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Article

Migration, transformation and bioaccumulation of mercury in technogenically transformed soils, Svirsk city, Irkutsk Region

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Abstract. This study focuses on distribution, bioaccumulation and speciation of mercury in technogenically transformed soils on the area of the former Angarsk Metallurgical Plant (AMP) located in Svirsk town, Irkutsk Region, Russia. The study was conducted in 2019–2020, 5 years later after the soil reclamation. The maximum Hg concentrations (up to 15.7 mg/kg), which significantly exceed maximum permissible concentrations, MPC (2.1 mg/kg) and regional background levels (0.020 mg/kg) are found in the soils around the waste dumps. Amongst the Hg fractions, mercury mainly occurs in organic and strongly-bound fractions, characterized by lower mobility. The study of the "soil-plant" system exemplified by the couch grass (*Elytrigia repens* L.) shows that Hg is mainly accumulated in roots, therefore the translocation of this element in plants is limited. Despite the performed soil reclamation, a residual mercury contamination is still observed in the upper soil horizons. The predominance of stable Hg fractions indicates a low risk for Hg remobilization under current environmental conditions, though continuous monitoring of Technosols is required for assessing a long-term ecological stability.

Keywords: soil contamination, Technosols, bioavailability, sequential extraction, couch grass

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Научная статья

Особенности миграции, трансформации и бионакопления ртути в техногенно трансформированных почвах г. Свирска

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Аннотация. В работе рассмотрены процессы распределения и бионакопления, а также формы нахождения ртути в техногенно трансформированных почвах территории бывшего Ангарского металлургического завода (АМЗ) г. Свирска (Иркутская область, Россия) в 2019–2020 гг., спустя 5 лет после проведения рекультивационных мероприятий. Максимальные содержания ртути (до 15.7 мг/кг) зафиксированы в зоне влияния остатков отвалов, что значительно превышает значение ПДК (2.1 мг/кг), а также региональные фоновые значения (0.020 мг/кг). Основная часть ртути находится в виде органически связанной и прочносвязанной фракций, характеризующихся низкой подвижностью. Изучение системы «почва–растение» на примере пырея ползучего (*Elytrigia repens* L.) показало, что наибольшее накопление ртути наблюдается в корнях; таким образом, транслокация элемента в растениях ограничена. Несмотря на проведенную рекультивацию, остаточное загрязнение ртутью сохраняется в верхних горизонтах почв. Преобладание устойчивых форм Hg свидетельствует о низком риске ремобилизации элемента в современных условиях, однако для оценки долговременной экологической стабилизации требуется постоянный мониторинг состояния техноземов.

Ключевые слова: загрязнение почв, техноземы, биодоступность, последовательная экстракция, пырей ползучий

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Introduction

Mining and metallurgical industries generate significant amounts of waste, which can pose an environmental hazard due to high concentrations of heavy metals, including mercury (Qiu et al., 2005). In mining, mercury can occur as primary minerals (cinnabar HgS) and as impurities in other sulfide minerals including pyrite (FeS) and sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$). Technogenic processes such as ore grinding, smelting, flotation, and waste storage release mercury into the environment, causing long-term effects on ecosystems. Soil plays an important role in the biogeochemical Hg circulation, as it accumulates this element and serves as a source for other components of the environment.

Mercury is recognized as a highly toxic, persistent, and mobile contaminant, as it does not decompose in the environment and is volatile (Gworek et al., 2020). In addition, mercury is extremely chemically and biologically active and can exist in different chemical forms. Even at low concentrations, mercury has toxic effects on plants and animals (Gworek et al., 2020; Singh et al., 2020). In agriculture, mercury compounds were previously used as seed disinfectants and herbicides, which additionally contributed to mercury entry into the soil (Gao et al., 2010). The phytotoxicity of mercury results from its ability to induce oxidative stress in cells, leading to increased lipid peroxidation, reduced activity of cytoplasmic and membrane proteins, photosynthetic pigments, loss of turgor, and changes in the respiration of plant organisms. It inhibits the plant vitality and decreases the plant growth rate (Azevedo and Rodriguez, 2012; Khan and Chaudhry, 2006).

Of particular interest is the behavior of mercury in Technosols, which are generated in areas of intense anthropogenic impact. These soils demonstrate altered chemical composition, structure, and physical and chemical properties. In Technosols, mercury can exist in various forms, including insoluble substances, mobile ions, organic complexes, and volatile compounds. The geochemical behavior of mercury depends on a number of soil characteristics such as organic matter content, pH levels, microbial activity, and hydrological conditions (Biester et al., 2002).

Studying mercury migration and transformation in Technosols is important in terms of the sustainability of ecosystems and environmental safety of areas affected by technogenic pollution. These studies are particularly relevant for areas with the long-term exposure to industrial pollution including town of Svirsk (Irkutsk Region), the zone of the Angarsk Metallurgical Plant (AMP) influence.

This study was aimed at identifying the patterns in distribution, migration and transformation of mercury compounds in the soil-plant system after the remediation actions on the contaminated industrial site of the former AMP in Svirsk town.

Materials and methods

The town of Svirsk lies on the left bank of the Angara river within the Irkutsk-Cheremkhovo Plain (Southern Baikal, Russia) (Fig. 1**A**). The area is a part of the southern Siberian Platform, where Lower Cambrian carbonate rocks overlain by alluvial deposits are predominant. The topography here is characterized by gently hilly terrain, composed of the ancient alluvial Quaternary deposits overlain by a layer of loams and clays with carbonates. The clay layers demonstrate poor water permeability therefore forming natural geochemical barriers, limiting the migration of mercury and other heavy metals to depth (Shen'kman, 2016).

The area of Svirsk town had experienced significant anthropogenic impact due to the activities of the AMP, which operated until 1949. The Plant produced arsenic compounds for defense purposes using the ores with high contents of arsenopyrite and sulfide minerals. After the enterprise ceased operations and was abandoned for a long period, the industrial site and adjacent areas were subjected to remediation in 2009–2014 (Bogdanov et al., 2014). The major remediation actions included collection and removal of contaminated soil, treatment with lime solution and adding of the conditionally fertile soil (Bogdanov et al., 2014). Despite the remediation measures, the area around the AMP industrial site still retains higher concentrations of arsenic and other heavy metals (Baenguev et al., 2022; Belogolova et al., 2025; Kachor et al., 2024).

In 2019–2020, ecological and geochemical studies were conducted on the territory of the AMP industrial site and in its vicinities (Fig. 1**B**). According to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015), the studied soils are classified as Technosols. In terms of the "Classification and Diagnostics of Russian Soils" (Shishov et al., 2004), they can be classified as chemozems. To assess the spatial distribution of mercury in the surface soil layer, 70 soil samples were collected from a depth of 0–20 cm. Taking into account differences in physical and chemical properties and the level of technogenic impact, 3 areas were conditionally identified: site 1 – zone of former arsenic dumps; site 2 – zone of former buildings of industrial facilities; site 3 – area in the vicinities of the major pollution zone. Two soil profiles up to 70 cm were sampled to study the vertical Hg migration. Profile 1 (N 53°05'44,2" E 103°20'18,8") lied in the area of former dumps (site 1), profile 2 (N 53°05'49,3" E 103°20'27,2") was located on site 2. Sampling points were fixed with the navigation system (GPS) receivers (GARMIN Montana 650t, Garmin Ltd., Taiwan) for further construction of geochemical contamination maps (Fig. 1**B**).

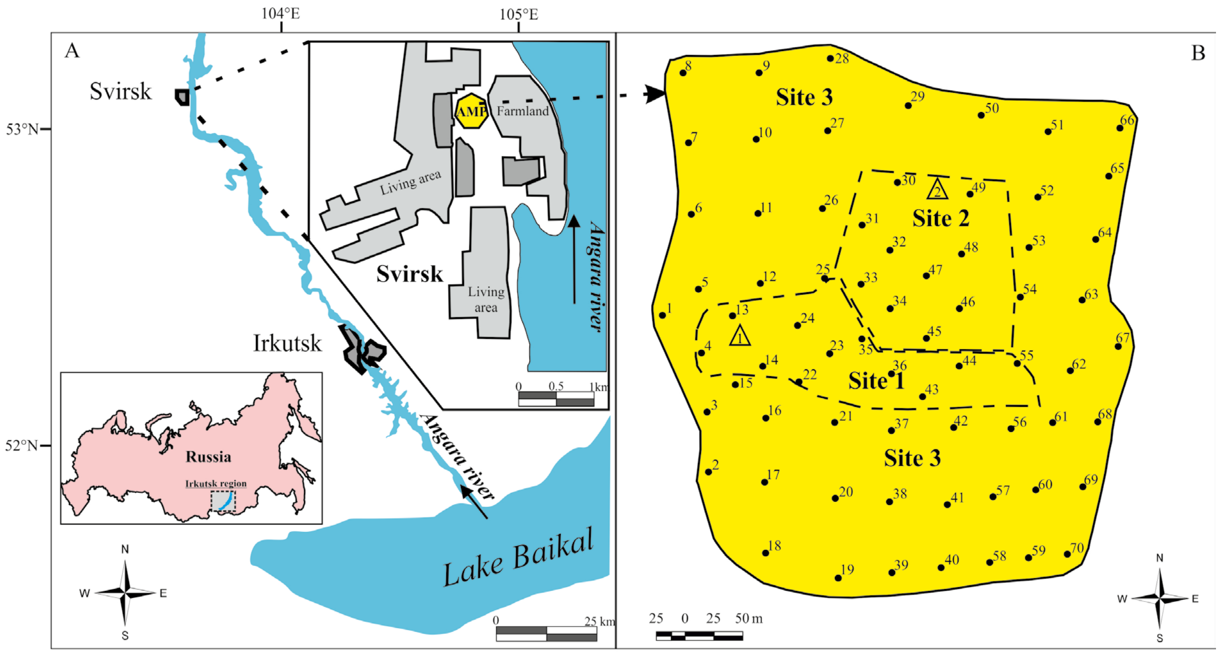

Fig. 1. Map of the study area (**A**) and sampling sites of Technosols (**B**). Sites: 1 – major contamination zone, 2 – former area of the plant buildings, 3 – area located outside sites 1, 2. Triangles in the figure indicate soil sections.

The study area is covered with herbaceous plants dominated by creeping couch grass *Elytrigia repens* (L.) Nevski. This species was chosen to assess Hg bioavailability as it is the dominant species in the phytocenosis and demonstrates tolerance to high levels of heavy metals in soils (Kaznina et al., 2016; Laidinen et al., 2018). Previous studies reported that *E. repens* is able to accumulate significant amounts of heavy metals in the roots (Chaplygin et al., 2022; Shtangeeva, 2021; Štofejová et al., 2021; Yun et al., 2018). For the analysis, the plants were collected in the amount of 45 samples. Then the plant samples were dried to an air-dry state at room temperature and were separated into shoots (30 samples) and roots (15 samples). Plant roots were pre-washed with running water.

All chemical analyses were accomplished using the scientific equipment of the certified analytical center of collective use 'Isotopic and Geochemical Research' of the Institute of Geochemistry, SB RAS. Soil samples were pre-sieved through 2 mm sieve.

In soil samples from site 1with the highest Hg abundances, the mercury species were studied by the method of sequential extraction described by N.S. Bloom et al. (2003). The obtained fractions included:

1 – water soluble (the samples were treated with distilled water);

2 – acid-soluble (the solid residue remaining from the first step (1) was treated with a mixture 0.1 M solution of CH_3COOH and 0.01 M HCl);

3 – organic (the residue from (2) was treated with 1 M NaOH);

4 – tightly bound within mineral matrices (the residue from (3) was treated with 12 M HNO_3);

5 – sulfide or residual (residue from (4) was digested in aqua regia).

The precipitate from each fraction was air-dried and then treated with a reagent to obtain the next fraction. Total Hg concentrations in soils plants and soil extracts were measured by the atomic absorption spectrometry with a RA-915+ analyzer coupled with Rp-91 attachment (Lumex, Russia). The following reference materials were used as control samples: SCT-3 (typical chernozem soil) and SDS-2 (sandy-loamy sub-podzolic soil).

The soil organic matter (C_{org}) was analyzed using the Tyurin method following the GOST 26213-2021[1]. The pH values were determined in soil suspension (soil: water ratio 1:5) using potentiometry.

Mercury accumulation by plants was estimated by calculating biological accumulation coefficients for the shoots (BCF_s) and roots (BCF_r) of the studied plants and translocation factor (TF) using the following formulas:

$$BCF_s = \frac{C_{shoot}}{C_{soil}};$$

$$BCF_r = \frac{C_{root}}{C_{soil}};$$

$$TF = \frac{C_{shoot}}{C_{root}},$$

where C_{root} and C_{shoot} – mercury concentrations in the aboveground biomass and roots (dry weight), respectively; C_{soil} – mercury concentration in soil.

Statistical processing of the obtained data was accomplished using PASW Statistics 10.0 software. The maps of Hg concentrations distribution in soil and plants were constructed in the Golden Software Surfer.

Results and discussion

According to literature data, background mercury content in soil varies from 0.03 to 0.1 mg/kg with an average value of 0.06 mg/kg (Li and Jia, 2018; Wang et al., 2012). The maximum mercury concentrations in the studied soils reached 15.7 mg/kg in the zone affected by former waste dumps (site 1). The average Hg content for this site amounts to 2.61 mg/kg which exceeds both the MPC for soils (2.1 mg/kg) in accordance with SanPiN 1.2.3685-21[2], and the regional geochemical background of 0.02 mg/kg (Grebenshchikova et al., 2008). On sites 2 and 3, the average Hg concentrations are significantly lower amounting to 0.3 and 0.2 mg/kg, respectively (Table 1).

[1] GOST 26213-2021, 2021. Soils. Methods of organic matter analysis.

[2] SanPiN 1.2.3685-21, 2021. Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors to humans

The spatial distribution of Hg concentrations (Fig. 2) shows that after the conducted reclamation the primary Hg contamination zone is concentrated around the remaining waste dump and its surroundings. On site 2, owing to the reclamation actions, Hg concentrations are significantly lower as compared to other sites. The average Hg concentration here is lower than the background level for the region.

To better understand the mechanisms of Hg accumulation and its subsequent transport pathways, we studied the pattern of Hg migration and variations of Hg concentrations through the vertical soil sections and determined the major zone of Hg accumulation. In soil profile 1 (site 1), maximum Hg concentrations (up to 11.9 mg/kg) were observed in the surface humus layer (0–10 cm), which demonstrated the higher organic matter content (C_{org} = 6.47%) (Table 2). Hg concentrations quickly decreased with increasing depth thus indicating a weaker migration ability of this element and its accumulation restricted to the upper horizon. These data confirm a higher Hg binding capacity to organic matter and fine-dispersed components of the upper soil horizon and are in agreement with other studies (Butakov et al., 2017).

Variations in pH values in the soil profile (site 1) were found to strongly influence the Hg behavior. In the upper horizons of technogenic soils, pH was low (3.0–3.5), being the result of oxidation zones of widespread sulfide mineralization on site 1 (Table 2). Such acidic conditions accelerate the release of individual ions from secondary minerals; however, the high organic matter levels compensate for this effect, binding mercury by forming stable organic complexes. Below the 30–40 cm depth, there was a sharp transition to a neutral-alkaline environment (pH 6.8–8.0), therefore leading to the predominance of insoluble Hg forms and minimal migration of this element into deeper soil layers.

Table 1. Hg concentrations in soils of the former AMP, Svirsk town, mg/kg; n – sample size, min and max – minimum and maximum values, M – the mean value, σ – standard deviation, Me – median, D – the sample variance.

Site no.	n	min	max	M	σ	Me	D
1	18	0.04	15.7	2.61	4.52	0.72	20.4
2	15	0.04	2.96	0.31	0.80	0.05	0.65
3	37	0.04	0.66	0.20	0.18	0.17	0.03

Table 2. Distribution of Hg concentrations (mg/kg), C_{org} (%) and pH in soil profiles.

Parameter	Depth, cm						
	0–10	10–20	20–30	30–40	40–50	50–60	60–70
Profile 1 (site 1)							
Hg	11.9	0.04	0.03	0.04	0.03	0.02	0.07
C_{org}	6.47	4.02	3.02	1.52	1.42	0.89	0.71
pH	3.0	3.1	3.5	6.8	7.7	7.9	8.0
Profile 2 (site 2)							
Hg	0.04	0.03	0.04	0.04	0.03	0.03	0.05
C_{org}	4.74	4.13	2.89	2.31	1.09	0.83	0.61
pH	3.8	3.8	4.1	7.4	7.9	8.1	8.1

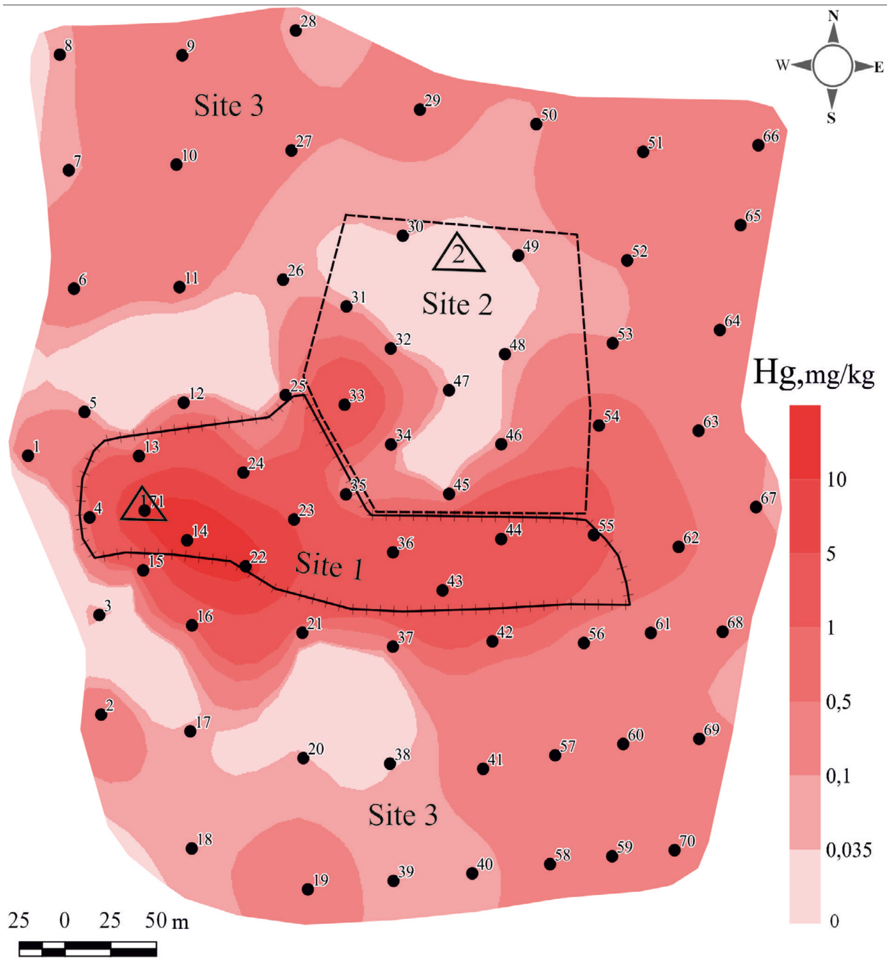

Fig. 2. Map representing the distribution of Hg concentrations in soils, mg/kg. Legend as in Fig. 1.

In soil profile 2 (site 2), Hg concentrations remained relatively constant and varied between 0.03 and 0.05 mg/kg. As opposed to site 1, low pH values (3.8–4.1) in the soil upper layers here were not followed by the increased Hg levels, that was a result of the reclamation efforts. A lack of clear vertical variation in Hg contents indicates relatively weak Hg migration mobility under such conditions.

It is known that determining of only total Hg concentrations are insufficient for understanding the biogeochemical cycle of this metal, since total Hg concentrations do not provide useful information on its reactivity, bioavailability and toxicity in soils (Issaro et al., 2009). Our results of the sequential extraction of Hg compounds showed that the percentage of Hg occurring in the organic and tightly bound fractions was high, while the smallest fractions included water-soluble and acid-soluble (Fig. 3), thus indicating low mobility and limited bioavailability of mercury in the studied soils.

On site 1, the major source of Hg contamination is likely cinnabar (HgS), a stable mineral form in the oxidation zone (Kim et al., 2004; Wang et., 2011). Our results are consistent with the data for the contaminated soils near former chlor-alkali and metallurgical plants (Biester et al., 2002; Gordeeva et al., 2017). On site 1 (source of contamination), Hg mainly exists as sparingly soluble compounds. It reduces its further migration and entry into biological objects. On sites 2 and 3, Hg may occur in more mobile forms, similar to As and Pb (Baenguev et al., 2022; Belogolova et al., 2025).

A lower proportion of acid-soluble Hg fraction points out a lack of higher Hg concentrations associated with carbonates and other readily soluble secondary minerals. So, mercury entering the soil underwent long-term technogenic transformation, during which the element mainly existed as more stable compounds: sulfides, tightly bound mineral forms, and also as part of organomineral complexes. This type of element behavior is typical of areas with long-term technogenic pollution, when mobile forms of mercury gradually transform into tightly bound and residual forms (Wang et al., 2012).

The formation of the water-soluble Hg fraction in conditions of prolonged atmospheric exposure can be explained in terms of the hypergenesis of sulfide material. Oxidation of arsenopyrite (FeAsS), pyrite (FeS_2) and other sulfides characteristic of arsenic production wastes breaks down the structure of primary minerals releasing associated elements, including mercury, which exists as impurities in sulfide minerals. Hypergenesis reactions lead to the formation of acidic sulfate solutions and mobile forms of metals, including mercury, which transforms into more mobile and soluble complexes, often containing chloride and sulfate ions in the oxidation zones. However, local oxygen saturation, periodic humidification and drainage effects are not able to stabilize the entire volume of mercury released, therefore water-soluble fraction may be detected (Fig. 3).

Comparison of our results with the data for the 'Usolyekhimprom' sludge storage area, located 50 km away from Svirsk town (Gordeeva and Pastukhov, 2023), shows that organically bound and tightly bound Hg fractions dominate in both studies, therefore confirming that under conditions of strong technogenic pollution, mercury tends to stabilize in less mobile forms.

For a complete evaluation of Hg bioavailability and its potential entry into food chains, the plant component is to be considered as well. The analysis of concentrations of heavy metals, including mercury, in plant tissues allows determining the degree to which the element accumulated in the soil transports into the biological system and participate in environmental processes. Numerous studies recognize the essential role of terrestrial plants in the Hg biogeochemical cycling (Fantozzi et al., 2013; Mazur et al., 2014). According to A. Kabata-Pendias (2011), the accepted background mercury levels in herbaceous plants range within 0.001–0.1 mg/kg. In this study, Hg concentrations in *Elytrigia repens* plant samples vary within 0.008–0.054 mg/kg in the aboveground biomass and 0.012–0.093 mg/kg in roots (Table 3). The maximum Hg concentrations are recorded on site 1 (the remaining waste dump) which demonstrates the highest soil contamination (Fig. 4).

Critical Hg levels for many plants range between 1 and 8 mg/kg (Kabata-Pendias and Szteke, 2015), so the recorded values are not higher than the toxic limits. Elevated Hg concentrations in *Elytrigia*

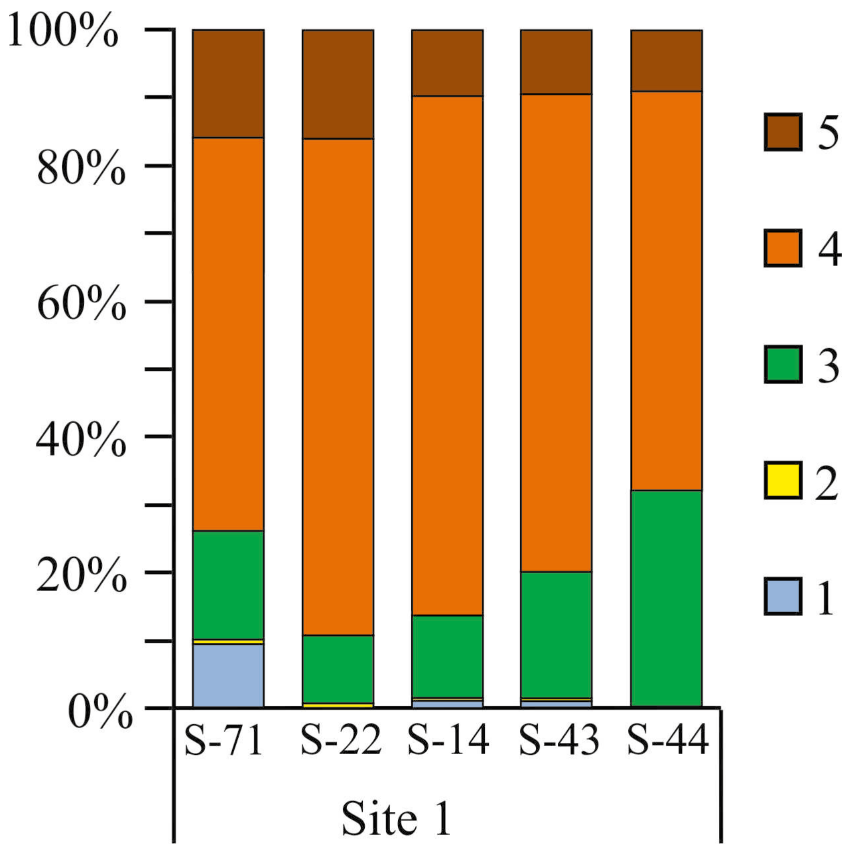

Fig. 3. Distribution of Hg concentrations by fractions (%), site 1. Fractions: 1 – water-soluble, 2 – acid-soluble, 3 – organic, 4 – tightly bound compounds, 5 – solid residue.

repens roots can result both from the absorption of bioavailable Hg forms and Hg sorption on roots as well as binding with soil aggregates.

The bioaccumulation coefficient (BCF) and translocation indices (TF) were used to evaluate the Hg translocation in the soil-plant system (Table 4). The results obtained align with the previous data indicating that Hg is mainly accumulated in roots (Schwesig and Krebs, 2003; Windham-Myers et al., 2014), which serve as natural barriers (Patra and Sharma, 2000; Zare et al., 2020).

The highest BCF_r values are recorded on site 2 (0.631), which is characterized by relatively low Hg concentration in soil. Translocation factors (TF) for plants on sites 2 and 3are almost two times higher as compared to those on site 1, which may be explained by stronger barrier mechanisms in plants. In response to high mercury concentrations in soil, plants can increase root selectivity and limit Hg uptake into cellular structures (Gworek et al., 2020).

Table 3. Hg concentrations (mg/kg dry weight) in aboveground parts / roots of couch grass (*Elytrigia repens*).

Site no.	Number of samles	Minimum	Maximum	Mean value
1	11 / 5	0.008 / 0.027	0.054 / 0.093	0.017 / 0.066
2	6 / 6	0.008 / 0.012	0.012 / 0.052	0.009 / 0.030
3	13 / 4	0.007 / 0.013	0.015 / 0.05	0.010 / 0.028

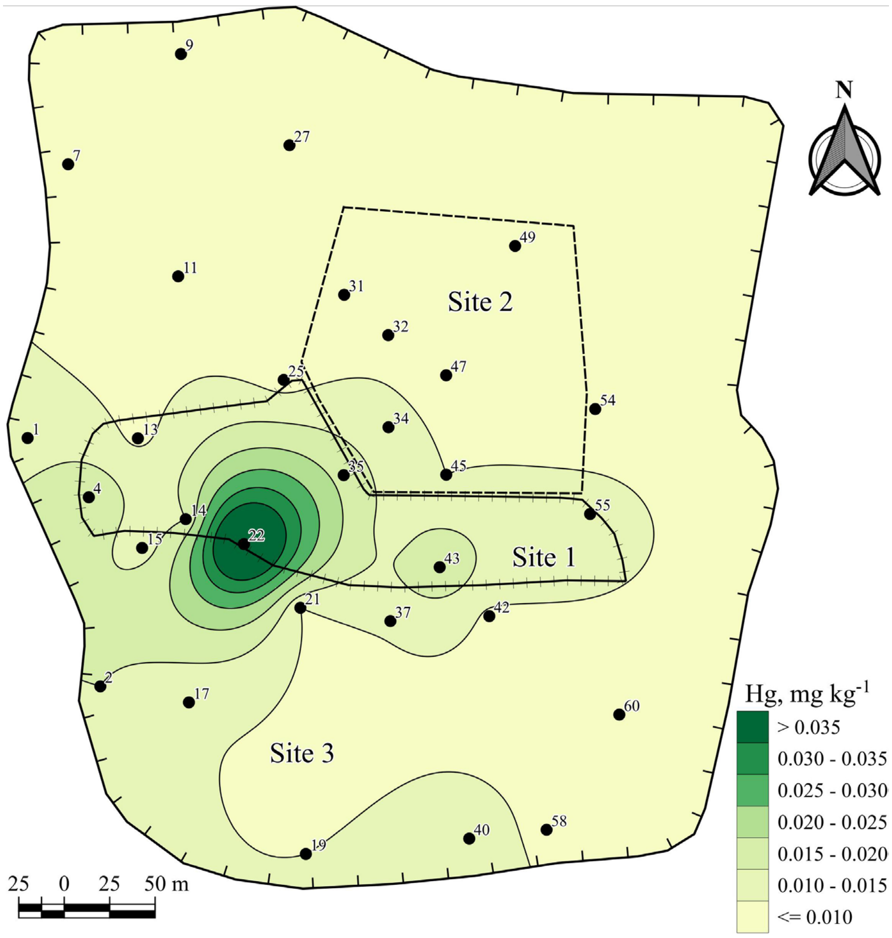

Fig. 4. Map of the distribution of Hg concentrations in the above-ground parts of *Elytrigia repens* plants, mg/kg.

Table 4. Distribution of Hg in plants (*E. repens*) and soil, as well as calculated indices. C_{shoot} – concentration in the aboveground biomass, C_{root} – concentration in roots, C_{soil} – concentration in soil (mg/kg dry weight); BCF_s – bioconcentration factor in the shoots, BCF_r – bioconcentration factor in roots, TF – translocation factor.

№ пробы	C_{shoot}	C_{root}	C_{soil}	BCF_s	BCF_r	TF
			Site 1			
36	0.013	0.093	2.18	0.006	0.043	0.14
37	0.011	0.027	0.168	0.065	0.161	0.407
42	0.009	0.056	0.702	0.013	0.08	0.161
43	0.02	0.086	3.4	0.006	0.025	0.233
55	0.012	0.07	1.17	0.01	0.06	0.171
Mean	0.013	0.066	1.524	0.02	0.074	0.222
			Site 2			
31	0.008	0.042	0.041	0.195	1.024	0.19
32	0.009	0.031	0.038	0.237	0.816	0.29
34	0.012	0.026	0.117	0.103	0.222	0.462
45	0.01	0.052	0.048	0.208	1.083	0.192
47	0.008	0.015	0.045	0.178	0.333	0.533
49	0.009	0.012	0.039	0.231	0.308	0.75
Mean	0.009	0.03	0.055	0.192	0.631	0.403
			Site 3			
40	0.012	0.029	0.051	0.235	0.569	0.414
54	0.007	0.013	0.875	0.008	0.015	0.538
58	0.009	0.021	0.186	0.048	0.113	0.429
60	0.008	0.05	0.178	0.045	0.281	0.16
Mean	0.009	0.028	0.323	0.084	0.244	0.385

In the case of *Elytrigia repens*, the calculated BCF values show that potentially toxic elements are mainly accumulated in its roots. Increased BCF and TF indices recorded on site 2 likely result from lower Hg concentrations in soil and more mobile Hg forms. Our data agree well with the results by O.N. Gordeeva et al. (2017) for the Southern Baikal region, showing that Hg accumulation coefficients in roots were almost 2–3 times higher than those values in the above-ground biomass. It confirms a general tendency of Hg accumulation primarily in the root system of herbaceous plants and its limited translocation to the above-ground part, resulting from both Hg forms in the soil and physiological barriers of element translocation to plants (Yuan et al., 2022).

Conclusion

The present study revealed Hg forms, its distribution and bioaccumulation in technogenically transformed soils (Technosols) in Svirsk town after the reclamation measures on the area of the former Angarsk Metallurgical Plant. The highest Hg concentration (15.7 mg/kg) was recorded in the vicinities of the former arsenic dump and was more than 7 times higher than the MPC value and significantly exceeded the regional geochemical background. Most mercury was found in in organically bound and tightly bound fractions, which resulted in its relatively low mobility and limited bioavailability. In the case of *Elytrigia repens* plants, Hg was mainly accumulated in the roots with low translocation to the above-ground part of the plant, therefore indicating a barrier function of the root system. The comparison of 3 sites demonstrated that the mercury bioavailability depends not only on the metal concentrations, but on its speciation.

The data obtained indicate that the Hg migration reduced, herewith the residual contamination still remained in the upper soil horizons. The predominance of stable mercury forms reduced the risk of its remobilization under the current conditions. However, changes in the hydrological or acid-alkaline regime may lead to the re-entry of the element into the biogeochemical cycle.

It is vital to continue long-term ecological monitoring of Technosols, to assess the role of microbiota in Hg transformation, and to develop phytoremediation techniques using sustainable plant species to stabilize mercury in soils of contaminated areas.

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