

Mercury in Soils and Plants in the Vicinity of Chlor-Alkali Product Manufacturers (Irkutsk Region)

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Abstract – The research presents the results of integrated studies focusing on accumulation and migration of Hg in soils and plants in the vicinity of former chlor-alkali product manufacturers in Irkutsk region. The fractioning showed the prevalence of Hg compounds with organic and mineral components in soils and low concentration of mercury in soluble and movable forms. The low mobility of Hg in soils means its concentration in plants doesn't exceed permissible norms. However, in the area of chlor-alkali product manufacturers, the amount of Hg in plants is above background. There is a clear trend of higher concentrations of Hg in aboveground parts of plants both wild and agricultural. This indicates additional absorption of atmospheric Hg, especially against the background of a relatively low level of soil pollution and Hg mobility in it.

Keywords – soil; mercury; fractioning; plants; bioaccumulation; chlor-alkali manufacturing.

I. INTRODUCTION

Chlor-alkali product manufacturers that use metallic Hg in technological processes are one of the main man-made sources of Hg in the environment [1–2]. It is known that Hg emitted into the atmosphere by these manufacturers is usually in the gaseous form of Hg(0), Hg(II) and can travel on significant distances [3–4]. One of the main sorption barriers for Hg is soil where mercury is fixed with organic and mineral substances to form both stable, low-mobility compounds and compounds, loosely connected with soil matrix.

The increase in Hg concentration in soils can lead to its accumulation in plants. However, mercury is not a biogenous element and negatively affects all living organisms [5]. Some mineral compounds of Hg are highly toxic for plants, as this chemical element causes oxidative stress in cells [6]. It is well-known that Hg can form compounds with different organic substances, many of which, especially low-molecular Hg-organic compounds are highly toxic and well-absorbed by living organisms, including plants [7–8]. In response to man-

made pollution, it is necessary to carry out researches that show the peculiar features of Hg migration in the soil–plant system and risks of its inclusion in food chains. The purpose of this work is the assessment of mercury pollution and its bioaccessibility in the soil–plant system in the area of former chlor-alkali product manufacturers.

II. METHODS AND MATERIALS

The research of Hg bioaccumulation was carried out in the area of impact of industrial manufacturers, in particular, Sayanskhimplast (SKP) and Usoliekhimprom (UKP) where metallic Hg was used in manufacturing processes until 2006 and 1998 respectively. The soils around these factories are classified predominantly as grey forest or sod carbonate soils. The contaminated samples 1–4 (fig. 1), collected along the creek are represented by meadow-bog and alluvial-meadow soils, polluted by SKP effluents, containing particles of a man-made slug. The research also studied agriculturally modified soils from private farms in the village of Ukhtuy, which is near the city of Zima and agriculturally modified soils of the city of Usolie-Sibirskoye. Wild plants are represented by herbs from the genera of *Carex*, *Equisetum*, *Geranium*, *Vicia*, *Sanguisorba*, *Achillea*, *Elytrigia*, a *Salicornia europaea* species and two species of birch – *Betula pendula*, *Betula pubescens*. Agricultural plants, including potato, carrot, beetroot, radish, cucumber, and eggplant were taken from private farms. Grain plants, such as oat and rye were also studied in the vicinity of SKP.

All samples were air-dried, while soils were screened through 2 mesh screens. The total concentration of Hg in samples was measured by atomic absorption analysis using PA-915+ spectrometer. A separate experiment was carried out to determine the fractional composition of Hg compounds in some soils in the vicinity of SKP (fig. 1): 1 – meadow-bog soil located 700 meters from SKP; 2 – alluvial-meadow soil with man-made wash, 1.8 km; 3–4 – alluvial-meadow soil, 3.2 km (birch outlier

(3), the bank of the creek (4)); 4 – grey forest automorphic soil, 1.6 km; 6–7 – agriculturally modified soils from the village of Ukhtuy, 7 km. The results of the analysis of Hg occurrence forms in the soils near Usoliekhimprom were presented earlier [9]. The fractioning was carried out using a stage-by-stage extractions method [10] that resulted in obtaining water-soluble, acid-soluble, organic, tightly bound and sulphide fractions, analyzed by atomic absorption method. The detection threshold of Hg in soils and plants is 0.005 mg/kg. The threshold in extracts from soils is 0.0005 mg/kg. The validation of analysis results was carried out on standard samples – birch leaf LB-1, GSO 8923-2007, Canadian waterweed EK-1, GSO 8921-2007, grass mixture Tr-1, GSO 8922-2007, for soils analysis control – SSK-1 (carbonated grey soil), SDPS-2 (man-made soil). The chemical analysis of soils and plants was performed on the equipment of the Common use centre for isotope geochemical research in Vinogradov Institute of Geochemistry SB RAS

III. RESULTS AND DISCUSSION

Total concentrations of Hg in soils are shown in table 1. The amount of Hg doesn't exceed standards (2.1 mg/kg), but its average and maximum values in all soils are higher than regional background (0.02 mg/kg [11]). The percentage of exceedance in relation to the regional background is 92–100%.

TABLE I. THE CONCENTRATION OF Hg IN THE TOPSOIL, MG/KG

Sampling point	Level	Number of samples	Mean	Min	Max
<i>Forest soils and new soils</i>					
SKP vicinity	A _{0s} , Ad	14	0.303	0.016	1.440
UKP vicinity	A _{0s} , Ad	13	0.160	0.006	0.466
<i>Agricultural soils</i>					
the city of Zima (village of Ukhtuy)	A _{max}	6	0.051	0.029	0.098
the city of Usolie-Sibirskoye	A _{max}	10	0.046	0.013	0.081

The highest concentration of Hg was found in the topsoils around SKP which is due to man-made pollution. This is supported by the analysis of the impact of run-offs that drain the territory of SKP industrial zone and emissions near the central heating and power plant that influence on the increase of Hg in soils [12]. The excessive concentration of Hg in respect to the regional background is also found in the topsoils near UKP. The obtained data indicate that Hg is an indicating element of chlor-alkali manufacturing in particular that used metallic Hg in the past.

The study of fractional composition of Hg compounds in soils near SKP (fig. 1) showed the presence of Hg primarily in organic and tightly bound fractions and to a lesser degree in sulphide fraction. These results show low mobility of Hg in soils near SKP because mercury, constituting the mineral lattice and bound with sulphides is hard to release in relatively stable environmental conditions. The destruction of stable Hg compounds happens when some physicochemical parameters of soils change, for example after the increase in humidity or a change in pH from neutral or alkaline to acidic. In this

respect, Hg compounds are a potential source of bioaccessible mercury in soils. High concentrations of Hg in the organic fraction have importance as these are Hg-organic compounds that define mobility or immobility of Hg in soils. Depending on the nature of formed organic compounds, the mobility of Hg in soils can both increase and decrease [7, 14].

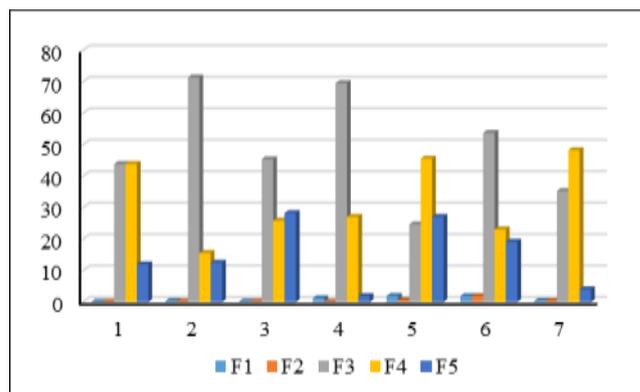


Fig. 1. The distribution of different Hg fractions in the topsoils near SKP (the percentage from the sum of fractions). F1-F5 – fractions: water-soluble fraction F1, acid-soluble fraction F2, organic fraction F3, tightly bound fraction F4, sulphide fraction F5.

The low mobility of Hg in studied soils is confirmed by its low concentrations in movable and bioaccessible fractions, i.e. acid soluble and water soluble, that in combination constitute less than 1% for most samples. One sample of agriculturally modified soils, taken 7 km away from SKP, showed a sequence higher total percentage concentration of Hg in acid-soluble and water-soluble fractions than other soils, in particular, 2.6–3.9 %. However, total concentrations of Hg in this soil are lower than in the rest. The increase of the movable Hg amount in agriculturally modified soils can relate to features of their use and cultivation, using different fertilizers, which increase the mobility of Hg.

Highly humid man-made soil from plot 2 and the soil from the bank of the creek (plot 4) stand out from the studied samples as they have the highest concentrations of Hg in organic fraction (fig. 1). The soil of plot 2 was collected in a relatively boggy flood of the creek with low flowage; the concentration of total carbon C_{org} in it is 5.2%, which is higher than in other soils. As Hg is highly capable to bind with organic components, its accumulation in the organic fraction is natural. Alluvial-meadow soil from plot 4 was sampled at the bank of the creek with high flowage. The concentration of Hg in water-soluble fraction here is a sequence higher than in other soils, but also a sequence lower in sulphide fraction. This can be due to the washability of soil that results in the dissolution of some mineral Hg compounds and an increase in its mobility. The concentration of C_{org} here is lower and account for 3.0%, but the main part of Hg is still bound with organic substances of this soil.

The results of Hg fractioning in the soils near Sayanskhimplast (SKP) match the results for the soils near Usoliekhimprom, presented earlier [9]. The feature that distinguishes the distribution of Hg in the soils near SKP is that the amount of sulphide fraction was higher in comparison with

the soils of UKP, where the amount of sulphide Hg was insignificant. This increase in sulphide Hg near SKP can be explained by man-made pollution by slags that are secondary minerals in fact. The study of Hg thermal forms in the soils near SKP [12] showed that the amount of mineral forms of Hg constitutes 7–35%. Also, physically sorbed Hg prevails that is due to the sorption of Hg by the organic substance in soils. The research results [12] confirm the data of Hg compound fractioning.

In general, the transformation of Hg in soils are defined by the original anthropogenic form of Hg. The atmospheric Hg emitted by chlor-alkali manufacturers is represented by Hg(0) и Hg(II) [3–4]. The gaseous Hg is sorbed in soils by different components and, as research shows, by humic substances primarily. Mercury that enters the soil as a component of minerals, especially sulphides, is hard to destroy. That is why it stays in corresponding forms, which is confirmed by the analysis of soils near SKP.

The research showed that *wild plants* near SKP and UKP (table. 2) accumulate Hg in amounts exceeding background concentrations, i.e. 0.017 mg/kg for tree leaves and 0.012–0.088 mg/kg for herbs [15].

TABLE II. THE CONCENTRATION OF Hg IN WILD PLANTS, MG/KG

Sampling point	Birch leaves	Birch branches	Herbs
<i>SKP mean</i>	0.079 (6) ^a	0.075 (6)	0.065 (38)
<i>min-max</i>	0.012-0.185	0.011-0.194	0.002-0.267
<i>UKP mean</i>	0.027 (24)	0.013 (11)	0.066 (15)
<i>min-max</i>	0.014-0.066	0.005-0.030	0.018-0.161

^a The number of samples is given in brackets.

The plants near SKP have an elevated concentration of Hg in respect to the plants near UKP. Apparently, such bioaccumulation of Hg is the result of its higher amount in soils near SKP in comparison with other plots (table 1). There are significant positive relationships ($p < 0.05$) between total concentrations of Hg in soils and plants near SKP: soils–birch leaves – 0.86, soil–herbs – 0.35; in the vicinity of UKP the relationship soil–birch leaves is 0.50. The relationships between different fractions of Hg and its concentration in plants were not found. Apparently, low concentration of Hg in water soluble and acid soluble fractions of soils weakly determine the bioaccumulation of Hg by wild plants. It is possible to suppose that there are other bioaccessible forms of Hg that should be studied further. It has been suggested that plants absorb Hg from the atmosphere primarily [16–17].

Hg is unevenly distributed in different parts of plants (table 3). Thin and especially ligneous bark of birch contained the maximum amount of Hg, while seeds and branches contained the minimum. Plant leaves accumulate more Hg than branches and the difference sometimes reaches one sequence.

Such distribution of Hg is apparently due to the peculiarities of different parts of plants and can be a mechanism for self-regulation of toxic elements accumulation. Tree bark is a natural biological barrier where the maximum accumulation of Hg occurs. This is due to both mechanical joining and binding of its insoluble organic and mineral compounds that are present in plant tissue. Trees also shed leaves that accumulate Hg

during leaf fall. When accumulating Hg in vegetative organs, a plant keeps reproductive organs from the negative effect of high doses of this metal. Apparently, Hg is accumulated in leaves not only from soils but from the atmosphere [16–17]. This might explain a higher concentration of Hg in leaves in comparison with branches. The latter primarily perform the transport function for Hg and don't accumulate it in high amounts. In herbs, Hg is also accumulated in herbs primarily. The concentration of this metal in the roots of herbs was lower than in leaves.

TABLE III. THE CONCENTRATION OF Hg IN DIFFERENT PARTS OF PLANTS, MG/KG

Sample		SKP	UKP
<i>Birch</i>	leaves	0.185	0.034
	branches	0.168	0.025
	seeds	–	0.024
	thin bark	0.668	0.081
	old bark	0.537	0.202
<i>Peas</i>	leaves	0.186	0.124
	caulis	0.056	0.012
	Pods	0.015	0.010
	seeds	0.005	0.014
	roots	–	0.057
<i>Milfoil</i>	leaves	0.044	0.062
	caulis	–	0.010
	flowers	0.041	0.028
	roots	0.021	0.029
<i>Soil</i>		1.440	0.410

The research also studied the *bioaccumulation of Hg in crops* in the vicinity of SKP (fig. 2). The permissible level of Hg in crops is 0.03 mg/kg in the dry matter [19]. The amount of Hg in crops near SKP is lower than this level. Such bioaccumulation of Hg relates to a low level of soil contamination, where these plants were growing – the concentration of Hg in the plough layer (0–25 cm) is 0.029 mg/kg. This is the lowest value for the soil near SKP. It should be noted that the accumulation of Hg primarily happens in darnels and caulis of plants, while in seeds this amount is one sequence lower, which is a classic example of plants protecting their organs from excessive accumulate of a toxic element.

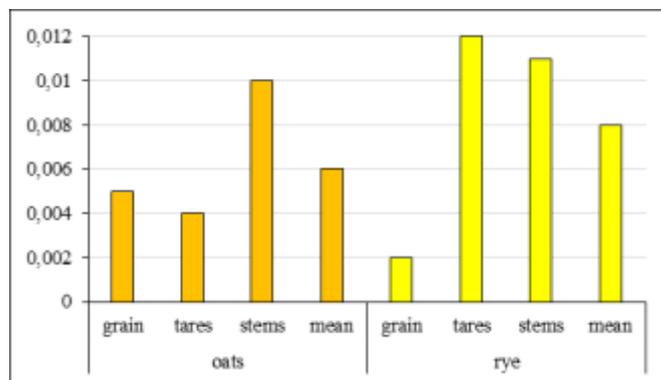


Fig. 2. The concentration of Hg in the crops near SKP, mg/kg

The concentration of Hg in vegetables, grown in the gardens of the city of Zima are represented in table 4. The data about vegetables in the city of Usolie-Sibirskoye is given as a

reference (table 5). According to the data [20], the permissible concentrations of Hg in vegetables are no more than 0.02 mg/kg. The concentration of Hg in the studied vegetables are lower than this norm. In general, the amounts of Hg in the vegetables of the cities of Zima and Usole-Sibirskoye match.

Mercury is not evenly distributed in different parts of vegetables. The amount of Hg in potatoes from plot 1, where the concentration of mercury in the soil is higher, exceeds the amount from plot 2 (table 4). However, plants from plot 1 concentrate Hg mainly in the bark, which is a natural barrier for a toxic agent in this case. The maximum accumulation of Hg on plot 2 is in leaves of vegetables, which can relate to additional Hg consumed from the atmosphere. The differences between Hg concentrations in bark and vegetables without bark are insignificant or not present.

TABLE IV. THE CONCENTRATIONS OF HG IN THE VEGETABLES OF THE CITY OF ZIMA (PLOTS 1 AND 2), MG/KG

Plant:	Hg	Plant:	Hg
(1) Potato without bark	0.006	(2) Potato without bark	0.004
(1) Potato, bark	0.016	(2) Potato, bark	0.004
(1) Radish without bark	0.005	(2) Potato, leaves	0.022
(1) Radish, bark	0.014	(2) Carrot without bark	0.006
(1) Radish, leaves	0.006	(2) Carrot, bark	0.004
(1) Cucumber without bark	0.010	(2) Carrot, leaves	0.008
(1) Cucumber, bark	0.019	(2) Egg-plant without bark	0.002
(1) Soil	0.098	(2) Egg-plant with bark	0.002
(2) Beetroot without bark	0.002	(2) Cabbage leaves	0.006
(2) Beetroot, bark	0.003	(2) Cabbage, pith	0.007
(2) Beetroot, leaves	0.025	(2) Soil	0.045

The trend of Hg amount increasing in vegetable leaves was also present in the city of Usole-Sibirskoye (table. 5). The concentration of Hg in the vegetables of indicated cities matches the background territories, represented by the villages on the shores of Lake Baikal, where the amount of Hg is 0.002–0.005 mg/kg and the background concentrations mentioned in [20] – 0.003 mg/kg.

TABLE V. THE CONCENTRATIONS OF HG IN THE VEGETABLES OF THE CITY OF USOLIE-SIBIRSKOYE (1) AND 30 KM AWAY FROM THE CITY (2), MG/KG

Plant:	Mean	Min	Max
(1) Potato, tubers (n=7)	0.003	0.002	0.007
(2) Potato, tubers (n=7)	0.004	0.002	0.006
(1) Carrot, leaves (n=3)	0.023	0.012	0.030
(1) Carrot, root plants (n=6)	0.005	0.003	0.007
(2) Carrot, root plants (n=2)	0.005	0.004	0.006

IV. CONCLUSION

The concentration of Hg in the vicinity of chlor-alkali product manufacturers in Irkutsk region doesn't exceed maximum permissible concentration but is higher than average in the region in most of the samples, sometimes substantially. The processes of Hg immobilization are prevailing in studied soils, which is confirmed by the high concentration of mercury in organic and tightly bound mineral fractions and low concentration in water soluble and acid soluble fractions, which represent the group of the most bioaccessible Hg compounds. However, both organic and mineral compounds are a potential

source of Hg in soil. The increase in humidity, a change in soil pH, microorganism activities or some other factors lead to the destruction of compounds and the release of Hg an increase of its mobility and bioaccessibility. Wild plants near chlor-alkali product manufacturers have elevated concentrations of Hg in respect to the background. The concentration in agricultural plants doesn't exceed the norm. However, the increase in the amount of mobile Hg in agriculturally modified soils can lead to an increase in mercury concentration in vegetables, predominantly bark, which performs a protective function. The increase in the concentration of Hg in aboveground parts of plants, both wild and agricultural, is an important trend. It indicates the consumption of atmospheric Hg, especially with respect to the low level of soil contamination (not exceeding norms) and Hg mobility.

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