfer were revealed. Quantitative characteristics of migration of the various forms of mercury being transferred from the industrial zone of the Aktash mining and metallurgical enterprise were assessed. A progressive decrease of their content in the waters that transmit pollution of fifth-second order rivers (Yarlyamry, Chibitka, Chuya, and Katun) was shown.

Keywords: Gorny Altai, environmental media, content and forms of mercury, peculiarities of migration

INTRODUCTION

Having high toxicity and unique geochemical properties, mercury has a special place among pollutants of natural ecosystems. The main sources of its ingress are natural and anthropogenic. Moreover, the first source is due to the specific character of the metallogenic geological environment, the second one – to the use of mercury in household activities [1, 2].

In the territory of Altai Republic, natural Hg source group is presented by a number of mercury deposits, developments, lithochemical areolas, and leakage fluxes within the Salair-Altai mercury-silver-polymetallic and Altai-Kuznetsk mercury-iron-gold-ore mineragenic regions (Fig. 1).

The second group of mercury sources is related to Hg extraction in the past and use in the territory of the region. The main factors of technogenic mercury emission into the mountain Altai ecosystems are long-term development of the Aktash Deposit and mercury-containing wastes processing by the homonymous mining and metallurgical enterprise (AMME), and also wide use of metallic mercury for fine-grained gold amalgamation in the development of hard-rock and placer gold deposits in the northeast of the region [3].

Currently, pollution of environmentally unfavourable territories of the past extraction and use of mercury, especially, of the industrial zone of AMME has become the key issue for the sustainability of the Altai Republic, as it limits one of its priority, *i. e.* tourism and recreation development. To successfully rehabilitate these territories, primarily to conduct mercury-polluted soils sanation, the information on forms of its occurrence in natural media depositing and transferring environmental pollution is required [4, 5].

The purpose of the performed investigation was to reveal forms of occurrence and migration of mercury in the main components of ecosystems of Gorny Altai.

MATERIALS AND METHODS

The research objects were soil profiles of sites of the past extraction (use) of mercury and waters (bottom sediments) transmitting (accumulating) it from the rivers of the region. For this purpose, testing single landscape-geochemical profiles of the tested soils of the former AMME, gold mining companies (Veseliy mine," the mine "Altay"), as well as water, coastal soils, and bottom sediments of the rivers in the zones of influence of these objects was carried out. To assess the natural ingress of mercury, components of the subaquatic landscape of Katun river (Elanda-Cuius segment), where the reservoir of the Katun hydroelectric power station was designed (Fig. 1) were explored.

Fig. 1. Overview diagram of investigated sites of mercury pollution in Altai Republic territory. Punches (deposits and occurrences of mercury): *1* and *2* are industrial area of AMME and valley of Yarlyamry river, and that of Veseliy mine; *3* is Maisky village and valley of Kaurchak river; *4* is reservoir project of Katun hydroelectric power station.

Soil profile samples were collected from A and B levels (0-10, 10-20, and 20-40 cm intervals) within industrial zones of enterprises and in floodplains of draining rivers. Assays of bottom sediments are represented by small-sand-clay-silt material of river braids and shallows.

The content of mercury and its thermoforms in samples of soil and bottom sediments was determined by atomic absorption (pyrolysis) using RA-915+ mercury analyzer with the prefix PIRO-915+ in the Uranium Geology MINOC of the School of Natural Resources of Engineering of the National Research Tomsk Polytechnic University (analyst E. E. Lyapina). The detection limit of the method is 5 ng/g. To monitor the accuracy of mercury determination, there were used standard samples of the composition of sod-podzolic sandy loam soil UPDS-3 (GEO 2500-83). Mercury thermoforming was determined by increasing the temperature of samples to 850 °C for 15 min at an average heating rate of 0.8 °C/s.

To assess the migration potential of mercury in polluted soils of AMME industrial zone, the content of its main forms (water-soluble, exchange, and acid-soluble) in 15 samples was determined. The determination was performed by atomic absorption using the method of MVI 80-2008 at The V. S. Sobolev Institute of Geology and Mineralogy, SB RAS (analyst N. V. Androsova).

RESULTS AND DISCUSSION

It was found that in polluted soils of AMME industrial zone with concentrations of gross mercury of 3.5–121 mg/kg, the content of its water-soluble form varied within 0.06 and 0.39 mg/kg with an average value of 0.19 mg/kg. The fraction of this form, in which mercury can be transmitted with surface runoff, varies from 0.3 to 2.5 % with an average of 1 % of the gross

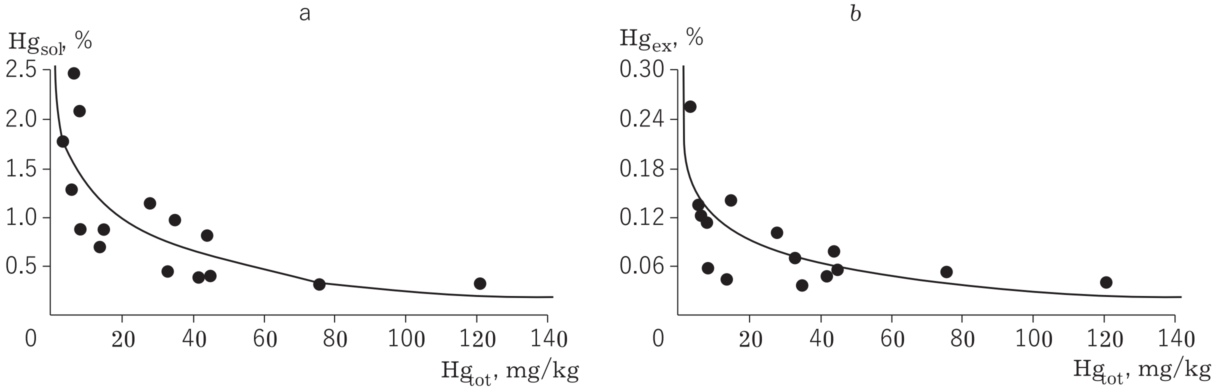

Fig. 2. Connection of water-soluble (*a*) and exchange (*b*) forms of mercury with its gross content in soils of industrial zone of AMME.

content in the soil. The share of the exchange form assimilated by vegetation is an order of magnitude lower than that of water–soluble and is 0.04–0.25 % of the gross, with an average value of 0.1 %.

The acid-soluble forms (94–99 % with an average value of 98 %) that do not participate in migration processes due to the lack of necessary natural conditions makes the main contribution to the gross content of mercury in polluted soils.

Analysis of the correlation between water-soluble and exchange forms of mercury with its gross content in soils revealed the presence of feedback hyperbolic dependence between them (Fig. 2), which lied in an increase of the fraction of mobile forms when reducing gross mercury content especially in the 1–10 mg/kg range. This points to a more intense formation of mobile forms of mercury in case of its low content in the soil, in other words, upon the scattered occurrence of mercury in the soil.

This regularity is well apparent in the distribution of mobile forms of mercury along with the soil profile. Thus, in all the profiles explored the content of water-soluble and exchange forms decreases with depth, and the content of the latter on average decreases three times faster. On the contrary, the relative fraction of these forms in the soil profile increases in 2–4.5 times, and that of water-soluble forms increases twice as fast as the exchange one (Table 1).

These trends in the behaviour of water-soluble and exchange forms of mercury in polluted soils determine the main peculiarities of their spatial distribution in the territory of the AMME industrial zone: an increase in their content in the profile of the central parts of pollution sites against a decrease in the relative fraction of these mobile forms.

Lately, in geoenvironmental research, thermodesorption analysis of solid natural environments that allows simultaneous determination of all forms of mercury has been widely used. According to its results, one may judge of the nature of the transformation of the initial mercury carriers and peculiarities of migration of its compounds, which is important for the development of methods for the remediation of environmental pollution [4–7].

TABLE 1

Mercury movable forms content in generalized soil profile of AMME industrial zone

Interval, cm	Water-soluble form		Exchange form	
	Content,		Content,	
	mg/kg	%	mg/kg	%
0–5	0.16–0.39 (0.24)	0.30–0.40 (0.35)	0.020–0.070 (0.040)	0.05–0.06 (0.06)
5–20	0.07–0.36 (0.18)	0.70–2.07 (1.22)	0.006–0.034 (0.014)	0.04–0.13 (0.09)
20–40	0.06–0.34 (0.16)	0.87–2.46 (1.51)	0.005–0.016 (0.009)	0.05–0.25 (0.12)

Note. Number of samples for each interval n = 15. 2. Average value is given in brackets.

TABLE 2

Relative fraction of solid-phase forms of mercury in the components of subaquatic ecosystems of Gorny Altai , %

Components	Mercury form				
	Free	Physically sorbed	Chemisorbed	Sulphide	Isomorphous
Soils:					
level A	71.9–99.8 (83.0)	1.9–25.5 (14.8)	2.1–4.6 (3.3)	0.6–1.1 (0.9)	0.0–0.1 (0.0)
level B	38.5–88.8 (73.7)	10.6–59.8 (25.1)	0.2–1.3 (0.7)	0.1–0.5 (0.3)	0.0–0.4 (0.2)
Bottom sediments	68.4–98.6 (84.3)	1.4–20.5 (10.8)	0.0–8.0 (3.2)	0.0–2.7 (1.1)	0.0–1.8 (0.6)

Note. Average value is given in brackets.

TABLE 3

Average relative fraction of solid-phase forms of mercury in soils and sediments of studied objects, %

Object	Mercury form				
	Free	Physically sorbed	Chemisorbed	Sulphide	Isomorphous
Veseliy mine	46.8	38.4	12.4	1.5	0.9
AMME industrial zone	73.7	25.1	0.7	0.3	0.2
Maisky village	81.6	14.2	2.6	1.2	0.4
Valley of Katun river	91.4	6.7	1.5	0.4	0.0

Within the performed investigation using a small factual material (12 samples of soils and sediments), for the first time, there were acquired data on the relative fraction of solid-phase forms of mercury in the studied areas of its natural and man-made emissions (Tables 2 and 3).

It was preliminarily found that the free form of mercury prevailed in polluted soils and sediments of Mountain Altai rivers, the fraction of which was 38.5–99.8 % with an average value of 80.3 % of its gross content. The average fraction of physically sorbed forms of mercury is 16.6 %, chemisorbed – 2.1 %, mineral (sulphide) – 0.7 %, isomorphic – 0.3 %. It is noteworthy that down the profile of soils, the fraction of the free form is significantly reduced due to the transition to the physically sorbed one.

The findings allowed distinguishing two prevailing types of thermo forms of mercury in soils and bottom sediments of rivers in the region. The first from them mainly represent-

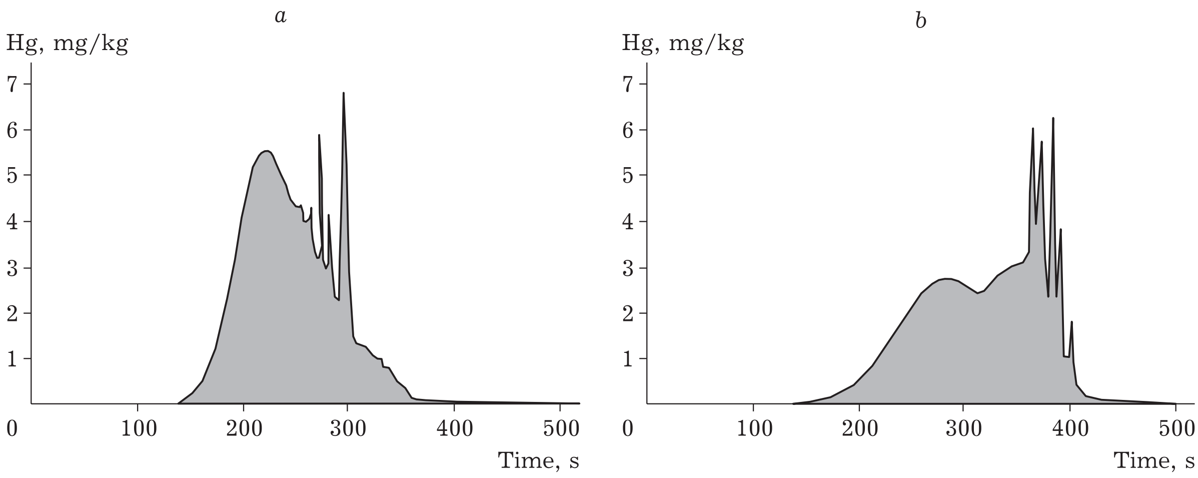

Fig. 3. Thermal images of mercury in soil profile of industrial zone of AMME with prevalence of its free (*a*) and physically sorbed (*b*) forms.

ed by free and, to a lesser extent, sorbed forms of mercury, is typical for soils and river sediments of mercury-free territories (conditionally-natural type). The second type, which contains all thermoforms under the prevalence of the first two forms, is more often apparent in the areas of past mining and using mercury (conditionally natural-technogenic type) (Fig. 3).

Almost the same ratio of thermoforms in the surface layer of coastal soils and in bottom sediments of rivers presumably indicates a close relationship between these components of subaquatic landscapes and the nature of mercury pollution of river sediments inherited from soils. When transferring river muds, the ratio of forms of mercury varies: free (atomic) mercury prevails over its sorbed form in suspended particles.

It is known that mercury in surface waters of the land migrates in two main phase conditions, i.e. in the dissolved form and as part of the suspension. In the first case, it can be present as a bivalent ion, mercury hydroxide, complex compounds with chlorine, organic matter, *etc*. [8–11]. Suspension and bottom sediments of water bodies are the crucial accumulators of mercury in conditions of pollution of aquatic landscapes [12].

On an example of Katun river and its tributaries transmitting mercury pollution of AMME industrial zones, trends in the ratio of forms of mercury to its content in water and sediments, and also the level of its bottom accumulation in different hydrological periods are outlined (Fig. 4).

It is found that the minimum fraction of water-dissolved mercury is typical for the rivers of the region in the spring flood (maximum – in the autumn low) [13, 14]. Trends in the ratio of its suspended form to the content in bottom sediments and variations in bottom accumulation coefficient (BAC) are antiphase in nature and increase by 3–4 orders of magnitude for diverse rivers.

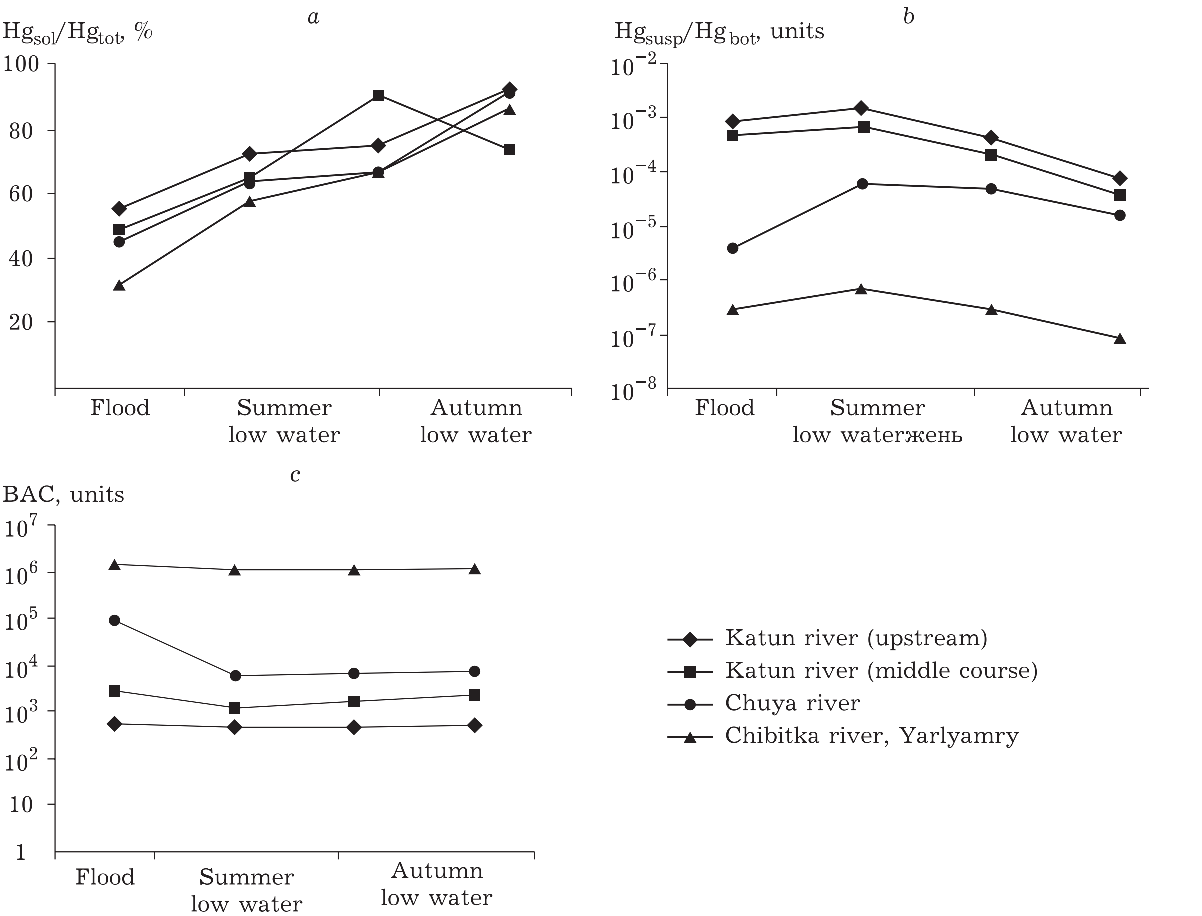

Fig. 4. Changes in mercury soluble form fraction in river water (*a*), ratio of its weighted form to contents of bottom sediments (*b*), coefficient of bottom accumulation of mercury (*c*) in diverse hydrological periods.

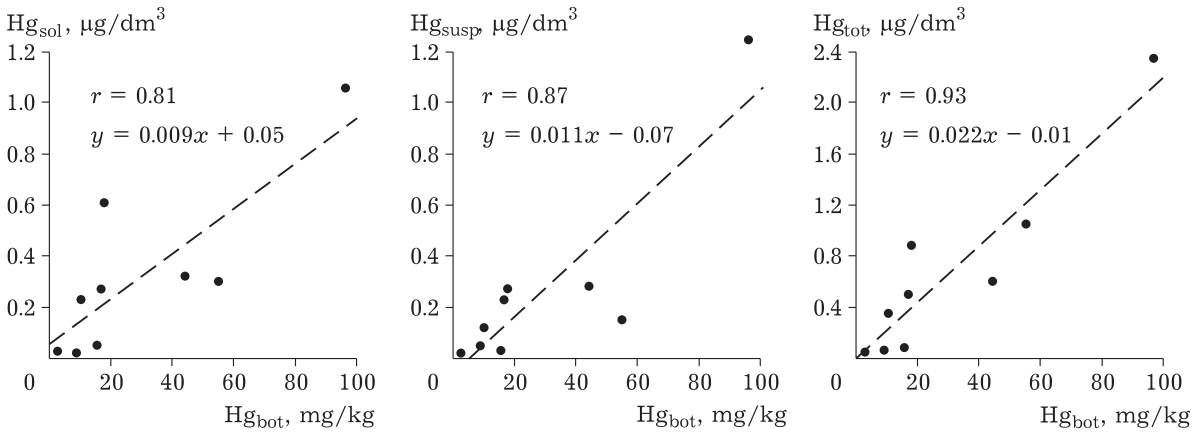

Fig. 5. Correlation of total and phase forms of mercury in river water (*Y*-axis) with its content in bottom sediments (*X*-axis).

The extensive examination of mercury distribution in components of aqueous systems (water, suspended matter, bottom sediments) that has been carried out from the late 1980-is [15, 16] has allowed revealing the specifics of mercury migration in the rivers of the region, wherein it comes both from natural sources and from polluted land in the industrial zone of AMME. In particular, a direct significant relationship between dissolved, suspended, and total forms of mercury in river water from its content in bottom sediments that are a source of secondary pollution (Fig. 5).

Examining the distribution of forms of mercury in Yarlyamry river water flowing through the industrial area of AMME, revealed a strong linear correlation between the mass of suspended particles and mercury sorbed therein, and also between its sorbed and dissolved forms. The ratio of the latter does not depend on mercury content and naturally varies from the upper reaches of the river [17].

In the industrial area of AMME, mercury content in river water increases significantly, herewith, the sorbed form is still prevailing over the dissolved one. In the 5–10 km range below the enterprise, gross mercury content in water decreases, dissolved form begins to prevail over sorbed. This indicates a gradual deposition of suspended particles and the transition of the sorbed mercury to the soluble form [18].

The distribution of mercury dissolved, sorbed in suspended solids, and total forms of in river water in the way of its migration from the territory of AMME industrial zone is characterised by a steady decrease in the content of all forms of mercury in water, and also in bottom sediments of Yarlyamry–Chibitka–Chuya rivers. A consistent reduction (1.5–2 times) in concentrations of technogenic mercury is replaced by its slight increase in the segment of the project of the Katun hydroelectric power station reservoir (Table 4), due to the additional supply of mercury from a se-

TABLE 4

Content of mercury in water and river bottom sediments during its transit from AMME (according to Altai-Geo JSC, 2005)

River/Order	Dissolved, μg/d^3	Suspended, μg/d^3	Total		BAC, units
			in water, μg/d^3	in bottom sediments, mg/kg	
Yarlyamry/5	0.035–0.089 (0.062)	0.004–0.065 (0.034)	0.039–0.154 (0.096)	47–368 (188.0)	1 960 000
Chibitka/4	0.024–0.026 (0.025)	0.002–0.050 (0.022)	0.026–0.074 (0.047)	28.3–74.6 (51.4)	1 117 000
Chuya/3	0.014–0.023 (0.019)	0.003–0.013 (0.009)	0.021–0.035 (0.028)	0.15–2.36 (0.73)	22 800
Katun*/2	0.011–0.031 (0.020)	0.002–0.023 (0.010)	0.016–0.045 (0.030)	0.01–0.28 (0.07)	2650

Note. Average value is shown in parentheses.

*Middle course below mouth of Chuya river.

TABLE 5

Gradients of mercury forms content in water and bottom sediments of region rivers

Mercury form	Rivers			
	Yarlyamry	Chibitka	Chuya	Katun
		River waters, μg/(dm^3 · km)		
Dissolved	0.06	0.003	0.00007	0.000006
Suspended	0.06	0.001	0.0002	0.000005
Total	0.12	0.004	0.00027	0.000011
		Bottom sediments, μg/(dm^3 · km)		
Gross	45.7	11.4	0.75	0.011

ries of its displays and scattering halos in the basin of the middle course of the Katun river below the mouth of the Chuya river.

In a series of Yarlyamry–Chibitka–Chuya–Katun rivers, the gradients of the content of the explored forms of mercury in water is progressively reduced on average, by an order of rivers (Table 5). The gradient decrease for bottom sediments of these rivers is more complex, close to exponential functions of type $y = 1/4^x$ (y is gradient of mercury content for water course in pollution migration beginning (Yarlyamry river), μg/(dm^3 · km); x is number of host contamination of larger watercourse (1 – Chibitka, 2 – Chuya, and 3 – Katun). The ratio of gradients of mercury content in water and in bottom sediments of neighboring multi-ordinal rivers in this series is close to each other (1/4 : 1/15 : 1/68), which indicates the sustained nature of its distribution in components of aquatic ecosystems in the way to passing.

It is worth to note the low levels of mercury transition from the accumulated metallurgical slags (ashes) of AMME (1.8 million tons) in the dissolved state. On an example of surface runoff from slag heaps of ashes, it was found that about $7 \cdot 10^{-5}$ of mercury contained therein passes to the aqueous phase. The biological uptake of mercury by vegetation is equally low. Thus, within the industrial area of AMME only 1–1.5 % of total Hg content of its gross content passes to soil-connected herbaceous plants [3].

CONCLUSION

1. Mobile (water-soluble and exchange) forms of mercury are present in polluted soils of the region in minor amounts (tenths-hundredths of mg/kg) and their relative fraction is inversely proportional to the gross content of mercury. Mobile forms of mercury are generated more intensively at its low concentrations in the soil.

2. Migration of mobile forms of mercury from polluted soils is limited and does not lead to hazardous pollution of aquatic ecosystems. Transit of mercury-containing technogenic silts of Yarlyamry river determines an elevated level of mercury pollution of bottom sediments and secondary pollution of water of the rivers in the basin of Katun river.

3. For soils and bottom sediment of “mercury-free” territories of the Region the presence of free and physically sorbed thermoformas of mercury is charastics, and in the places of its previous extraction and usage all forms were present with the predominance of the above mentioned two forms.

4. Both seasonal dynamics and a progressive decrease in pollution transportation by surface watercourses are typical for dissolved and suspension-sorbed forms of mercury and its bottom accumulation coefficient.

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