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Correlations between Mercury in Soils and Bottom Deposits of Bol'shoye Yarovoye Lake

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Abstract

It was found that mercury contents in saline soils of Bol'shoye Yarovoye Lake met the average content in solonetz soils of the steppe zone of Altai Territory. Differences between types of soils are explained by the peculiarities of solonetz and solonchak processes. The distribution of mercury in bottom deposits is uneven both along cores on depth of individual wells, and in different wells. The average content of mercury and the value of the Hg/Al ratio in bottom deposits are significantly higher than their values in soils because of local pollution. Low mercury contents and Hg/Al ratios were found in coastal wells only. Factor analysis and pair correlation method detected differences in correlations of mercury between soils and bottom sediments both in granulometric fractions, and the initial samples. Correlation analysis results in the initial samples of soils and bottom sediments give the overall picture of mercury distribution in the sedimentation process. Mercury in soils has positive correlations with the terrigenous component that is its major natural source. A negative correlation with the "carbonate group" (Ca, Mg, Sr) and antimony is typical. Mercury in bottom deposits has positive correlations with antimony and manganese, and is bound with the major composition of precipitates indirectly only. These results argue of a change in the deportment of mercury in the sedimentation process, which confirms its local entrance into precipitation from a technogenic source that is accompanied by antimony.

Key words: mercury, Altai Territory, Bol'shoye Yarovoye Lake, soils, bottom deposits, factor analysis

INTRODUCTION

The study of the distribution of elements along the water area of Bol'shoye Yarovoye Lake in soils and bottom sediments is of both theoretical and practical value. The lake is an important promising source of chemical raw materials and the therapeutic sludge, preparation base of valuable biological feed raw materials (*Artemia salina* maxillopod). The lake area represents a balneological resort area, however, the location on its shore of the Altaykhimprom JSC, wastes of which contain mercury, are hazardous for the environment. Pollution of snow/water slurry, zooplankton, and local pollution of soils and bottom deposits was detected [1–5].

Bol'shoye Yarovoye Lake is found in the central part of the Kulunda depression and it is drainless. Landscape and climatic conditions with low rainfall levels (250–300 mm a year) and increased evaporation are causes of a high degree of salinity of the lake water and soils of its catchment area.

According to mineralization, the lake water was assigned to sulphate-chloride type, according to O. A. Alekin's classification [6], and by some data, to sodium chloride [7]. The lake receives water from snow water and ground water numerous springs. Sandy silts represent bottom deposits of the lake. Isolinear maps of grade distribution of microelements (the Statistica 12 program) in soils and bottom deposits detected local zones of increased concentrations of mercury associated with waste area of the chemical combine and wastewater discharges of Yarovoye city [9].

The soils of the area were formed on the base of integumentary loess-like loams. Complex-mosaic soil cover from more ancient chestnut soils and black soils of south solonetzic to younger salines and solonetz. Meadow salines were formed in the southeastern lowered part of the catchment area. Chestnut soils and southern solonetzic chernozems are located at the elevated areas in the eluvial landscapes.

EXPERIMENTAL

Testing of soils was carried out by genetic horizons in the catchment area up to the source rocks in 14 through cuts (74 samples). Bottom deposits were tested from a catamaran using special samplers in 15 wells (74 samples) to depths to 90 cm (Fig. 1). Samples were collected through each 3 cm and carefully packaged. Granulometric analysis was carried by the elutriation method in some soil sections and bottom sediment cores and fractions for analysis (>0.25, 0.25–0.16, 0.16–0.02 and <0.02 mm) were isolated. The major part in the mechanic composition of soils determined by Kachinsky method is represented by a large-silty fraction 0.05–0.01 mm. According to the content of physical clay (fraction 0.01–<0.001 mm), they refer to light and medium loam [8].

According to X-ray structural analysis, bottom deposits consist of quartz, plagioclase, potassium feldspar, calcite, occasionally interlayers of mirabilite ($Na_2SO_4 \cdot 10H_2O$) and traces of halite (NaCl), in addition to organic matter.

Instrumental atomic absorption determination of mercury was carried out by the method of cold vapour using a MHS-20 mercury hy-

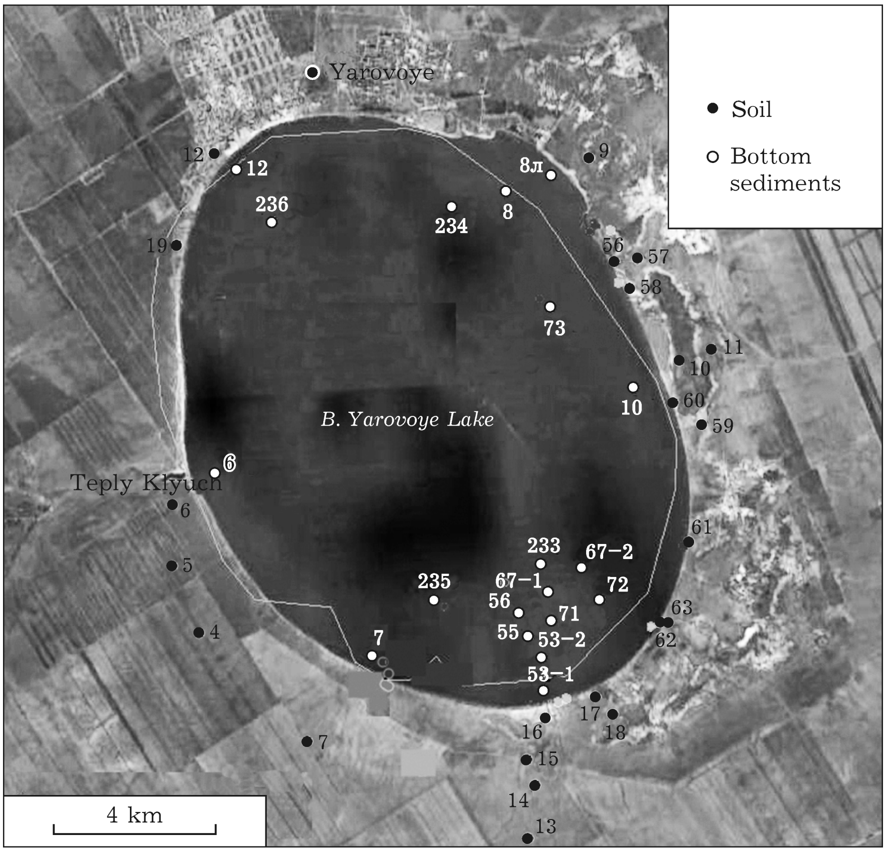

Fig. 1. Sampling scheme of Bol'shoye Yarovoye Lake.

TABLE 1

Average content of mercury ($\bar{X}$) and the Hg/Al ratio in soils

Soil types	n	$\bar{X}$, mg/kg		Hg/Al, 10^{-6}	
		Average	Variation limits	Average	Variation limits
Chestnut	5	0.040	0.031–0.047	0.009	0.006–0.012
Chernozems southern solonetzic	15	0.036	0.014–0.097	0.007	0.003–0.019
Solonchaks	8	0.021	0.011–0.033	0.005	0.002–0.008
Solonetzes	20	0.048	0.022–0.071	0.009	0.004–0.016
Saline solonetz	6	0.028	0.019–0.036	0.009	0.003–0.034
Solodized solonetz	5	0.034	0.024–0.045	0.008	0.006–0.062
Solonchak on solonetz	5	0.065	0.041–0.091	–	–
Meadow and meadow-marsh solonchaks	10	0.058	0.026–0.12	–	–
Average	74	0.040	0.011–0.097	0.008	0.002–0.062

Notes. 1. Here and in Tables 2, 3: n is number of samples. 2. Dash – aluminum in the samples was not determined.

dride console to a PerkinElmer device at the Sobolev Institute of Geology and Mineralogy of the SB RAS (analytics are Z. O. Badmaeva, N. V. Androsova) according to the accredited technique with a detection limit of 0.01 g/g. The laboratory was accredited by the Association of Analytical Centers "Analytics" and registered in the State register No. ROSS Ru 0001.510590. In addition to analysis for mercury, another group of macro- and microelements was analyzed.

The distribution of elements in bottom deposits and soils of the catchment area is driven by many factors, including salinization conditions. To detect the effect for the distribution of mercury contents of other elements pair correlation method and factor analysis were used. They were performed both for the original samples, and granulometric fractions.

TABLE 2

Average content of mercury ($\bar{X}$) and the Hg/Al ratio in bottom sediments

Well No.*	n	$\bar{X}$, mg/kg		n	Hg/Al, 10^{-6}	
		Average	Variation limits		Average	Variation limits
			Coastal water area			
6, 7, 12, 81	20	0.018	0.010–0.040	12	0.04	0.002–0.009
			Northeastern part of water area			
8	5	0.052	0.020–0.120	3	0.016	0.005–0.031
73	12	0.233	0.039–0.360	12	0.058	0.010–0.280
			Southern part of water area (carbonate coast)			
53	14	0.057	0.037–0.083	14	0.009	0.007–0.015
56	6	0.064	0.040–0.110	6	0.015	0.07–0.021
67	6	0.217	0.084–0.360	6	0.038	0.014–0.065
71	11	0.060	0.022–0.120	11	0.011	0.004–0.023
Average	74	0.089	0.010–0.360	52	0.025*	0.004–0.280

Note. For design. see Table 1.

*Coastal wells not considered.

RESULTS AND DISCUSSION

Table 1 presents results of mercury determination in various soils of the catchment area of Bol'shoye Yarovoye Lake. As a whole, mercury content in all soils is lower than the average value for soils of Altai Territory [10] and meets solonetz soils of this landscape zone. Average contents of mercury are close in zonal chestnut soils and southern chernozems. The formation of solonchaks happens at strong evaporation under acid conditions. Soil ground water currents rise up to the surface, where readily soluble salts are accumulated. This may cause a partial transition of mercury into a gas phase, which, apparently, reduces its content in soil sections. In solonetzes, colloids and readily soluble salts formed at desalination move down, where an illuvial salt horizon is formed, which, apparently, contributes to the preservation of mercury in soil section. These peculiarities are reflected in mercury content in soils. Increased contents of mercury are typical for meadow and meadow-marsh solonchaks because of higher contents of organic matter in them. Average contents of mercury in granulometric fractions of chestnut soils are 0.006–0.016 mg/kg. They considerably increase in solonetzes, especially in <0.02 mm (0.034–0.188 mg/kg) fraction.

The mercury content in bottom deposits is distinguished by the nonuniformity (Table 2). As a whole, its average content in them is much higher than in various soils. The lowest contents are typical for coastal wells. This is a consequence of the fact that the bulk of the precipitate is formed due to the collapse of soils and rocks of the coastal area and represented mainly by the macrofragmental component. Wells of the northeastern part of the water area are found in the zone of meadow-marsh soils, where the contents of organics are elevated and near the location of wastes of the combine that are located in the northern part of the catchment area. Here, high mercury contents in many precipitation depths are a consequence of technogenic pollution. Precipitation of the southern part of the water area are located in a soil area with a high content of carbonates. In addition to Ca, the Mn contents are increased in them; Mn compounds have high sorption capacities. Substantial amounts of Mn were also detected in meadow-marsh sediments of the coastal zone. Thus, mercury enrichment of bottom deposits is related to their capacity to accumulate this element from both natural, and technogenic sources.

The primary natural source of mercury is mainly aluminosilicate rocks. Solubility of aluminium hydroxide compounds is low during weathering, especially under weakly acidic and weakly basic conditions typical for this region. Consequently, aluminosilicate components mainly preserve initial aluminium contents, which is also testified by its insignificant migration into an aqueous phase: aluminium content in water of the lake is 0.12–0.25 mg/L. This allows isolating its entrance in soils and bottom deposits from natural and technogenic sources by an aluminium normalization of mercury contents (see Tables 1 and 2). Comparison demonstrates that soils generally differ much from bottom sediments by this indicator. The average value of the Hg/Al ratio in soils is $0.008 \cdot 10^{-6}$, and in bottom sediments, it varies greatly from well to well, depending on their location and depth of core recovery: from $0.004 \cdot 10^{-6}$ in the coastal part to $(0.038–0.058) \cdot 10^{-6}$ in other parts of the water area. This is also confirmed by values for granulometric fractions. Thus, values of Hg/Al ratios in bottom sediments in many cases are several times higher the ratios in soils. Herewith, mercury can be found both in mineral and organic forms. This is confirmed by the results of calculations for bottom sediments of many lakes of Altai Territory and the Novosibirsk Region: the average value of the Hg/Al ratio in bottom sediments of the terrigenous composition is $0.005 \cdot 10^{-6}$, and in sediments with a larger content of organics and a lower content of Al, including in sapropels – $0.080 \cdot 10^{-6}$ [12]. Here, mercury from the natural and remote natural and anthropogenic sources is present. The correspondence of the Hg/Al ratio in soils of the catchment area of Bol'shoye Yarovoye Lake to the ratio in terrigenous precipitation of lakes confirms that mercury contents in them are close to background. It is obvious that as a whole, the effect of the technogenic component in soils due to atmospheric mercury transfer is quite insignificant. Pollution was detected in several samples in immediate proximity to the location of combine wastes (taken from the upper soil horizon and not included in sampling).

The factor analysis results for >0.25 and 0.25–0.16 mm fractions of soils demonstrated the following: the major part of elements except for the carbonate group (Ca, Mg, Sr) is connected to each other by positive correlations, which testifies their entrance mainly to the detrital component of soil. Thus, one can conclude that mercury in these fractions does not enter into it and is probably present mainly as free form Hg^0.

Mercury in 0.16–0.02 mm and <0.02 mm fractions has positive correlations with many elements. Thus, this is polymetal group (Cd, Zn, Cu, Pb), iron group (Fe, Ni, V, Mn, Co) and partially feldspathic group (Al, K, Ba, Be). Mercury, like many other elements, has negative correlations with Ca, which is part of the carbonate group. Thus, mercury in this fraction is a part of the general system of correlations of an aluminosilicate matrix. The number of positive correlations in mercury in <0.02 mm fractions decreases. From polymetal group, positive correlations with Cu and Pb are preserved, from the second group – with V and Mn, from third – with Al, Na, Be. Mercury has negative correlations with Ca and Sr entering into the carbonate group. This result can be interpreted as transition of the bulk of mercury from bonds of the mineral part of soil to its organic component and magnesium isolations. The negative effect of carbonate formation is displayed.

Factor analysis results for fractions give cause to assess mercury behaviour in joint sedimentation process, Mercury in >0.25 mm fraction does not have direct positive correlations with elements of the aluminosilicate part of precipitation and is connected with it through only positive correlations with Mn and Co, forming group Hg, Ca, Co, Mn. One can assume this is mainly the detrital carbonate fraction with manganese crusts. Like most elements, mercury has negative correlations with Na, which testifies the effect of the salinity of precipitation. Mercury in 0.25–0.16 mm fraction has only one positive correlation with Sb that is connected, in its turn, with the greater part of elements of the aluminosilicate component. The carbonate group is stood apart due to positive correlations of Ca with Mg, Sr and Li.

Most elements in 0.16–0.02 mm granulometric fraction are positively connected, forming the main composition of the clastic part of precipitation. Mercury and antimony like and in the previous case having positive correlations are not directly a part of it. Mercury joins to it as a result of positive correlations with Be and Ni. As a result, by connection with one another, a group of elements is formed: Hg, Cd, Zn, Be, Ni, Sb, Mn, Al, Cr. Most of them are connected with the detrital component, which the carbonate group (Ca, Sr, Mg) is stood apart from.

The granulometric fraction >0.02 mm is generally characterized by a significant decrease in overall positive correlations among all elements and an increase in the number of negative. There are particular positive correlations with many others in a series of elements with positive correlations (Fe, Ni, V, Al, Be), among them, correlations with Hg, Co, Ba are typical for Ni. Resulting from such correlations, group Hg, Cd, Ni, Sb, Mn, Co, Ba is formed, where mercury is directly connected with Sb, Cd, Ni, and Cd – with Hg, Mn and Sb. Another series of elements presented by Li, Mg, Sr, Na, to which Ca is adjacent due to positive correlations with Sr and Na, is completely separated from the first series by negative correlations. These elements have general migration ways in the lake system.

Thus, there are differences in correlations of mercury in soils and bottom deposits. There are no correlations in mercury in large fractions. There are positive correlations of mercury with Mn and Co in bottom sediments for >0.25 mm fraction, which makes it necessary to consider the part of manganese isolations in concentrating of Hg and Co. Positive correlations of mercury and Sb in 0.25–0.16 mm fraction and its indirect connection with the aluminosilicate component are of importance. Correlations with Sb in soils for mercury are not observed at all, and they are preserved in bottom sediments and in 0.16–0.02 and <0.02 mm fractions. Mercury in 0.16–0.02 and <0.02 mm fractions in bottom deposits has only indirect correlations with the clastic component, and directly enters into it in soils. Positive correlations of mercury in fractions of bottom sediments <0.02 mm are reduced due to the carbonate group and Na completely separated by negative correlations.

The results of the pair correlation method additionally used confirmed the main factor analysis results (Table 3).

Correlations of elements in the initial samples are determined by their interconnections in fractions depending on the mechanical composition. They provide a general picture of mercury distribution in the sedimentation process.

According to the factor analysis results of the initial soil samples, the major part of elements has positive correlation between them (Fig. 2). Here, Al, Fe, Co, Ni, Ba, K, Pb, Hg, Th comprise the main aluminosilicate frame, that is, mercury here is directly connected with the clastic component. In addition to these connections, mercury has positive correlations with Mn, Cu, Cd, Zn and, like many other elements, negative ones with the carbonate group (Ca, Mg (Li), Sr). Negative correlations with Sb are typical.

Most elements in bottom deposits preserve positive correlation (see Fig. 2). There are almost no negative correlations, except for Sr that has positive ones with Ca and Mg only. Mercury is basically not connected with the major composition of precipitation. Indirect correlations are performed only due to positive ones of mercury with Sb and Mn. Likewise, in soil isolation of the carbonate group (Ca, Mg, Sr) in bottom sediments is observed where elements have positive correlations with each other. Only Sr has negative correlations with the aluminosilicate component in bottom sediments. Obviously, this is due to greater solubility of Sr, in comparison with Ca and Mg that mainly pass into precipitates.

TABLE 3

Correlation coefficients for mercury in soils and bottom sediments

Elements	Soils					Bottom sediments				
	Initial	Granulometric fractions, mm				Initial	Granulometric fractions, mm			
		>0.25	0.25−0.16	0.16−0.02	<0.02		>0.25	0.25−0.16	0.16−0.02	<0.02
Li	−0.3	−0.2	0.0	0.1	−0.1	0.0	0.3	0.4	0.2	−0.2
Be	0.3	−0.1	0.0	0.7	0.5	0.1	0.2	−0.0	0.4	0.5
Na	−0.2	0.1	−0.0	−0.0	0.5	0.2	−0.7	−0.3	−0.0	−0.5
Mg	−0.3	−0.1	−0.0	−0.2	−0.3	0.1	0.3	0.3	−0.0	−0.2
Al	0.3	−0.1	0.2	0.6	0.5	0.1	0.4	0.6	0.4	0.2
Sb	−0.3	0.1	0.0	0.3	0.3	0.4	0.1	0.7	0.7	0.6
K	0.4	0.0	0.1	0.6	0.4	0.1	0.2	0.2	0.3	−0.1
Ca	−0.4	−0.0	−0.1	−0.5	−0.6	0.1	0.8	0.3	−0.1	−0.2
V	0.2	−0.2	0.2	0.6	0.6	0.0	0.4	0.4	0.3	0.2
Cr	0.2	−0.4	−0.6	0.2	0.1	0.0	0.4	0.5	0.4	−0.1
Mn	0.5	−0.1	0.3	0.6	0.5	0.4	0.6	0.1	0.5	0.4
Fe	0.3	−0.1	0.2	0.6	−0.1	0.0	0.4	0.4	0.3	0.0
Co	0.4	−0.1	0.1	0.5	0.4	0.0	0.7	0.5	0.4	0.3
Ni	0.5	−0.2	0.1	0.7	0.3	0.1	0.5	0.6	0.5	0.6
Cu	0.4	−0.1	0.2	0.7	0.7	0.1	0.5	0.5	0.3	−0.2
Zn	0.4	−0.2	0.3	0.7	0.4	0.0	0.4	0.5	0.4	0.5
Sr	−0.4	−0.1	−0.0	−0.4	−0.5	0.1	0.3	0.1	−0.1	−0.2
Cd	0.5	−0.3	0.4	0.8	0.3	0.1	0.5	0.5	0.9	0.8
Ba	0.4	−0.1	−0.0	0.4	0.2	0.3	0.3	0.5	0.2	0.2
Hg	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Pb	0.4	0.0	0.1	0.5	0.6	0.2	0.5	0.5	0.2	0.5
Th	0.5					0.0				
U	0.1					0.1				
n	59	21				63	17			

Note. For design. see Table 1.

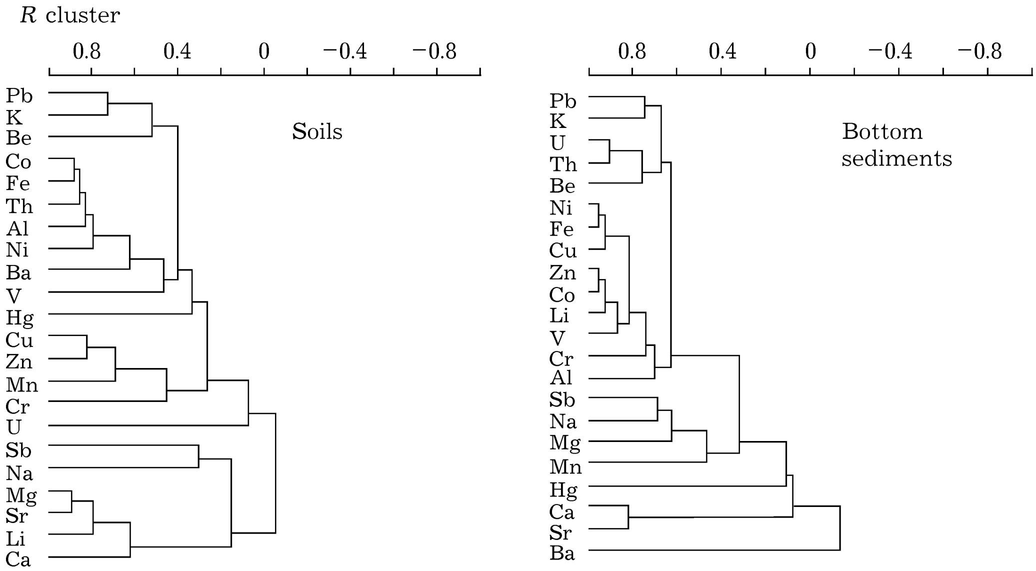

Fig. 2. Dendrograms of R-type cluster analysis of contents of macro- and microelements in soil sections and columns of bottom sediments.

Thus, differences in correlations of mercury and other elements in granulometric fractions led to significant differences of these correlations in precipitation from soils (Fig. 3). As shown by comparison the results on fractions and the initial samples, 0.16–0.02 mm fraction in soils and 0.16–0.02 and <0.02 mm fractions in bottom sediments exert the maximum effect for total mercury distribution.

It is noteworthy that contents of organic matter in soils and bottom deposits were not considered in correlation analysis. Strictly speaking, the obtained results relate to the mineral part only, and conclusions on the role of organics are indirect. On average, its content in bottom sediments of the lake are about 6 %, according to the results of losses determination. Earlier, according t the factor analysis results of over 100 lakes and soils of their catchment areas of Siberia, positive correlations of mercury and cadmium with losses during calcination were found [11].

The uneven distribution of mercury in bottom sediments at expense of its presence from the technogenic source reduces its correlation level with the content of other elements. Data in analyses with low mercury contents (at the detection limits) are the second complicating factor, which is especially typical for soils. This is found according to the pair correlation data (see Table 2) and clear in appropriate graphs. A trend to the direct correlation of mercury with

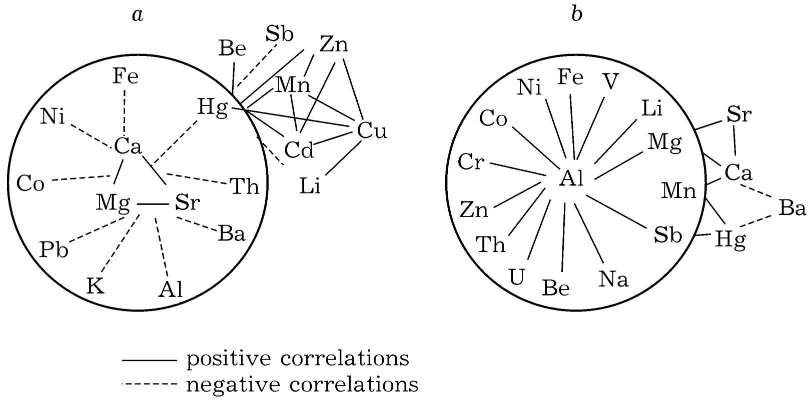

Fig. 3. Scheme of mercury correlations in soils (a) and bottom sediments (b).

other elements is most clearly expressed in a range of its contents of 0.03–0.100 mg/kg. The absence of correlations in the region of increased contents or its second branch testifies a change in deportment form, including the entrance of mercury from technogenic sources. Thus, the study of correlations of mercury detected a series of important peculiarities in the sedimentation process.

CONCLUSION

1. Comparison of average mercury contents in soils of the catchment area and bottom sediments of Bol'shoye Yarovoye Lake demonstrates a significant increase of the mercury content in precipitation relatively to all types of soils. Values of the Hg/Al ratio that allows assessing the contribution of the aluminosilicate component in the total mercury content confirm this.

2. Factor analysis and the pair correlation method identified differences in mercury correlations between soils and bottom deposits in fractions and the initial samples. Mercury in soils is connected with the clastic part: with aluminosilicates and a group of polymetals (Cd, Cu, Zn); negative correlations with a group of Li, Ca, Mg, Sr and Sb. Mercury in bottom sediments has positive correlations with Sb and Mn only and relates to the main matrix indirectly. This testifies a change in mercury deportment during sludge formation, which is mainly caused by the entrance of mercury from a source not connected with the terrigenous material of soils.

3. The study results of correlations in bottom sediments confirm the availability of local technogenic mercury pollution that is accompanied by antimony. Its effect in soils is insignificant. Correlation analysis methods can also be used when studying other lake systems.

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