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Characteristics of Heavy Metal Migration in the Natural–Anthropogenic Anomalies of the Northwestern Altai

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Abstract—The abundances and migration characteristics of the main ore and accompanying metals (Cu, Pb, Zn, Cd, Fe, and Hg) were investigated in the natural and cultural landscapes of the northwestern Altai. Elevated metal concentrations (compared with the background and guideline values) were observed in the material of tailings of the Altai Mining and Processing Complex and Zmeinogorsk Gold Recovery Plant, as well as in the waters of anthropogenic lakes, snow cover, and vegetation. It was found that Zn and Cd are more actively transported into solutions than Pb and Cu during the oxidation dissolution of sulfides in waste heaps. The spatial migration of heavy metals was evaluated. Species-dependent features were established in the accumulation of elements by plants in the phytocoenoses of anthropogenic ecosystems.

Keywords: mining industry, tailings, environment, anthropogenic landscapes, metals, migration, soil, vegetation, water, snow cover.

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INTRODUCTION

Erosion and deflation processes in the tailings of mining and processing enterprises present a serious environmental hazard. The input of heavy metals and aggressive sulfate waters into the constituents of natural landscapes results in significant transformations and changes in the physicochemical properties of soils and gradual degradation of the vegetation cover of ecosystems adjoining mining centers. It is believed that the remediation of anthropogenic anomalies with the complete oxidation of sulfate acid solutions formed owing to the dissolution of sulfide ores requires more than 90 yr [1, 2]. As the technologies of waste disposal are followed more strictly in western countries, a number of investigations of submerged mine tailings have been reported in the international literature [3], for instance, on the behavior of metals in plants of moist and waterlogged areas of anthropogenic ecosystems [4].

In the Russian Federation, most abandoned tailings dumps are dried up. It was found that a wind gust can remove from the surface of a waste heap 1000 ha in area approximately 60000 m^3 of sand-sized mineral particles [5]. Investigations have been reported on the physicochemical and biogenic processes of the formation and distribution of secondary minerals in mine tailings [6–9] and the microbiological oxidation of ores [10, 11]. Some studies focused on the distinguishing of stages in the development of anthropogenic geosystems [12] and types of technogenesis [13]. Anthropogenic mass fluxes and their influence on the hydrogeochemistry of surface waters have been explored by experimental methods [9, 13, 14].

On the other hand, the migration and deposition of metals in soils and plants in anthropogenic landscapes are not adequately understood [13]. Therefore, our study focused on the estimation of heavy metal migration in the anthropogenic landscapes of the Rudnyi Altai.

OBJECTS AND METHODS

The Altai is one of the richest regions of Russia in terms of mineral resources, including metals, nonmetals, and fuels. The transitional zone of the mountain belts of the northwestern Altai in the Loktevskii, Rubtsovskii, Tret'yakovskii, and Zmeinogorsk administrative districts hosts the main resources of base metal ores. They are represented mostly by sheet and lenticular bodies of Cu–Pb–Zn ores at the northeastern termination of the Rudnyi Altai [15]. For more than 50 years, these ores from a number of deposits were processed at the Altai Mining and Processing Complex (AMPC), where Pb and Zn concentrates were produced. During the period of AMPC operation, two large tailings dumps with a total area of ~1 km^2 and a volume of 11 million cubic meters were accumulated near the town of Gornyak [16] (Fig. 1). The AMPC was closed in 1995.

The Zmeinogorsk Gold Recovery Plant (ZGRP) processed up to 1956 the ores of the oldest gold deposit of the Altai. The tailings dumps of the ZGRP are older

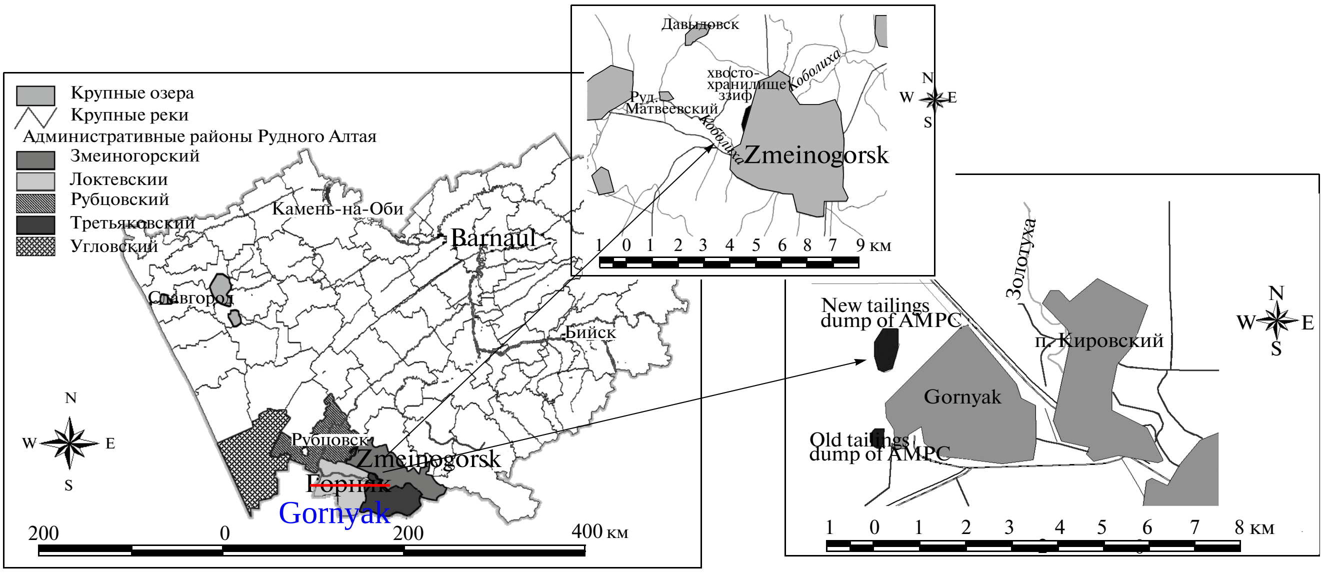


Fig. 1. Region studied and location of the tailings dumps of the Altai Mining and Processing Complex and the Zmeinogorsk Gold Recovery Plant.

than the waste heaps of the AMPC; they are smoothed, vegetated at the periphery, and located on the right-bank terrace above the flood plain of the Korbolikha River within the water protection area of the town of Zmeinogorsk (Fig. 1). During spring flood, the body of the settler is washed out, and the anthropogenic material is transported into the floodplain and further into the Gilevskoe reservoir on the Alei River.

Since the shutting down of plant operations, one of the main environmental problems in the areas adjoining the waste heaps has been the dispersion of dust enriched in heavy metals (small particles of processed ore, salt crystals, and secondary minerals) from the bottom surface of the dried tailings dumps. An additional contribution to the contamination of natural objects is related to the water removal of solid materials, evaporation and emission of toxic gases, and seasonal infiltration of solutions into the underlying soils. The residential areas of Gornyak near the tailings are threatened by the seepage of toxic mining waters, because the cessation of water pumping out of the mine resulted in mine flooding, sagging, and a rise of the groundwater level.

The following objects were investigated: solid materials from the AMPC waste heaps, anthropogenic materials and plants from the sides of the tailings dumps of the AMPC and the periphery of ZGRP heaps, waters of anthropogenic lakes, and snow cover (solid and water phases), as well as soils and plants from the background areas of the northwestern Altai.

The surface sampling of mine tailings was carried out radially from rim to rim through the center of the dumps from depths of 0–30 cm. In addition, refilled (technically remediated) areas of waste heaps and soils from the vicinity of the tailing dumps were sampled. One-kilogram samples were dried, sieved, and stored in polyethylene bags until further processing. Samples of all the available species of existing phytocoenoses were collected at the soil sampling sites. The plants were divided before analysis into subterranean and subaerial parts, washed with distilled water, dried in a ventilated room, and finely powdered.

In order to evaluate the air transport of main pollutants and estimate the anthropogenic contamination of the atmosphere, a snow cover was analyzed in the AMPC area. The snow was collected in March through its whole thickness. The pit area and the time of snow cover formation were recorded. The samples were at least 6 kg in weight, which is sufficient for metal analysis. The snow samples were melted and filtered. The filtered precipitate was weighed, and the total amount of dust falling from the atmosphere per unit area per unit time was determined. The dust loading was calculated as $P_n = P_o/(St)$, where P_o is the mass of dust (solid residue) in the sample, S is the projective area of deposition, and t is the time from the onset of snow cover formation [17]. The contents of heavy metals in snow were determined separately for the solid residue and the water phase.

Water was sampled in accordance with guides specified by Russian State Standards (GOST 17.1.5.01-80, GOST 17.1.5.05-85, and GOST R 51592-2000) for the investigation of water objects. Samples were collected in clean polyethylene containers, conserved with HNO_3 (2 ml per 0.5 l) following the procedure of [18], and rapidly delivered to the laboratory.

During the field work, the archived data of the AMPC and ZGRP were inspected for obtaining data on the chemical composition of processed ores, technological protocols of beneficiation, methods of storage, and conditions of dump monitoring.

Table 1. Detection limits and characteristics of errors*

Element	Water samples			Plant materials		
	Detection limit, mg/l	Range of measurements, mg/l	Characteristic of measurement error, accuracy, ±δ, %	Detection limit, ppm	Range of measurements, mg/l	Characteristic of measurement error, accuracy, ±δ, %
As	0.0005	0.0005–0.3	60–15	2.5	10–100	50–25
Fe	0.01	0.01–15	38–15	0.04	10–200	55–15
Hg	0.00002	0.00002–1000	60–23	0.0002	0.01–1.0	50–25
Cd	0.00001	0.00001–0.01	45–20	0.0004	0.01–1.0	40–9
Cu	0.0001	0.0001–100	60–15	0.004	0.5–30	29–8
Pb	0.0002	0.0002–0.1	60–25	0.004	0.01–1.0	50–14
Zn	0.002	0.002–500	48–14	0.02	1.0–100	26–9

* Characteristics of errors correspond to values specified for the analytical methods.

The laboratory stage of investigations included sample preparation, analysis, and interpretation of the obtained data.

The grain size composition of soils and waste heap materials was determined by the physicochemical method of Kachinskii [19].

The chemical elements were determined in water and plants by atomic absorption spectrometry at the certified analytical center of the Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, using atomic absorption spectrophotometers with flame and electrothermal atomization. Mercury was analyzed by the cold-vapor amalgamation technique using a Perkin Elmer HGA-600 (electrothermal atomization with Zeeman background correction) and Pye Unicam SP-9 (flame atomization) analyzers. The organic components of plant samples were decomposed by the method of dry ashing in an electric furnace at a gradual temperature increase up to 480°C and subsequent treatment of the obtained ash with various acids. Wet salts were dissolved in acid solutions. The acid digestion of plant and soil materials for Hg determination was carried out using a water bath. The detection limits and analytical uncertainties are given in Table 1.

Soils and waste heap materials were analyzed by the multielement atomic emission method using an argon-arc double-jet plasmatron equipped with a DFS8 spectrograph at the Institute of Soil Sciences and Agrochemistry, Siberian Branch, Russian Academy of Sciences. The samples were preliminarily powdered in an agate mortar, mixed with a buffer (powder of specpure carbon), and injected into the plasma jet with an argon flow. The detection limits of the ore and accompanied elements of interest (27 elements were simultaneously measured) in soils by the above method were (wt %) 1×10^{-4} for Zn and As, 3×10^{-4} for Fe, 3×10^{-5} for Pb, 5×10^{-5} for Cu, 1×10^{-7} for Cd, and 1×10^{-8} for Ba. The relative errors of quantitative determination (variation coefficients of measured contents relative to the mean) were within 10% for Fe, Pb, Zn, and As and 20% for Cd and Cu.

The degree of soil contamination was estimated by comparison with the maximum permissible concentrations (MPC), provisionally permissible concentrations (PPC) [20], regional background contents of metals, guidelines accepted in other countries [21], and the mean contents of elements in soils [22]; the contamination of plants was estimated by comparing with the global mean background values [23].

RESULTS AND DISCUSSION

The contents of most chemical elements in the AMPC waste heaps were not higher than the permissible levels. However, the contents of the main ore-forming elements (Cd, Cu, Pb, and Zn), as well as Ba and As were significantly higher than the public health limits (PPC and MPC) and background contents (Table 2). Anomaly ~~and hazard~~ indexes were calculated for such elements (Table 2 [24]), which are the ratios of the mean content of the element in anthropogenic material to the background content ~~and PPC for loamy soils, respectively [21]~~.

The examination of the chemical composition of the AMPC waste heaps indicated both their environmental hazard and the expediency of the secondary extraction of Cu, Zn, and Pb. The contents of these metals are up to several tens of grams per one kilogram of waste heap material. Modern technologies allow metal extraction at such abundances, and the reprocessing of these materials may appear profitable. The calculated resources in the waste heaps of the AMPC are 68000 t of Cu, 83 000 t of Zn, and 46 000 t of Pb.

Note that the anomaly parameters (Table 2) of Cu and Pb in the waste rocks of the AMPC are significantly higher than the background-normalized contents of Cd and Zn. The ratios of metal contents in the waste heap materials to the guidelines accepted in various

Table 2. Contents of the main ore and accompanying elements in the anthropogenic materials of the AMPC tailing dumps, ppm

Object, parameter	As	Ba	Cd	Cu	Pb	Zn
Tailings (surface):						
old*	**207** ± 31	**91596** ± 21344	**7.1** ± 2.1	**2773** ± 536.7	**1669** ± 178	**4269** ± 1041
new*	**135** ± 24	**230025** ± 54560	**9.5** ± 1.8	**7794** ± 2308	**4476** ± 1066	**6703** ± 1634
PPC [20] and MPC (Ba)	2; 5; 10	100	0.5; 1.0; 2	33; 66; 132	32; 65; 130	55; 110; 220
Mean content in soils [22]	5	500	0.5	20	10	50
Background content	9.6	n.d.	0.15	26	22	74
Anomaly index, C/C_b [24]**	18 / (2–45)	n.d.	55 / (7–107)	203 / (37–1039)	140 / 7–488	74 / (5–196)

Note: Mean ± confidence interval. ** The numerator is the mean value, and the denominator is the range.

countries (after Kloke [21]) show a similar sequence: Cd (2.8 MPC) < Zn (18 MPC) < Pb (30 MPC) < Cu (53 MPC). The ratios of metal contents in the waste heap materials to the mean abundances in soils [22] form the same sequence with the maximum values for Cu and Pb: 17 (2–32) for Cd, 110 (7–330) for Zn, 264 (27–1350) for Cu, and 307 (15–1075) for Pb.

Since the materials of the AMPC waste heaps show usually sand and loamy sand grain-size characteristics, it is more plausible to compare the contents of heavy metals in the samples from the surface of the AMPC waste heaps with PPC for sandy soils, although this level is more stringent. The enrichment factors of the tailings relative to PPC are on average 16 (up to 42) for Cd < 18 (up to 48) for Zn < 52 (up to 270) for Cu < 83 (up to 290) for Pb.

Thus, the solid material of the AMPC waste heaps shows both anomalous contents of the main ore and accompanying elements and significant shifts (relative to the mean and background levels) in metal proportions owing to preferential enrichment in Cu and Pb. The metal ratios in soils from the uncontaminated areas of the northwestern Altai (ordinary and southern chernozems) correspond to the mean levels for soils [22] and abundances in the uncontaminated soils of the world [23].

Erosion and deflation processes in the AMPC waste heaps cause the spatial migration of heavy metals and their additional enrichment in the adjacent components of natural landscapes. Enclaves of anthropogenic materials were observed in soils at distances of up to 300 m. In winter, the surface of the waste heaps is almost free of snow, because mixtures of snow and anthropogenic particles are transported by wind to the surrounding areas.

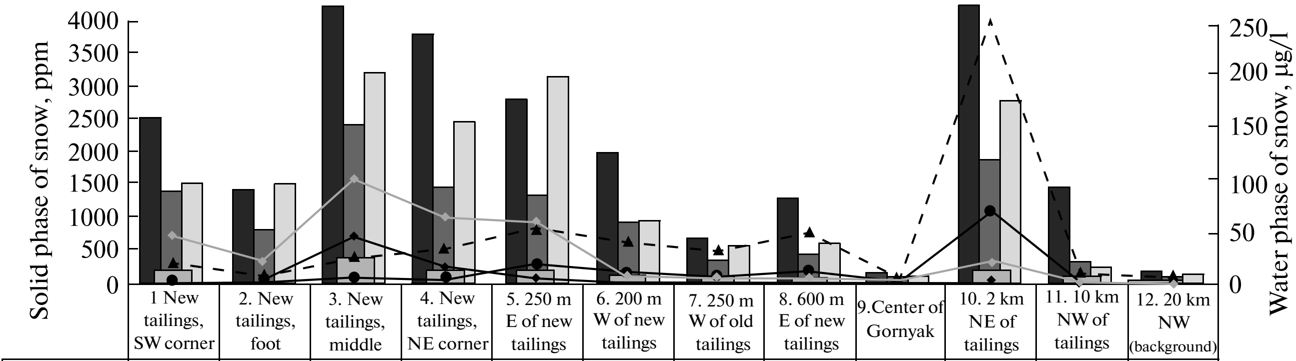
It is known that a snow cover has high sorption capacity and accumulates all atmospheric contaminants reflecting the existing air pollution [17]. According to our data, the solid phase of snow from the surface of the AMPC tailings and adjacent areas are enriched relative to PPC by a factor of 10 for Zn, Pb, As, and Ba, 7 for Cu, and 3 for Cd. The maximum daily dust loading and content of heavy metals in the solid phase of the snow cover were observed in the central part of the large tailings dump and areas east and northeast of it (sites 3, 4, 5, and 10 in Fig. 2). Since the material of the old tailings dump is poorer in heavy metals (Table 2), the snow near the old waste heap (site 7 in Fig. 2) shows lower Cu, Zn, Pb, and Cd contents. Note that the proportions of elements in the filtered solid phase of snow are more uniform that those of the waste heaps.

In the center of Gornyak (site 9), which is affected mainly by a heat and electric power plant, elevated dust content was observed in the snow cover, but the contents of heavy metals in the solid residue of snow were lower than those in other samples.

As to soluble metal species, snow from the surface of the tailings dumps is enriched in Cd and Zn relative to MPC_w [18] by factors of 10–40 (up to 44 μg/l) and 1.5 (up to 1580 μg/l). Snow from the surface of natural ecosystems remote from the pollution source is distinguished by elevated Cu, Pb, and Ba contents in the water phase (two times higher than MPC_w for Pb and Ba). The center of the impact is also characterized by higher ratios of Zn and Cd concentrations in soluble and solid fractions, whereas a decrease in the influence of the pollution source is accompanied by an increase in the ratio of dissolved and solid species of Cu and Pb (Fig. 3).

The lowest contribution of water-soluble compounds (relative to the solid fraction) is observed for Pb in all snow samples, because various Pb compounds show low solubilities [25]. According to data from the literature, the ability of the elements to form soluble compounds decreases from Cd and Zn to Cu and Pb: Ni > Cd > Ca $\gg$ Zn > Mn > Mg $\gg$ Co > Cr > Cu > Pb > Ag [26].

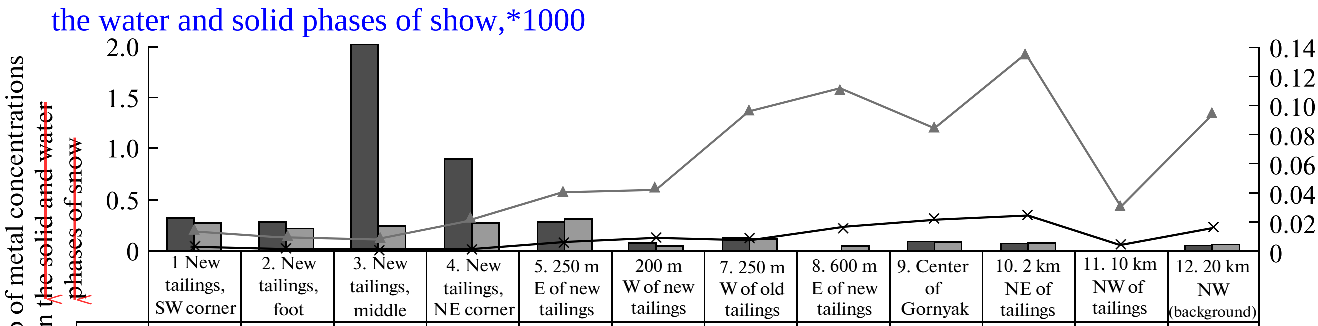
The slightly alkaline pH values (8) in the snow on the surface of the waste heap depress in general the migration of cation-forming elements. It is known that Zn can be somewhat more mobile in an alkaline environment [26, 27] compared with Cu and Pb. Copper and



	1 New tailings, SW corner	2. New tailings, foot	3. New tailings, middle	4. New tailings, NE corner	5. 250 m E of new tailings	6. 200 m W of new tailings	7. 250 m W of old tailings	8. 600 m E of new tailings	9.Center of Gornyak	10. 2 km NE of tailings	11. 10 km NW of tailings	12. 20 km NW (background)
Zn	2500	1400	6600	3800	2800	2000	660	1300	146	4600	1460	187
Cu	1370	775	2420	1450	1330	910	320	452	65	1875	324	76
Pb	1500	1470	3180	2470	3170	947	565	603	45	2800	258	129
Cd	8.6	3.5	51	13	11	5.6	4.6	4.5	0.58	13	6.5	1
Cd water	2.8	1.0	44	12	3	0.3	0.5	0.05	0.05	0.8	0.05	0.05
Cu water	18	5.7	55	31	53	39	31	50	5.5	253	10	7.2
Pb water	2.7	1.8	4.5	1.7	17	8.7	5	10	1	70	1	2
Zn water	660	312	1580	1000	914	76	68	68	13	344	11	9.3

Sampling sites

Fig. 2. Contents of heavy metals in the water phase (µg/l) and solid residue (ppm) of the snow cover of the AMPC tailings and adjacent areas.



	1 New tailings, SW corner	2. New tailings, foot	3. New tailings, middle	4. New tailings, NE corner	5. 250 m E of new tailings	200 m W of new tailings	7. 250 m W of old tailings	8. 600 m E of new tailings	9. Center of Gornyak	10. 2 km NE of tailings	11. 10 km NW of tailings	12. 20 km NW (background)
Cd	0.326	0.286	2.095	0.923	0.273	0.054	0.109	0.011	0.086	0.062	0.008	0.050
Zn	0.263	0.223	0.239	0.263	0.326	0.038	0.103	0.052	0.089	0.075	0.008	0.050
Cu	0.013	0.007	0.009	0.021	0.040	0.043	0.097	0.111	0.085	0.135	0.031	0.095
Pb	0.002	0.001	0.001	0.001	0.005	0.009	0.009	0.017	0.022	0.025	0.004	0.016

Sampling sites

Fig. 3. Ratios of metal contents in the solid and water phases of the snow cover of the AMPC tailings dumps and areas near the waste heaps.

Pb sulfates produced by the oxidation of primary sulfide ores are classic examples of poorly soluble compounds. According to published data, up to 100% Cd and 75% Zn occur in an exchangeable state in the solid phase of aerosol fallouts, whereas the exchangeable forms of Pb and Cu account for only 50 and 30%, respectively [26]. It was experimentally established that the oxidation of sulfide ores is accompanied by more rapid dissolution of Zn compounds compared with the other metals considered here. In addition, the period of half-removal from contaminated soils is relatively short for Zn and Cd: from 70 to 510 yr for Zn, 13–110 yr for Cd, 310–1500 yr for Cu, and 740–5900 yr for Pb [29]. The geochemical similarity of Cd and Zn and their extensive isomorphism [27, 30] suggest their joint migration and identical degrees of leaching.

The elevated (relative to MPC) content of Pb in the water phase of snow from areas remote from the waste heaps is explained by the influence of a highway: Pb halides are unstable and readily transformed into oxides, carbonates, and sulfates soluble in the weakly acidic media of natural landscapes [26].

Table 3. Annual airborne load of chemical elements on the environment in the area near the AMPC waste heaps, kg/km^2 yr

Sampling site	Chemical element					Total dust load, tonne
	As	Cd	Pb	Cu	Zn	
Central part of the waste heap (epicenter)	457	51	7684	5847	15948	2416
250 m east of the waste heap	461	22	6433	2700	5682	2029
2 km northeast of the waste heaps	65	6	1267	850	2082	453
Southwestern corner of the waste heap	74	5.1	887	810	1478	591
200 m to the west	12	0.5	76	73	161	80
10 km to the northwest	1.2	0.5	15	19	85	58
Background (20 km east of the waste heaps)	0.8	0.1	7.5	4.4	10.9	58

Using the data of snow sampling, we calculated the total environmental load of a chemical element owing to airborne pollution as the mass of the contaminant falling onto the unit area per unit time: $P_{tot} = CP_n$ (mg/km^2 day), where C is the element content in the snow, and P_n is the total mass of the contaminant (dust load). Given this value, the annual input of airborne toxicants into soil per unit area was determined (Table 3). ~~Since the composition of the contaminant is multielemental, integrated load was calculated.~~ It was established that the amount of elements precipitated per unit area owing to the air transport of dust decreases regularly with increasing distance, although the content of metals in the dust may be rather high (10 in Table 3 and Fig. 2). This is obviously related to the fact that fine particles are transported over considerable distances; they are especially rich in heavy metals but provide a minor contribution to the contamination of the territory. Thus, the data on heavy metals in the solid fraction of the snow cover give only qualitative estimates of dust for the area under investigation. In order to quantify the airborne environmental impact, the input of toxicants per unit area must be calculated.

It was shown that the spatial airborne migration of metals in the Altai is especially intense in the northeastern direction under the influence of prevailing southwesterly winds.

According to our measurements, the water of a lake on the surface of the tailings dump shows aggressive acidity (pH = 2–3) and chemical composition unfavorable for living activity. The concentrations of elements in the water of this lake are higher than the MPC values [18] by a factor 2.5 for Pb (79 μg/l), 6 for Ni (0.62 mg/l), 10 for Co (1 mg/l), 52 for Cu (52.3 mg/l), 250 for Zn (254 mg/kg), 940 for Cd (0.94 mg/l), and 1000 for Fe (304 mg/l).

Thus, the sequence of metal concentrations normalized to background values for natural water basins and MPC in the water medium of anthropogenic landscapes (Cd > Zn ⩾ Cu > Pb), including lakes, surface, and the water phase of the snow cover, is different from the sequence of MPC- and background-normalized metal concentrations in the solid components of the environment (Cu > Pb ⩾ Cd > Zn). The materials of tailings are relatively rich in Cu and Pb, and the liquid media are enriched in more labile Zn and Cd. According to literature data, among the two main paths of major ore component input into the soils and surface waters of areas adjacent to anthropogenic systems, water migration is most significant for Zn, and air migration is most significant for Pb [31].

The contents of major ore and accompanying elements in the anthropogenic materials of the walls, foots, and substrates of naturally vegetated and remediated parts of the tailings dumps of the AMPC and ZGRP are somewhat lower than in the waste heaps themselves, but are still higher than the background values in the soils of the natural landscapes of the northwestern Altai and PPC (Table 4).

The perimeters of the ZGRP tailings dumps are characterized by more uniform distributions of Cu, Pb, Zn, and Cd in the samples of anthropogenic material: the variation coefficients of Cu, Zn, Pb, Cd, and Hg are no higher than 36%. Since Au was extracted by the amalgamation method, the mean Hg content in the anthropogenic material of the ZGRP (1.74 ± 0.28 mg/kg) is twice the maximum content in the walls of the AMPC tailings (0.28–0.60 ppm).

Anomalous enrichment of a medium in heavy metals inevitably results in an increase in their contents in the biota (Table 4, Fig. 4). This is why the contents of the elements discussed here in the plants of primitive plant communities from the walls and foots of the tailings dumps of the AMPC and ZGRP are 8–100 times higher than the background levels in plants from uncontaminated ecosystems. For instance, alfalfa from the ZGRP waste heaps contains up to 14 ppm Cd, which is 467 times higher than the background level.

The most significant enrichment relative to the background contents in the plants of anthropogenic ecosystems was observed for Pb, Cd, and Zn. These metals are the first in the sequence of the degree of uptake by plants from the leaf surface owing to the precipitation of airborne dust (Cd > Pb > Zn > Cu > Mn >

Table 4. Mean contents of heavy metals in the subaerial part of plants, their roots, and substrates at foots, walls, and perimeters of the tailings dumps of the AMPC and ZGRP and uncontaminated areas in the northwestern Altai, ppm

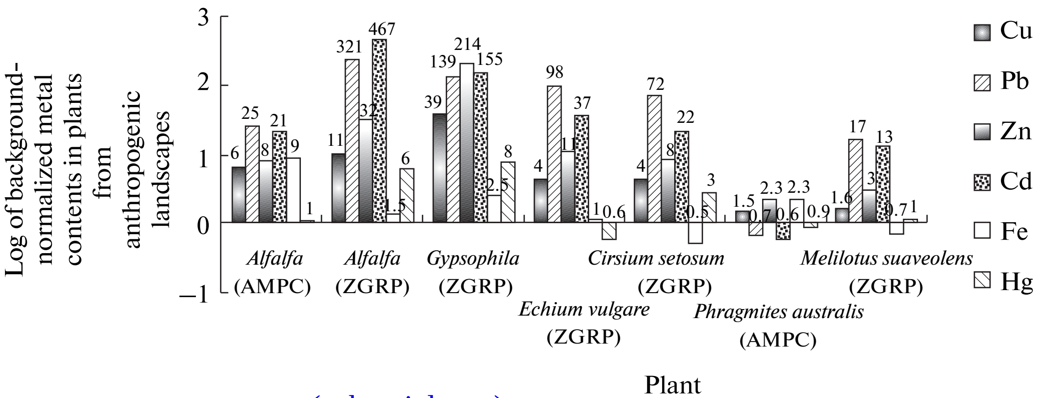
Object, reference			Cu	Pb	Zn	Cd	Fe	Hg
Walls of the AMPC tailings dumps ($n = 4$)	*Plants*	*subaerial part*	***63*** ± 38	***79*** ± 48	***340*** ± 277	***1.1*** ± 0.9	*3869 ± 348*	***0.07*** ± *0.03*
		roots	***229*** ± 76	***110*** ± 83	***1611*** ± 799	***15.1*** ± 8.3	*3070 ± 232*	***0.11*** ± *0.02*
	substrate		**793** ± 306	**647** ± 177	**1481** ± 777	**5.7** ± 3.6	**70875** ± 14713	**0.43** ± 0.07
Perimeter of the ZGRP tailings dump ($n = 7$)	*Plants*	*subaerial part*	*62 ± 20*	*347 ± 138*	*736 ± 498*	*7.1 ± 4.5*	*477 ± 171*	***0.23*** ± *0.09*
		roots	**81** ± *20*	**325** ± *109*	**1020** ± *476*	**30.5** ± *19.1*	**510** ± *171*	**0.17** ± *0.05*
	substrate		**398** ± 44	**2189** ± 268	**2055** ± 98	**8.9** ± 0.7	**10871** ± 3055	**1.73** ± 0.28
Background areas of the northwestern Altai ($n = 10$)	*Plants*	*subaerial part*	*8 ± 1.4*	***2.9*** ± *0.6*	*33 ± 6.1*	***0.13*** ± *0.05*	*798 ± 556*	***0.074*** ± *0.026*
		roots	*17 ± 2.5*	***2.4*** ± *0.4*	***18*** ± *2.7*	***0.08*** ± *0.03*	***1300*** ± *338*	***0.016*** ± 0.004
	substrate		**26** ± 1.7	**18** ± 0.8	**75** ± 3.5	**0.20** ± 0.02	**30030** ± 1145	**0.055** ± 0.005
Natural levels of contents in land grasses (published data)								
Kabata-Pendias, 1989 [33]								
Kabata-Pendias, Pendias, 2001 [23]			***1–20***	***0.1–10***	*12–47*	***0.07–0.27***	*18–1000*	***0.04–0.1***
Alekseev, 1987 [32]			n.d.	***1–5***	*7–95*	***0.2–0.8***	***n.d.***	***0.1–0.2***
Mean content in living matter (published data)								
Perel'man and Kasimov, 2000 [30]			***3.2***	***1***	***20***	***0.002***	***100***	***0.00n***
Standards for bulk content in soils: PPC [20], mean abundance [22]*, and MPC**								
Soil group (for PPC) a)			**33**	**32**	**55**	**0.5**	**38000***	**2.1****
b)			**66**	**65**	**110**	**1.0**		
c)			**132**	**130**	**220**	**2.0**		

Note: n.d. indicates no data. Soil groups: (a) sandy and loamy sandy; (b) acidic (loamy and clayey, $pH_{KCl} < 5.5$); and (c) near neutral and neutral (loamy and clayey, $pH_{KCl} > 5.5$KC). *After [22]. ** MPC.

Fe [32]), which is the main path of toxicant migration under the semiarid climate conditions of the northwestern Altai.

In order to obtain a comparative estimate for the intensity of trace element uptake by plants from background and contaminated areas, accumulation index, I_a, was calculated for the heavy metals as the ratio of element contents in the dry mass of plants and in the soil or substrate [33].

In all the plant species growing on anthropogenic substrates, the intensity of the absorption of Hg and other ore metals (except for alfalfa and Gypsophila) decreased. Despite the high (compared with the background) contents of Hg, Cu, Pb, and Zn (Table 4), their accumulation indexes in the plants of the waste heaps are lower than one. In most cases, the plants of anthropogenic ecosystems show an increase in the intensity of absorption of Fe, which is deficient in arid regions; this could be a protective mechanism, because the antago-



(subaerial part)

Fig. 4. Logarithms of metal contents in plants from anthropogenic substrates normalized to the background values (numbers are non-logarithmic values).

nistic interaction between Fe and heavy metals is known for a number of species [33]. For instance, the level of Fe content in the alfalfa from the ZGRP waste heap is not high, 570 ppm, whereas other metals (Cd, Zn, Pb, and Cu) are accumulated in this plant much more extensively. The Fe content in the alfalfa from the AMPC waste heap is up to 3310 ppm, but the contents of the main ore elements are significantly lower than those in the alfalfa from the ZGRP waste heap.

Note that the Fe content of the subaerial parts of the plant species is significantly higher or similar to that in the rhizomass (acropetal coefficient is lower than one), which is explained by the high ascending ability of the element in the pant organism: iron occurs at the beginning of the sequence of element mobility in plants: Fe > Cu > Mn > Cd > Zn > Pb [32].

Different plant species growing on contaminated soils near the waste heaps of the AMPC and ZGRP show more significant differences in element contents compared with individual samples of anthropogenic materials. The intensity of element uptake increases in some plants (alfalfa and Gypsophila) by a factor of several, and the contents of metals in plant tissues increases relative to the background values by a factor of several tens (Fig. 4). This is obviously related to the species-specific features of these plants.

The heavy metal contents are usually no higher than the background levels in the tissues of *Phragmites australis* (common reed) and *Melilotus suaveolens* (sweet clover). These are species with barrier-type element uptake.

Under the conditions of environmental pollution, the "background" accumulation indexes of element decrease in *Echium vulgare* (viper's bugloss) and *Cirsium setosum* (thistle); nonetheless, the high contents of heavy metals in the substrate results in an increase in their contents in tissues (especially Pb, up to 266 ppm and 315 ppm, and Cd, up to 2.2 ppm and 4.1 ppm, respectively) above the background level.

Both the content and the intensity of uptake of heavy metals, especially Pb, Zn, and Cd, increase by a factor of several in *Gypsophila patrinii* growing under the conditions of an anthropogenic impact. For instance, an increase in Cu content in the substrate by a factor of 16 (up to 350 ppm) results in plant enrichment in Cu by a factor of 39 (from 2 to 90 ppm), an increase in Zn content in the substrate by a factor of 26 (from 74 to 1920 ppm) is accompanied by plant enrichment by a factor of 213.5 (from 10 to 2135 ppm), and an increase in Cd content in the substrate by a factor of 43 (up to 8.7 ppm) is accompanied by plant enrichment by a factor of 155 (up to 17 ppm).

CONCLUSIONS

The contents of Zn, Cu, Pb, Cd, As, Hg, and Ba in the solid material of the tailings dumps of the AMPC and ZGRP are significantly higher than the MPC, PPC and background levels of the elements in zoned chernozems. The AMPC waste heaps are both sources of environmental pollution with heavy metals and materials for reprocessing and recovery of Cu, Zn, and Pb.

The eolian transport of the material of tailings dumps is one of important paths of heavy metal input into the environment under the semiarid climate conditions of the northwestern Altai. The spatial air migration of metals with dust from the surface of waste heaps occurs more intensely in the northeastern direction under the influence of southwesterly winds prevailing in the Altai.

In the tailings dumps, element sequences are shifted (relative to the background, MPC, and foreign standards) owing to relatively high Cu and Pb contents in the solid materials and enrichment of the liquid media (water and snow) in more labile and leachable elements (Zn and Cd).

The contents of the main ore and accompanying elements in the plants of the anthropogenic landscapes of the northwestern Altai are much higher than those in plants from the uncontaminated ecosystems (especially, Cd, Zn, and Pb) and significantly variable. The absorption indexes of the main ore metals (Cu, Pb, Zn, and Hg) in plants decrease under the conditions of anthropogenic contamination, whereas the uptake of Fe, which is deficient in arid regions, increases.

Gypsophila patrinii is characterized by barrier-free element uptake and significantly contributes to the formation of the phytocoenoses of anthropogenic landscapes. This species can be recommended for the phytomeditation of contaminated soils as a plant accumulating heavy metals.

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REFERENCES

1. T. A. Al, C. J. Martin, and D. W. Blowes, "Carbonate Mineral/Water Interactions in Sulfide-Rich Mine Tailings," Geochim. Cosmochim. Acta **64**, 3933–3948 (2000).
2. M. P. Boulet and A. C. L. Larocque, "A Comparative Mineralogical and Geochemical Study of Sulfide Mine Tailings at Two Sites in New Mexico, USA," Environ. Geol., Nos. 2–3, 130–142 (1998).
3. P. Madejon, J. M. Murillo, and T. Maranon, "Bioaccumulation of As, Cd, Cu, Fe and Pb in Wild Grasses Affected by the Aznalcollar Mine Spill (SW Spain)," Sci. Tot. Environ., Nos. 1–3, 105–120 (2002).
4. E. Stoltz and M. Greger, "Accumulation Properties of As, Cd, Cu, Pb and Zn by Four Wetland Plant Species Growing on Submerged Mine Tailings," Environ. Exp. Botany, No. 3, 271–280 (2002).

5. I. A. Turchaninov and M. A. Iofis, *Exploration of the Complex Ore Deposits of the Karelia–Kola Region,* Ed. by V. M. Busyrev (AN SSSR, Apatity, 1988) [in Russian].
6. V. N. Avdonin, "Anthropogenic Sulfide Oxidation at the Krasnogvardeiskoe Deposit, Urals," in *Materials on Mineralogy of the Uralian Deposits* (UNTs AN SSSR, Sverdlovsk, 1984), pp. 63–69 [in Russian].
7. L. N. Kovalenko, E. Yu. Kulagov, and G. N. Elistratova, "Mechanism of the Anthropogenic Oxidation of Highly Cupriferous Ore of the Talnakh Ore Cluster," Izv. Vyssh. Uchebn. Zaved., Geol. Razved., No. 7, 66–70 (1984).
8. I. A. Tarasenko and A. V. Zin'kov, *Ecological Consequences of the Mineralogical–Geochemical Transformation of the Mine Tailings of the Sn–Ag–Pb–Zn Ores* (Dal'nauka, Vladivostok, 2001) [in Russian].
9. S. B. Bortnikova, O. L. Gas'kova, and E. P. Bessonova, *Geochemisytry of Anthropogenic Systems*, Ed. by G. N. Anoshin (Geo, Novosibirsk, 2006) [in Russian].
10. N. P. Belkanova, G. I. Karavaiko, and Z. A. Avakyan, "Destruction of the Siloxane Bond of Quartz by *Vacillus mucilaginosus*," Mikrobiologiya **54**, 27–30 (1985).
11. L. K. Yakhontova, A. P. Grudev, and V. V. Zuev, "Problems of the Study of the Mineral Substrate–Microorganism System," Vestn. Mosk. Gos. Univ., Ser. 4., Geol., No. 5, 80–92 (1994).
12. E. F. Emlin, N. P. Konyukhova, and V. Yu. Ipanov, *Geochemical Principles of Urbanization on the Urals* (Sverdlovsk, 1988) [in Russian].
13. V. S. Arzhanova and P. V. Elpat'evskii, "Mining Type of Anthropogenesis: Methodical Aspects and Results," in *Reports on International Scientific-Practical Conference "Geochemistry of the Biosphere," Russia, 2006* (Moscow–Smolensk, 2006), pp. 42–44 [in Russian].
14. V. A. Chudaeva, *Migration of Chemical Elements in Far East Waters*, Ed. by S. L. Shvartsev (Dal'nauka, Vladivostok, 2002) [in Russian].
15. N. A. Roslyakov, *Oxidation Zone of Sulfide Deposits in the Western Altai* (Nauka, Novosibirsk, 1970) [in Russian].
16. *Results of Prospecting–Assessment Work for Gold and Silver within the Anthropogenic Deposits of the Zolotushinskii Concentrating Mill and the Loktevskii Silver-Refining Plant for 1999-2001. A Report.* (Zmeinogorsk, 2001) Book 1.
17. *Methodical Recommendations on the Estimation of the Degree of Pollution of Atmospheric Air of the Settlements by Metals on Their Content in the Snow Cover and Soil* (IMGRE, Moscow, 1990) [in Russian].
18. Yu. V. Novikov, K. O. Lastochkina, and Z. N. Boldina, *Methods of Basin Quality Study*, Ed. by A. P. Shitskova (Moscow, 1990) [in Russian].
19. *Agrochemical Methods of Soil Study* (Nauka, Moscow, 1975) [in Russian].
20. *Approximate Permissible Concentrations of Heavy Metals and Arsenic in Soils. Hygienic Standards 2.1.7.020-94* (Goskomsanepidnadzor Rossii, Moscow, 1995) [in Russian].
21. A. Kloke, "Richtwerte'80. Orientirungsdaten fur tolerierbare einiger Elemente in Kulturboden," Mitt. VDLUFA, Nos. 1–3, 9 (1980).
22. A. P. Vinogradov, *Geochemistry of Rare and Dispersed Elements in Soils* (Akad. Nauk SSSR, Moscow, 1957) [in Russian].
23. A. Kabata-Pendias and H. Pendias, *Trace Elements in Soils and Plants* (CRC Press, Boca Raton, 2001).
24. *Methodical Recommendations on Geochemical Studies for Estimating the Environmental Influence of Projected Mining Enterprises* (AN SSSR, IMGRE, Moscow, 1986) [in Russian].
25. @*Brief Reference Book on Chemistry*, Ed. by I. T.Goronovskii, Yu. P. Nazarenko, and E. F. Nekryach (Naukova dumka, Kiev, 1987) [in Russian].
26. M. A. Glazovskaya, *Methodological Principles of the Estimation of Ecological–Geochemical Resistivity of Soils to Anthtropogenic Impacts* (Mosk. Gos. Univ., Moscow, 1997) [in Russian].
27. V. V. Ivanov, *Ecological Geochemistry of the Elements. A Reference Book*, Ed. by E. K. Burenkov (Nedra, Moscow, 1996) [in Russian].
28. J. Jurjovec, C. J. Ptacek, and D. W. Blowes, "Acid Neutralization Mechanisms and Metal Release in Mine Tailings: A Laboratory Column Experiment," Geochim. Cosmochim. Acta **66** (9), 1511–1523 (2002).
29. Orlov, D.S., Malinina, M.S., and Motuzova, G.V., *Chemical Pollution of Soils and Their Protection*, (Agropromizdat, Moscow, 1991).
30. A. I. Perel'man and N. S. Kasimov, *Landscape Geochemistry* 3rd Ed. (Astreya, Moscow, 1999) [in Russian].
31. E. V. Pryanichnikova, Extended Abstracts of Candidate's Dissertation in Geology and Mineralogy (Moscow, 2005) [in Russian].
32. Yu. V. Alekseev, *Heavy Metals in Soils and Plants* (VO Agropromizdat, Leningrad, 1987) [in Russian].
33. A. Kabata-Pendias and H. Pendias, *Trace Elements in Soils and Plants* (CRC Press, Boca Raton, 1984).

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