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 men-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 in soil is 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, Sayanskikhimplast (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 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

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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 alkaliescent 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].

The lowest 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) \( \equiv \) 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          |
|----------------|--------------|----------------|----------------|
| **SKP mean**   | 0.079 (6)    | 0.075 (6)      | 0.065 (38)     |
| **min-max**     | 0.012-0.185  | 0.011-0.194    | 0.002-0.267    |
| **UKP mean**    | 0.027 (24)   | 0.013 (11)     | 0.066 (15)     |
| **min-max**     | 0.014-0.066  | 0.005-0.030    | 0.018-0.161    |

* The number of samples is given in brackets.

The plants near SKP have an elevated concentration of Hg in respect to the plants near SKP. 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 (\( \rho < 0.05 \)) 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   |
|--------|-------|-------|
| **Birch** |       |       |
| leaves  | 0.185 | 0.054 |
| branches| 0.168 | 0.025 |
| seeds   | 0.024 |       |
| thin bark| 0.668 | 0.081 |
| old bark| 0.537 | 0.202 |
| **Peas**  |       |       |
| leaves   | 0.186 | 0.124 |
| caulis   | 0.056 | 0.012 |
| pods     | 0.015 | 0.010 |
| seeds    | 0.005 | 0.014 |
| roots    | –     | 0.057 |
| **Milfoil** |     |       |
| leaves   | 0.044 | 0.062 |
| caulis   | 0.010 |       |
| flowers  | 0.041 | 0.028 |
| roots    | 0.021 | 0.029 |
| **Soil**  | 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 Usoolie-Sibirskoye match.

Mercure 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](attachment:table-iv.png)

The trend of Hg amount increasing in vegetable leaves was also present in the city of Usoolie-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 Usoolie-Sibirskoye (1) and 30 km away from the city (2), mg/kg](attachment:table-v.png)

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.

**Acknowledgment**

The research is carried out as part of the government task in IX.127.1 (0350-2016-0027) Project, financed by the №17-45-38808 r_a grant.

**References**

[1] A.G. Bravo, C. Cosio, D. Amouroux, et al., “ Extremely elevated methyl mercury levels in water, sediment and organisms in a Romanian reservoir affected by release of mercury from a chlor-alkali plant”, Water Res., vol. 49, pp. 391–405, 2014.

[2] S. Lakshman, T. Murugesan, “The chlor-alkali process: Work in Progress”, Clean Technol. Environ., vol. 16 (2), pp. 225–234, 2014.

[3] M. Lodenius, “Dry and wet deposition of mercury near a chlor-alkali plant”, Sci. Total Environ., vol. 213, pp. 53–56, 1998.

[4] H. Biester, G. Müller, H.F. Schöler, “Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants”, Sci. Total Environ., vol. 284, pp. 191–203, 2002.

[5] W. Clarkson, L. Magos, “The toxicology of mercury and its chemical compounds”, Toxicology, vol. 36 (8), pp. 609–662, 2006.

[6] S. G. Skugoreva, S. Yu. Ogorodnikova, T. K. Golovko et al., Fito-tekhnichnost fosfororganicheskikh soedinen i ruty, edited by T. K. Golovko, Ekaterinburg: UB RAS, 2008, 155 p.

[7] A. Kabata-Pendias, Trace elements in soils and plants, 4th ed. Boca Raton: FL, USA: CRC Press; Taylor & Francis Group, 2011, 505 p.

[8] G.M. Varshal, N.S. Buachidze, T.K. Velyukhanova, et al., “The role of organic matter in mercury cycle”, In: Global and regional mercury cycles: sources, fluxes and mass balances, 2. Environment, vol. 21. Dordrecht; Boston; London: Kluwer Academic Publishers. 2006, pp. 403–414.

[9] O.N. Gordeeva, G.A. Belogolova, M.V. Pastukhov, “Mercury speciation and mobility in soils of industrial areas in the Baikal region, Southern Siberia, Russia”, Environ. Earth Sci., vol. 76 (16), p. 558, 2017.

[10] N.S. Bloom, E. Preus, J. Katon, et al., “Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils”, Anal. Chim. Acta, vol. 479, pp. 233–248, 2003.

[11] V.I. Grebenshikova, E.E. Lustenberg, N.A. Kitae, et al., Environmental geochemistry of the Baikal region (Baikal geological polygon). Novosibirsk, Academic Publ. H. «Geo», 2008, 234 p.

[12] E.V. Butakov, M.S. Khodorova, V.I. Grebenshikova, et al., “Mercury in soils of the agro-industrial zone of Zima city (Irkutsk oblast)”, Eurasian Soil Science, vol. 50 (11), pp. 1334–1361, 2017.

[13] A. Manceau, M. Merkulova, M. Murdzek, et al., “Chemical Forms of Mercury in Pyrite: Implications for Predicting Mercury Releases in Acid Mine Drainage Settings”, Environ. Sci. Technol., vol. 52 (18), pp. 10268–10296, 2018.
[14] I. Cattani, H. Zhang, G. Beone, “The role of natural purified humic acids in modifying mercury accessibility in water and soil”, J. Environ. Qual., vol. 38 (2), pp. 493–501, 2009.

[15] V.V. Ivanov, Ecologicheskaya geohimiya elementov, vol. 5. Moscow: Nedra, 1997, 576 p.

[16] J.A. Ericksen, M.S. Gustin, D.E. Schorran, et al., “Accumulation of atmospheric mercury in forest foliage”, Atmos. Environ., vol. 37, pp. 1613–1622, 2003.

[17] F.X. Han, Y. Su, D.L. Monts, et al., “Binding, distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA”, Sci. Total Environ., vol. 368, pp. 753–768, 2006.

[18] P.V. Elpatievskiy, Geohimiya migratsionikh potokov v prirodnikh i prirodno-tehnogennikh sistemakh. Moscow: Nauka, 1993, 253 p.

[19] V.M. Poznyakovsky, Gigienicheskie osnovi pitaniya i ekspertizi prodovolstennikh tovarov. Novosibirsk: Novosibirsk State University publishing house, 1996, 432 p.

[20] L.I. Kuzubova, O.V. Shuvaeva, G.N. Anoshin Metilrtut v okruzhayushey srede (rasprostranenie, obrazovaniye v prirode, metodi opredeleniya). Novosibirsk: GPNTB SB RAS, 2000, 82 p.