

Forms of mercury in soils and its accumulation by herbs in the zone of influence of the sludge storage of a chlor-alkali plant (Southern Baikal region)

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Abstract. Total concentrations of Hg in soils and the narrow-leaved fireweed *Chamaenerion angustifolium* L., as well as the forms of Hg presence in soils by the method of sequential extractions were examined to study the processes of mobilization-immobilization of Hg in the soils of the territory of the chlor-alkali plant sludge storage and the features of the bioaccumulation of this element in herbs. The determination of Hg in all samples was carried out by the atomic absorption method. High concentrations of Hg in soils near the sludge storage have been established. In almost all soil samples the amount of Hg is above the regional background. Fractionation showed that Hg in soils is found mainly in organic, strongly bound and sulfide fractions. Due to the low concentrations of Hg mobile fractions, water- and acid-soluble, a relatively low accumulation of Hg in *Chamaenerion angustifolium* L. was found, which was also facilitated by the barrier properties of the herb roots. Nevertheless, the accumulation of predominantly organic and strongly bound forms of Hg in soils indicates a high potential for Hg mobilization from these fractions due to changes in various physicochemical and biogeochemical properties of soils.

1 Introduction

Hg migration processes in the environment are determined by complex biogeochemical factors. Studies of the ability of Hg to migrate from one environment to another have shown the difficulty of complete exclusion of Hg from migration cycles, in connection with which it accumulates in human biosubstrates [1–6]. Numerous domestic and foreign studies show that in case of technogenic environmental pollution, it is often the soil that is one of the main deposits of Hg due to the sorption properties of soil components [2, 4, 7, 12, 17, 21, 34]. Poorly soluble Hg compounds can persist in soils for a long time and serve as a potential reserve of bioavailable Hg [7–9]. As a rule, elevated concentrations of Hg in soils lead to an increase in its bioaccumulation by herbs. At the same time, mercury has an extremely negative effect on herbs [4, 10–11]. The level of Hg accumulation by herbs during root intake

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depends not so much on its total concentrations in soils, but on the forms of occurrence, namely, bioavailable compounds [10, 12–13]. In addition, the root system of herbs, together with microorganisms living in the root zone, form acidic exudates capable of dissolving bound soil Hg compounds and absorbing them from solutions [14–16]. The process of Hg methylation in soils under the influence of microorganisms is of great importance, which contributes to an increase in the bioaccumulation of this element [17–22]. A significant part of Hg can be accumulated by herbs from atmospheric air during foliar absorption [10, 23–27]. Thus, the pathways of Hg accumulation by herbs are diverse and require careful study, especially under conditions of technogenic pollution. The purpose of this study was to research the forms of Hg occurrence in soils and its accumulation in herbs near and in the vicinity of the highly polluted territory of the sludge storage of chlor-alkali plant (CAP), which in the past specialized in organochlorine production and used Hg as a catalyst in production processes. The company has now completely ceased production and is in the process of being liquidated.

2 Materials and methods

Sampling of soils and herbs was carried out at different distances from the CAP (Figure 1). Technogenic transformed alluvial-meadow and soddy forest soils, as well as gray forest and soddy forest soils at a depth of up to 20 cm from the sludge storage, were selected from a root-inhabited depth of up to 30 cm near the sludge storage. Soils taken near the sludge storage were often contaminated with material, iridescent over the dam, due to which many soil samples had a gray-blue color, there were layers of reddish color. Background plot 29 was located 6.3 km from the sludge storage, where alluvial-meadow soil was selected. Among the herbs, one dominant species was chosen, which grows everywhere in the study area – narrow-leaved fireweed *Chamaenerion angustifolium* L., separately aboveground part and roots. All soil and herb samples were dried to an air-dry state, the soils were sifted through a 2 mesh sieve. Total concentrations of Hg in herbs were determined after decomposition of 1 g of a herb sample with concentrated nitric acid. The total concentrations of Hg in soils were measured after treatment of a sample weighing 1 g with aqua regia.

In some soil samples, the forms of Hg occurrence were studied, which are based on the method of sequential extractions by N. S. Bloom et al. (2003). Five fractions were obtained: F1 – water-soluble – the soil sample was treated with distilled water, F2 – acid-soluble – the residue from the previous fraction was treated with a mixture of 0.1 M CH_3COOH solution and 0.01 M HCl solution, F3 – organic – the residue from fraction 2 was treated with 1 M solution NaOH, F4 – strongly bound in the lattice of minerals – the residue from fraction 3 was treated with 12 M HNO_3 solution, F5 – sulfide – the residue from fraction 4 was treated with aqua regia. The precipitate from each fraction was dried to air dry before being treated with a reagent to obtain the next fraction. Total concentrations of Hg in soils and herbs, as well as in extracts from soils, were measured by the atomic absorption method on a RA-915+ spectrometer with an attachment RP-91S (Lumex, Russia). The lower detection limit for total Hg in soils and herbs is 0.005 mg/kg, and in soil extracts it is 0.0005 mg/kg. As a chemical analysis control, standard samples were used: SChT-3 (typical chernozem), SDPS-2 (sandy loamy soddy-podzolic soil), obtaining yields of 103.1% and 101.5% of the concentration certified, respectively. The precision expressed as the relative standard deviation (RSD) was 3.46% and 4.02%, respectively.

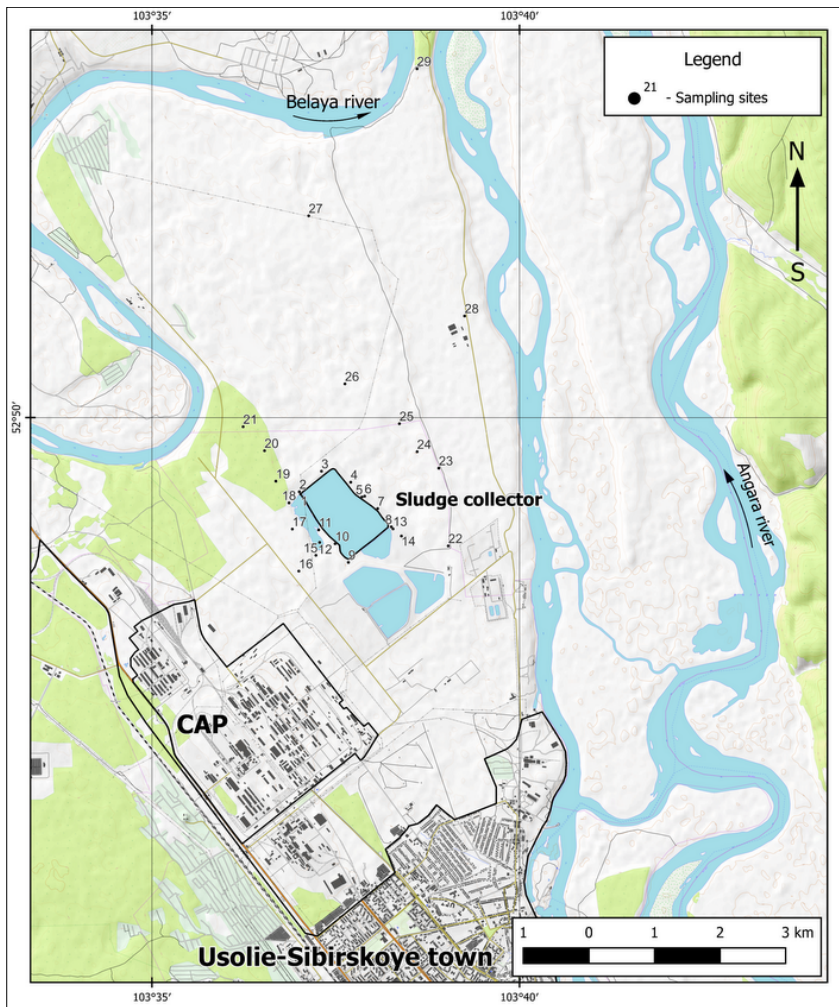


Fig. 1. Map-scheme of the work area. 1-29 – soil and herb sampling points.

Before determining Hg, soil pH was measured in an aqueous filtered solution at a soil-distilled water ratio of 1 to 5 on an Expert-rn pH meter (Russia). The C_{org} concentration was determined by wet combustion according to the Tyurin method [29]. All analytical work was performed on the equipment of the Center for the Collective Use of Isotope Geochemical Research of the Institute of Geochemistry named after A.P. Vinogradov SB RAS. Statistical data were processed in Statistica 6.0, Excel 2013 programs. A map-scheme of soil and herb sampling was created in QGIS 3.28.5 program.

3 Results and discussion

3.1 Hg and C_{org} concentrations in soils, pH value

The data are presented in Table 1. Soils near the sludge storage are characterized by the predominance of slightly alkaline and alkaline pH_{water} , which is apparently associated with the production of soda at this enterprise and the discharge of alkaline waste into the sludge storage.

Table 1. Concentrations of Hg, C_{org} and pH_{water} in the soils of the vicinity of CAP.

Soils (number of samples)	Hg, mg/kg	pH _{water}	C _{org} , %
Near sludge storage (19)	37.6±142	7.76±0.98	1.85±1.59
	0.028-621	5.44-9.12	0.24-6.46
Away from sludge storage (17)	0.13±0.18	6.64±0.46	2.2±1.21
	0.027-0.81	5.91-7.34	0.42-4.3

Significant alkalization of nearby soils occurred due to the overflow of technogenic alkaline material through the sludge storage dam. In general, 68% of the studied soils near sludge storage have an alkaline reaction with pH > 8.0. With distance from the sludge storage, the value of pH_{water} approaches neutral, which is typical for uncontaminated soils in this area. C_{org} concentrations in soils vary widely, but their average values in soils near and far from the sludge storage are comparable. There is a tendency for C_{org} to increase in soils far from sludge storage. Probably, this was facilitated by forest fires that occurred in the vicinity of the sludge storage in recent years.

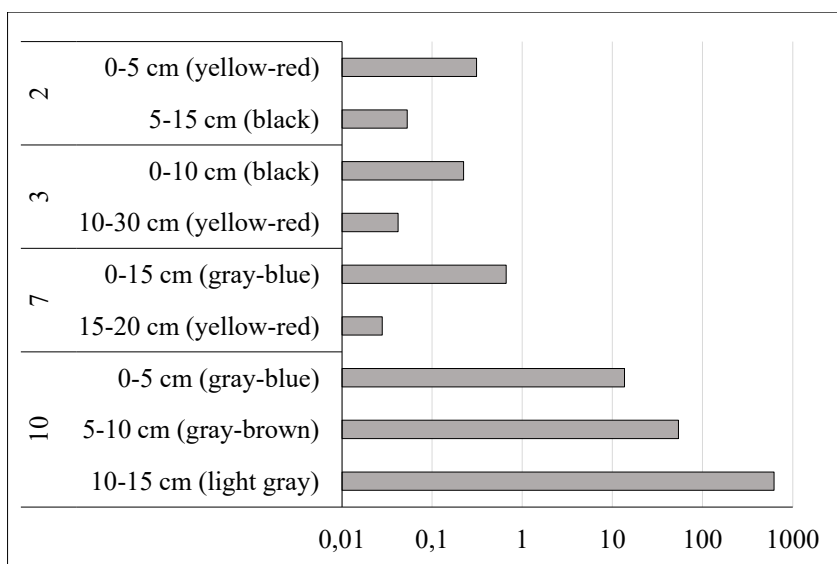


Fig. 2. Distribution of Hg over soil layers near sludge storage, mg/kg. 2-10 – soil sampling points.

The data in Table 1 indicate a large scatter of Hg concentrations in soils near sludge storage, which is typical for technogenically polluted areas. The maximum concentrations of Hg in some soils reach hurricane values, 2 orders of magnitude higher than the MPC (2.1 mg/kg) and 4 orders of magnitude higher than the regional background (0.02 mg/kg, [30]). In 30% of soil samples taken near the sludge storage, Hg concentrations are higher than MPC. The amount of Hg in soils decreases with distance from the sludge storage, but remains above the regional background in all soil samples. The same trend was established for the soils of the forest zone in the vicinity of CAP, 1.5 km – 5.0 km from the mercury electrolysis shop, where the average concentrations of Hg were 0.21-0.25 mg/kg [13]. This indicates that the boundaries of the halo of Hg dispersion are blurred, and its concentrations, which are elevated relative to the regional background, persist even at a considerable distance from the main sources of pollution, which is facilitated by the atmospheric transport of gaseous, ionic forms of Hg and polluted dust particles.

Figure 2 shows the distribution of Hg over the layers of technogenic soils. In this case, it is appropriate to speak of layers rather than horizons of soils, since the technogenic soils near

the sludge storage were often a stratum with clearly limited in color and density layers containing various technogenic material. Accumulation of Hg occurs mainly in the upper soil layer, which is due to the technogenic influx of Hg and its fixation by humus and mineral soil particles. The exception is soil 10, sampled on the southwestern side of the sludge storage, where the maximum concentrations of Hg were found among all the studied plots. Here, an increase in the amount of Hg with depth is observed, although the total thickness of the layer is only 15 cm. Each identified layer of this soil has its own color and significantly differs in Hg concentrations. In the 10–15 cm layer, the amounts of Hg amounted to 621 mg/kg, probably due to its accumulation on the geochemical barrier.

3.2 Forms of Hg in soils

To study the features of Hg migration in soils, we studied the occurrence forms of this element based on the fractionation method (Fig. 3). In 5 fractions, various groups of soil Hg compounds with different solubility and bioavailability were isolated. The most mobile fractions of Hg are water F1 and acid-soluble F2 available to herbs from soil solutions. The organic F3 and mineral F4 fractions represent a potential reserve of soil Hg, which, under changes in humidity, temperature, pH, under the influence of microorganisms and physicochemical interactions of soil components, can replenish the amount of bioavailable Hg in the soil [14–16, 31]. The most stable and poorly soluble are sulfide F5 Hg compounds, however, these Hg compounds can also be partially dissolved, for example, under the influence of microorganisms, soil acidification, and increased moisture [22, 32–33].

Figure 3 shows the percentage of different Hg fractions, calculated from the sum of the fractions, from which the proportion of bioavailable Hg for herbs can be estimated. In soil samples 2 and 3, taken from the northwestern side of the sludge storage, high concentrations of Hg in the sulfide fraction (49-60.5%) were established. In the rest of the soils sampled near the sludge storage, the amount of sulfide Hg is lower, and strongly bound Hg often predominates. The highest concentration of Hg in the sulfide fraction (90 %) was found in sample 15, taken at a distance from the sludge storage. In soil samples 16 and 22, distant from sludge storage, and in background sample 29, organic and strongly bound fractions predominate.

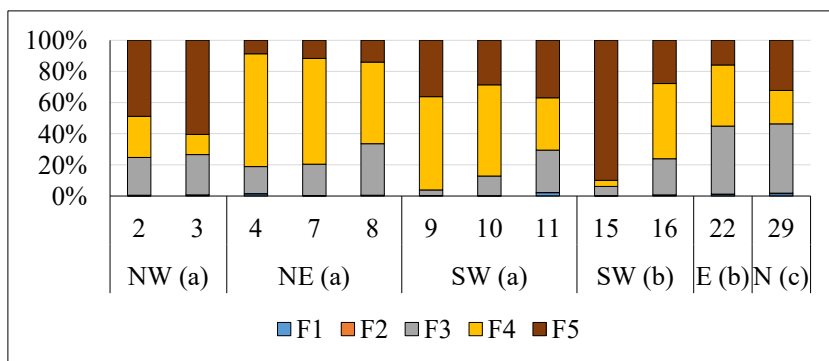


Fig. 3. Ratio of forms of Hg occurrence in soils near (a) and at a distance (b) from sludge storage, (c) background, percentage of the sum of fractions. NW, NE, SW, E, N – cardinal directions. Fractions: F1 – water soluble, F2 – acid soluble, F3 – organic, F4 – strongly bound, F5 – sulfide.

An increase in Hg in the organic fraction indicates a high potential for Hg mobilization in the soil and an increase in its bioaccumulation by herbs. It is known that the formation of mobile and bioavailable forms of Hg in soils depends mainly on the dissolution and biological destruction of its organic compounds [4]. In addition, soil organic matter is capable of

dissolving many mineral compounds, contributing to the release of chemical elements [31]. According to the method [28], the organic fraction of Hg is represented mainly by humic acids and methylmercury. Methylmercury is one of the most important Hg compounds that determine the bioavailability of Hg for all living organisms due to its ability to penetrate various biological barriers [34]. Methylated forms of Hg are easily absorbed by herbs. Despite the fact that methylmercury was not determined by direct methods, there is a high probability of its presence in the studied soils due to methylation of various Hg complexes by microorganisms. The possibility of such processes is shown in [17–22].

The strongly bound fraction is represented mainly by Hg in the mineral lattice [28] and has a lower dissolution potential. Nevertheless, it is known that plant roots are able to release carbon dioxide, various organic acids, which acidify the rhizosphere part of the soil and dissolve soil minerals, thereby facilitating the absorption of their constituent elements [14–16, 35]. Thus, despite the low concentrations of the most mobile fractions of Hg, water- and acid-soluble, there is a high probability of dissolution of its organo-mineral complexes under the influence of various biogeochemical processes in the soil.

3.3 Mercury in herbs

Table 3 shows the concentrations of Hg in the aboveground parts and roots of the fireweed *Chamaenerion angustifolium* L. near and far from sludge storage, as well as the amount of Hg in the soils on which these herbs grew. The Hg concentrations in soils and herbs near the sludge storage are higher and regularly decrease with distance from it. The levels of accumulation of Hg by herbs (aboveground part together with roots) near sludge storage exceed the Clarke for terrestrial vegetation, which according to H. J. M. Bowen (1976) is 0.015 mg/kg of dry weight. When moving away from sludge storage, the amount of Hg in herbs approaches the Clarke's.

Table 3. Hg concentrations in soils and herbs (dry wt.) in the vicinity of sludge storage, mg/kg.

Samples, place of sampling	Soil	Aboveground part	Roots
Near sludge storage (7)	5.34±7.77	0.042±0.022	0.173±0.21
	0.076-19.7	0.024-0.089	0.027-0.60
Away from sludge storage (3)	0.087±0.049	0.014±0.003	0.016±0.008
	0.052-0.143	0.012-0.017	0.008-0.024

There are conflicting opinions about the effect of total Hg concentrations in soils on its accumulation by herbs. Both the absence or weak correlation of the total concentrations of Hg in soils and herbs, as well as an increase in the bioaccumulation of this metal in contaminated soils, are noted. This is due to the fact that the soil is not always the main supplier of Hg for herbs. Often foliar uptake of Hg from atmospheric air is of paramount importance. In the present study, for the total sample, including all 10 herb samples, a positive correlation was established between the total concentrations of Hg in soils and roots. The correlation coefficient R is 0.71 ($p < 0.03$). No such dependence has been established for the above-ground parts. This is probably due to the fact that herb leaves are able to absorb atmospheric Hg, which is confirmed by many studies [10, 23–27]. The deposition of Hg-containing dust particles on the herb surface is not ruled out.

The obtained data show the predominant accumulation of Hg in the roots of fireweed *angustifolium Chamaenerion angustifolium* L., especially near sludge storage, where in 43% of root samples, Hg concentrations are increased relative to the natural level in herbs, which according to A. Kabata-Pendias (2011) is 0.10 mg/kg. At a distance from the sludge storage, the concentrations of Hg in the roots and aboveground parts of the fireweed are comparable, and in the background plot, they are somewhat lower in the roots (0.008 mg/kg) than in the

aboveground part (0.012 mg/kg). Probably, on more polluted soils near sludge storage, herb roots act as a natural biochemical barrier, limiting the supply of Hg to aboveground parts, including seeds. This plays an important role in the distribution of fireweed *Chamaenerion angustifolium* L. in the study area, contributing to the successful growth of the species on soils heavily contaminated with mercury. A slight increase in the amount of Hg in the aboveground parts of herbs in the background plot indicates an increase in foliar uptake of Hg, and, possibly, the accumulation of Hg-containing dust on the surface of stems and leaves.

3.4 Influence of Hg forms in soils on its bioavailability for herbs

Our study showed that the accumulation of Hg by herbs is determined not only by the total concentrations of Hg in soils, but also by the processes of mobilization-immobilization of this element in soils, its existence in various forms. Significant positive correlations between organic F3 and strongly bound F4 fractions of Hg and total concentrations in herbs, shown in Figure 4 by a linear trend, confirm the importance of organic and mineral Hg compounds in its accumulation by herbs.

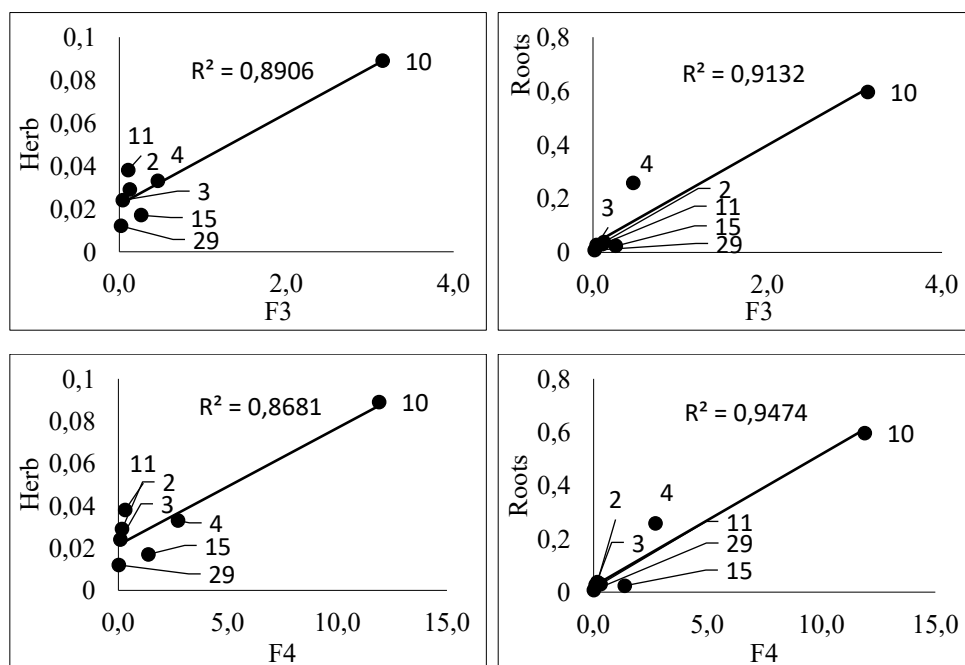


Fig. 4. Correlation coefficients R at $p < 0.01$ between organic F3, tightly bound F4 Hg fractions, and total Hg in various herb parts ($n = 7$). 2-29 – sampling sites.

For other Hg fractions, no such regularity was obtained. These results confirm previous studies on the important role of Hg-organic compounds in Hg migration from soils to herbs [13].

4 Conclusion

Thus, the CAP sludge storage remains one of the main sources of technogenic Hg in the region. Mercury emitted by this enterprise is carried over considerable distances, due to which an increase in Hg concentrations in soils relative to the regional background is

observed everywhere. In the immediate vicinity of sludge storage, Hg concentrations in soils can reach hurricane levels. At the same time, the amount of mobile Hg available to herbs directly from soil solutions is low, due to which there was no mercury contamination of herbs over a large area. A significant bioaccumulation of Hg is observed only in the immediate vicinity of the sludge storage. Under the conditions of technogenic stress, the defense mechanisms of herbs are activated – the accumulation of Hg occurs mainly in the roots, which contributes to the survival of the studied species in the territory heavily polluted with mercury. The results of fractionation showed the presence of a large number of organic and mineral forms of Hg in soils. It should be taken into account that these Hg compounds are not absolutely stable – complex biogeochemical processes in soils lead to their gradual dissolution and, as a result, an increase in Hg bioaccumulation. Significant positive correlations confirm the important role of organic and mineral complexes in Hg bioaccumulation.

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