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Geochemical disturbance of soil cover in the nonferrous mining centers of the Selenga River basin

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Abstract The anthropogenic geochemical transformation of soil cover in large nonferrous mining centers of the Selenga River basin was assessed. The results of the geochemical survey of 2010–2012 revealed the spatial distribution patterns and abundances of 18 hazardous heavy metals and metalloids in the soils of Erdenet (Mongolia) and Zakamensk (Buryat republic, Russian Federation). In both cities, mining activities disturbed soil cover which accumulates Mo, Cu, As, Sb, W in Erdenet and Bi, W, Cd, Be, Pb, Mo, Sb in Zakamensk. Maximum accumulation of elements in Erdenet is restricted to the industrial zone. In Zakamensk, it has spread on ½ of the territory with the degree of multielemental pollution exceeding the extremely dangerous level by 16 times. The effect of mining centers on the state of the river system is local and does not spread to the Selenga River. Downstream from Erdenet, an artificial pool intercepts heavy metal and metalloid flows of the Erdenetii-Gol River. By contrast, downstream from the tailing dumps of the Dzhida tungsten–molybdenum plant the concentrations of ore elements W and Mo and their accessories Bi and Cd in the Modonkul River exceed background values by 146, 20, 57, and 21 times, respectively, decreasing by an order of magnitude 30 km downstream.

Introduction

Mining nonferrous ores is one of the most powerful agents of anthropogenic impact on the environment in terms of its geographic extension and disturbance of landscapes adjacent to the mining areas. Large amounts of chemical elements arrive with metal ores into the environment and contaminate soils, plants, surface, and ground waters. The environmental and geochemical implications of development of deposits of nonferrous metals and other raw materials are actively studied in different regions (Elpat'evskii 1993; Milu et al. 2002; Avessalomova and Kasimov 2004; Owor et al. 2007; Blagodatskaya et al. 2008; Gomez-Alvares et al. 2009; Lizarraga-Mendiola et al. 2009; Garcia-Sanchez et al. 2010; Candeis et al. 2011; Hudson-Edwards et al. 2011; Rastmanech et al. 2011; Puzanov et al. 2012; Serbula et al. 2012; Rey et al. 2013; Tatsy 2013; Schaidera et al. 2014).

A great number of studies focuses on contamination of various natural media in the impact zones of ore-dressing enterprises. Associations of chemical

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elements in different physical and chemical phases of soil were revealed (Yurgenson et al. 2008; Favas et al. 2011; Mileusnic et al. 2014), and the environmental fate and transport of heavy metals (HMs) and metalloids in dust and aerosol from mining activities were observed (Brotons et al. 2010; Taylor et al. 2010; Csavina et al. 2012), with special attention to waste storage sites, tailing ponds and neighboring soils (Acosta et al. 2011; Anawar et al. 2011; Conesa et al. 2011; Martínez-Pagán et al. 2011; Martínez-Martínez et al. 2013). Biogeochemical studies deal with trace element concentration in roots and leaves of different plant species (Martínez-Sánchez et al. 2012; Santos et al. 2014), and technogenic changes in rates of HM migration in soil–plant system (Alloway 2012; Wahsha et al. 2012; Ghaderian and Ravandi 2012; Santos et al. 2012).

The analysis of publications on this issue showed that there are no common approaches to ecological assessment of mining landscapes that account for their lithological and geochemical features typical for natural ore anomalies. Behavior of different pollutants and properties of their geochemical fields are insufficiently understood, which hampers reliable estimation and development of spatial prediction models of contamination patterns of mining landscapes. In this context, the aim of the current work was to assess the anthropogenic geochemical transformation of soil cover in large nonferrous mining centers of the Selenga River basin, in the cities of Zakamensk and Erdenet. The Erdenet porphyry copper and Dzhida tungsten–molybdenum deposits are the largest in Trans-Baikal. Their geological structure and geochemical features have been determined, and geological–economic models were developed (Byambaa 2007; Gavrilova et al. 2010; Timofeev et al. 2015; Povilaitis 1960; Ecological-economic characterization of problem areas 1997; Yurgenson et al. 2008; Smirnova and Plyusnin 2013). However, the ecogeochemical state of landscapes in this region is poorly known. The following tasks were posed:

- determine the concentrations of heavy metals (HMs) and metalloids in background soils and specify priority pollutants of urban soils;
- assess the environmental hazard of soil contamination with HMs and metalloids in the main land-use zones of the cities; and

- reveal the effect of mining and processing plants (MPPs) on trace element composition of bottom and suspended sediments in the tributaries of the Selenga river which serve as an integral indicator of anthropogenic impact on their watersheds.

Objects of study

Natural conditions

Field studies were fulfilled in two mining regions: the city of Erdenet (Mongolia) and the city of Zakamensk (Buryat republic, Russian Federation). Current population of Erdenet is 87,000 people; that of Zakamensk is 11,400 people. Both cities are located in the basin of the Selenga, the largest river flowing into Lake Baikal (Fig. 1). The climate is sharply continental, with cold winters and warm humid summers delivering up to 60–70 % of annual precipitation.

Erdenet

The city occupies an area of 180 km^2 on the Selenga–Orkhon interfluve which is an elevated rolling plain with absolute heights of 1000–2150 m. The city is located in the valley of the Erdenetii-Gol River, the left tributary of the Orkhon River. The riverbed in the southern part of the Erdenet remains dry in the summer; in the center of the city, water flow appears due to groundwater discharge. Meandering riverbed is a few meters wide, embedded in poorly permeable clay sediments, with a small section cutting through gravelly deposits (Smirnov and Krashnikov 1976).

The ore body is composed of volcanogenic and volcanogenic-sedimentary rocks of the Permian Khanui Series penetrated by the Upper Permian granitoids of the Selenga complex. This is a porphyry molybdenum–copper body with commercial concentrations of Re, Ag, and Se; Pb, Zn, As, Sr, Bi, Co, Ni, Ge, Ta, Ga, In, and Cd are also present in the ores. The body comprises three rock associations: gabbroids, granitoids, and subalkaline granites with sienogranites (Berzina and Sotnikov 2007).

The studied area belongs to the zone of mountain steppes and forests, where the alternation of forest and steppe is controlled by mountain topography and slope aspects (Yunatov 1950). Natural vegetation persists on

Fig. 1 Location of the
study objects

the slopes of Erdenetii-Gol and Gaveli-Gol river
valleys; this is a low-grass steppe with crested hair-
grass (*Koeleria pyramidata*), bulbous bluegrass (*Poa
botryoides*), hairy feathergrass (*Stípa capilláta*),
prairie sagewort (*Artemisia frigida*), etc., (Vostokova
and Gunin 2005), as well as natural larch (*Larix*) forest
closer to the tops. In the city, vegetation consists of
larch and poplar (*Populus*) plantations, with grass
cover almost absent due to intensive pasturing.

The natural soils include deep slightly saline
solonetzic/deeply solonetzic dark chestnut and
slightly saline non-solonetzic dark chestnut soils
(Karpel 1975) which correspond Haplic Kastanozems
Sodic and Haplic Kastanozems according to the WRB
classification. In residential and industrial zones of the
city, the upper horizon consists of a filled mixed
humus-enriched layer with some construction, munic-
ipal, and industrial wastes; it is identified as urbic
(Dobrovol'skyi 1997). The parent rocks include (1)
Quaternary alluvial deposits, (2) Early Mesozoic
porphyritic intrusives, (3) Triassic volcanic series
and subvolcanic intrusives, (4) granodiorite and gran-
ite series of the Permian Selenga complex, and (5)

gabbro and diorite series of the Permian Selenga
complex.

Zakamensk

The study area of 45 km^2 is located 460 km southwest
of the city of Ulan-Ude in the southern part of the
Mongolian–Siberian mountain belt; it is confined to
the Selenga–Vitim zone (Ufimtsev 1991). This is a
strongly dissected upland with relative heights of
watershed ridges over the valley bottoms reaching
300–400 m (Zinov'eva et al. 2011). The city is located
on the Modonkul River 28 km in length, a right
tributary of the Dzhida River, which flows into the
Selenga. The valley at the boundary of watersheds is
3–7 km wide, with the bottom 300–350 m wide;
valley sides are mainly steep, with an erosion cut of up
to 2.0–2.5 m; riverbed width varies from 10 to 30 m.
The river has numerous tributaries: Barun-Naryn,
Zun-Naryn, Inkur, etc.

The area is located at the boundary of two regional
geological structures formed by Lower Paleozoic
carbonate-terrigenous   strata   of   the   Dzhida

synclinorium and granitoid intrusives of the Modonkul massif. In the Lower Paleozoic, the largest ore-controlling (confining the stocks dykes of the ore-bearing Gudzhir granitoids) and ore-enclosing (Pervomaiskoe, Inkur, and Kholtoson deposits) fault of northwestern orientation was formed; along the fault zone, the Lower Paleozoic volcanogenic-sedimentary rocks contact with granitoids of the Dzhida intrusion. Industrial Pervomaiskoe, Inkur, and Kholtoson deposits contain ore elements W, Mo and non-ore elements Cu, Zn, Pb, Be, Ag, Cd, Hg, Co, Ni, and Cr.

The natural forest vegetation includes white birch (*Bétula platyphýlla*) and Siberian larch (*Lárix sibírica*) in combination with partially anthropogenically modified meadow steppes (Papov 2007). There are poplar and larch plantations within the city.

Under undisturbed conditions, soil cover consists of soddy taiga, gray forest, and alluvial meadow soils (Nogina 1964) which relate to Cambisols, Luvisols, and Mollic Fluvisols according to the WRB classification. Within the city, as in Erdenet, large amounts of construction and municipal wastes are present in the upper soil horizon. The soils are developed from (1) Quaternary alluvial deposits composed of coarse gravel, loamy sands, and loams; (2) first stage of Paleozoic Dzhida complex (plagiogranites, granodiorites, and diorites); (3) Middle Permian–Lower Triassic Cherny Yar series (orthophyres, keratophyres, tuffs, and tuffolavas); and (4) Cambrian complex (sandstones, siltstones, and limestones).

Technogenic impact

Mining plants are city-forming enterprises. The Erdenet MPP is in operation since 1976 and now produces about 530 thousand tons of copper concentrate and 4.5 thousand tons of molybdenum concentrate per year. The open-pit method is used, with more than 440 million m^3 of rock mass extracted (www.erdenetmc.mn, 2013). The Dzhida tungsten–molybdenum plant functioned from 1934 to 1997; it developed the stockwork molybdenum (Pervomaiskoe), tungsten sulfide (Inkur and Kholtoson ore and placer deposits), and gold (Myrgensheno, Ivanovka) fields.

Mining waste is stored in tailings; in Erdenet, the tailing occupies more than 1500 ha in the Zuna-Gol River valley, where a dam more than 85 m in height was created; in Zakamensk, 44.5 million tons of waste is distributed among the Dzhida (bulk), Barun–Naryn

(slurry), and emergency tailings. In 2011, 3.5 million tons of waste is transferred from the latter tailing to the upper part of the Barun–Naryn tailing. Since 2010, the Zakamensk joint-stock company has been processing the tailings from the Dzhida tungsten–molybdenum plant with the formation of a new dump site in the Zun-Naryn River valley.

Sources of landscape contamination in Erdenet include the Erdenet thermal power plant, which is located between the mining and residential zones, and uses brown coal from the Sharyngol and Baganur quarries. As is with most sulfur coals, the used brown coal is enriched with chalcophilic elements (As, Bi, Mo, Sb, W, etc.). The closely located Erdenet Hivs Company produces wool carpets, machine tapestries, and clothes from sheep and camel hair, cashmere, and felt. Wool dyes contain Cr, Ni, Zn, and Cd (Saet et al. 1990), which can arrive with discharges to surface and ground waters.

There are thermal power plant which utilizes heating oil, enterprises of wood harvesting and conversion, crude iron, steel, bronze casting, construction materials plant and food production alongside mining enterprises in Zakamensk.

Land-use zoning

In the studied areas five land-use zones were distinguished: two residential—multistory and single-story (ger houses in Erdenet and dachas in Zakamensk) zones; an industrial zone; a traffic zone; and pasture (Erdenet) or natural recreation (Zakamensk) zone. The pastures and recreation zones along the periphery of the cities occupy the largest areas. The background areas include the top and upper parts of gentle slopes of the Erdenet-Gol and Modonkul River valleys. They locate within the same geological structures, thus can be regarded as natural analogues of urban areas.

Methods and materials

The soil-geochemical survey was performed in Erdenet in the summer of 2010 and 2011 and in Zakamensk in 2012. Mixed soil samples (in Erdenet, 226 samples, including 32 background ones; in Zakamensk, 129 samples, including 24 background ones) composed of 3–4 replications were taken from the surface 0- to 10-cm horizon in a grid pattern with

spacing of 500–700 m, which ensured the spatial resolution necessary for composing large-scale geochemical maps. The number and location of sampling points were determined with consideration for the geological heterogeneity of the area.

Bottom sediments were sampled from the rivers Erdenetii-Gol (3 samples, including 1 background sample), Modonkul (3 samples, including 1 background sample), and Dzhida (2 samples).

The bulk concentrations of 54 HMs and metalloids in soil and bottom sediment samples were analyzed by ICP-MS and ICP-AES at the All-Russia Institute of Mineral Resources (Moscow). For thorough analysis, 17 priority pollutants belonging to hazard classes I (Zn, As, Pb, Cd), II (Cr, Co, Ni, Cu, Mo, Sb), and III (V, Sr, Ba, W) were selected, as well as some others (Sn, Cs, Bi).

The obtained concentrations of HMs and metalloids in the background soil samples (C_b) were grouped depending on the parent rock and compared to their mean global values for soils C_g (Kabata-Pendias 2011) by calculating the global enrichment and dispersion factors: $EF_g = C_b/C_g$ and $DF_g = C_g/C_b$, respectively. The comparison was made with the global values for soils proposed by Kabata-Pendias (2011), as this work deals only with the surface horizons, where the leveling role of soil organic matter is high. Using the averaged EF_g and DF_g values, we plotted geochemical spectra, which characterize the geochemical features of background soils developed from different parent rocks. Enrichment and dispersion factors for background bottom sediments were calculated with respect to soils prevalent in the background conditions.

The geochemical transformation of urban soils was also assessed with consideration for the lithological–geochemical heterogeneity of the area: The local factors of enrichment $EF_l = C_u/C_b$ and dispersion $DF_l = C_b/C_u$ (where C_u is the concentration of the element in urban samples) were calculated against the background values for the same parent rock. The geochemical spectra of urban soils were plotted from the data averaged for the entire city and separate land-use zones; their analysis allowed to identify priority pollutants. Anthropogenic geochemical changes in bottom sediments were determined by comparison with non-contaminated river sediments in the upper reach.

The visualization of soil-geochemical data was performed by local interpolation, or kriging method in MapInfo 11.5 and Surfer 11 packages. The geochemical maps were based on the plans of the cities and geological maps for Erdenet (Watanabe and Stein 2000) and on sheet M-48-51-G, 1997 (Zinov'eva et al. 2011), for Zakamensk with the authors' correction. To prevent the overestimation of area contamination, points with concentrations of HMs and metalloids exceeding the average levels in the city soils by 3 standard deviations and more were excluded from the interpolation. They are denoted on the maps as point anomalies.

The data were statistically processed in Statistica 8 and MS-Excel packages. The means (m), errors of the means, standard deviations (σ), variation coefficients ($C_v = \sigma/m \times 100\%$), maximum (max) and minimum (min) values, correlation coefficients (r), and other statistical parameters were calculated for each sampled population.

The ecological–geochemical assessment of the state of urban soils is based on parameters developed for the joint environmental–geochemical and sanitary–hygienic studies of the urban environment:

- maximum permissible concentrations (MPCs) and provisional permissible concentrations (PPCs) adopted in the Russian Federation (GN 2.1.7.2041-06, GN 2.1.7.2042-06) and Mongolia (MNS 5850:2008);
- danger coefficients showing the excess of concentrations of particular elements over the MPC/PPC values $K_o = C_u/MPC$;
- integrated index of risk, which is proposed to be calculated against the global background C_g with consideration for the toxicity of pollutants (Timofeev et al. 2015): $IIR = \sum(EF_g \cdot K_T) - (n - 1)$, where $EF_g = C_u/C_g$ is the global enrichment factor, n is the number of elements with $EF_g > 1.3$, and K_T is the toxicity coefficient (1.5, 1.0, and 0.5 for the elements of hazardous classes I, II, and III, respectively) (Vodyanitskii et al. 2012). The IIR characterizes the environmental hazard of the increased concentrations of HMs and metalloids in urban soils and technogenic surface formations and has 5 gradations (Table 1). As a standard for comparison, we used global clarkes of topsoils rather than regional background with much higher concentrations of HMs and metalloids which often exceed health regulations.

Table 1 Levels of soil contamination with HMs and metalloids and the corresponding gradations of environmental hazard (Saet et al. 1990; Kasimov et al. 2012)

IIR	Degree of environmental hazard
<16	Permissible
16–32	Moderately dangerous
32–64	Dangerous
64–128	Very dangerous
>128	Extremely dangerous

Results and discussion

Geochemical specialization of background soils

The peculiar features of the local geochemical background were revealed by analysis of geochemical data for natural soils developed on different parent rocks: five rocks in Erdenet and four rocks in Zakamensk. Each rock is characterized by various concentrations of HMs and metalloids, which are also traced in the surface soil horizons (Table 2). The number of background samples taken at each plot is proportional to its area S.

The rocks of the Permian Selenga complex ($S = 50\%$ of the studied area), which were represented by 13 soil samples, are typical of Erdenet. The highest mean concentrations of V, Cr, Co, Ni, Zn, and Sr among the selected background soil groups were found in these samples, as well as the maximum concentrations of ore elements and their accessories: Cu, Zn, Mo, and W. Early Mesozoic porphyry intrusives are distributed in a limited area (3–4% of the studied area). High concentrations of As, Cd, Sn, and Pb are typical of the soils developed from these deposits. The lowest concentrations of the considered elements are observed in the surface soil horizons in the distribution range of the Triassic volcanic series and subvolcanic intrusives.

The background soils in Zakamensk developed from the Dzhida complex of Paleozoic age composed of granodiorites, diorites, and plagiogranites and are characterized by the highest mean concentrations of Zn, Co, Cu, Mo, Ba, and W. Similar geochemical features are revealed in the natural soils formed on the Permian Selenga complex in Erdenet, which consist of the same rocks. The background soils on alluvial

deposits have the highest mean values for As, Cr, Ni, Sr, Bi, Cs, and Sn. The lowest mean concentrations of almost all elements are noted in the soils on the Cherny Yar series and the Cambrian complex. Exceptions are Sb and V for the former, and Cd and Pb for the latter.

The generalized characterization of local geochemical background for each mining center was obtained by comparing the mean background values calculated for all the selected samples with the mean global values for topsoils (Kabata-Pendias 2011). For this purpose, geochemical spectra for each studied region were plotted (Fig. 2).

The background soils near Erdenet are enriched against the global background with $Mo_{3.0}Sr_{2.1}W_{1.8}$-$As_{1.4}$ (subscripts denote the EF_g values). Most of the elements, except Sr, are chalcophilic (Greenwood and Ernsho 1997). Granites and granosyenites are the main sources of HMs in background soils (Gavrilova et al. 2010). The highest dispersion is found for Cd ($DF_g = 1.6$) and Bi ($DF_g = 1.5$).

In the surface horizons of background soils in Zakamensk, a more wide association of elements was found: these are ore elements $W_{11.4}Mo_{4.0}$ and accessory metals $Sb_{2.9}Cs_{2.0}Bi_{1.9}Zn_{1.5}Co_{1.5}$. All elements, except for Cs, are also chalcophilic (Greenwood and Ernsho 1997); i.e., they occur in the environment as sulfide minerals, which is typical for this region—the Inkur and Kholtoson ore bodies have an elevated sulfur concentration, which is also manifested in the ore-enclosing and host rocks. The concentrations of the other elements (Ba, Sr, Cu, V, Ni, Pb, Sn, Cr, As, Cd) in the soils are similar to the mean global values for topsoils.

Thus, the elevated concentration of chalcophilic elements (W and Mo) is a common feature of background soils in the studied mining landscapes. Petrochemical features of morphostructures (confinement to the arsenic geochemical province) are also manifested in Erdenet, in contrast to Zakamensk.

Geochemical specialization of urban soils

Priority pollutants of urban soils in different land-use zones were determined from the local enrichment factors EF_l against the background soils developed on the same parent rocks (Table 3). The industrial zones are the most polluted in both mining centers. In the industrial zone of Erdenet, $Mo_{10.7}Cu_{10.6}As_{1.6}Sb_{1.5}$-$W_{1.5}$ are accumulated (subscripts denote the EF_l

Table 2 Statistical and geochemical parameters for HMs and metalloids in the surface (0- to 10-cm) horizons of background soils near the cities of Erdenet and Zakamensk

Parameter	V	Cr	Co	Ni	Cu	Zn	As	Sr	Mo	Cd	Sn	Sb	Cs	Ba	W	Pb	Bi
Erdenet																	
Soils on Quaternary deposits (n* = 8)																	
Mean, mg/kg	142.1	49.5	14.8	25.5	34.8	82.3	8.6	308.8	2.3	0.2	2.7	1.4	4.9	575.0	2.0	22.4	0.3
σ, mg/kg	30.5	11.4	4.1	7.2	6.3	21.5	1.4	82.0	1.8	0.1	0.5	1.5	0.6	94.3	0.5	5.1	0.1
EF_g (DF_g)**	1.1	(1.2)	1.3	(1.1)	(1.1)	1.2	1.3	1.8	2.1	(1.6)	1.1	2.1	(1.0)	1.3	1.2	(1.2)	(1.5)
Soils on Early Mesozoic porphyry intrusives (n = 2)																	
Mean	165.0	54.5	16.5	26.5	50.5	95.5	13.0	325.0	3.9	0.3	3.2	1.2	4.1	600.0	3.4	25.5	0.3
σ	7.1	0.7	0.7	0.7	10.6	20.5	1.4	7.1	0.8	0.0	0.7	0.0	0.4	113.1	1.0	4.9	0.0
EF_g (DF_g)	1.3	(1.1)	1.5	(1.1)	1.3	1.4	1.9	1.9	3.5	(1.5)	1.3	1.8	(1.2)	1.3	2.0	(1.1)	(1.3)
Soils on Triassic volcanic series and subvolcanic intrusives (n = 4)																	
Mean	165.0	47.0	16.0	23.5	50.8	80.5	8.5	340.0	2.9	0.2	3.1	0.8	3.3	792.5	5.4	23.8	0.3
σ	45.1	6.5	6.9	6.1	21.1	12.7	3.6	72.1	1.2	0.0	0.8	0.3	0.8	125.3	4.5	4.8	0.2
EF_g (DF_g)	1.3	(1.3)	1.4	(1.2)	1.3	1.2	1.2	1.9	2.7	(1.7)	1.2	1.2	(1.5)	1.7	3.2	(1.1)	(1.2)
Soils on granodiorite and granite series of the Permian Selenga complex (n = 13)																	
Mean	172.3	56.8	17.2	30.3	42.8	98.0	8.3	410.0	1.9	0.3	3.0	1.1	4.6	550.8	2.5	20.9	0.3
σ	42.3	19.9	5.1	8.8	11.0	16.7	3.4	153.0	0.6	0.0	0.7	0.5	1.2	154.8	1.9	4.5	0.1
EF_g (DF_g)	1.3	(1.0)	1.5	1.0	1.1	1.4	1.2	2.3	1.7	(1.6)	1.2	1.6	(1.1)	1.2	1.4	(1.3)	(1.7)
Soils on gabbro and diorite series of the Permian Selenga complex (n = 5)																	
Mean	170.0	47.40	15.0	27.8	54.2	89.6	9.9	410.0	5.6	0.23	2.62	0.96	3.40	586.0	1.84	19.20	0.23
σ	30.00	18.90	2.45	6.10	21.85	15.77	5.47	47.43	6.46	0.04	0.45	0.54	0.75	99.65	0.56	2.39	0.06
EF_g (DF_g)	1.32	(1.26)	1.33	(1.04)	1.39	1.28	1.45	2.34	5.05	(1.80)	1.05	1.44	(1.49)	1.27	1.08	(1.41)	(1.84)
Zakamensk																	
Soils on alluvial deposits (n = 6)																	
Mean	126.5	69.3	14.8	40.2	35.5	98.8	7.7	290.0	3.6	0.3	2.9	2.2	16.5	506.7	7.1	22.8	0.5
σ	25.3	13.0	3.0	9.6	9.0	15.0	4.2	72.9	1.4	0.04	0.7	1.8	13.7	52.4	2.4	3.5	0.1
EF_g (DF_g)	(1.0)	1.2	1.3	1.4	(1.1)	1.4	1.1	1.7	3.2	(1.3)	1.2	3.2	3.3	1.1	4.2	(1.2)	1.3
Soils on the Paleozoic Dzhida complex (n = 15)																	
Mean	175.5	47.8	22.8	34.1	81.0	133.5	4.9	274.0	7.8	0.4	2.6	1.6	10.8	698.0	34.3	31.7	1.3
σ	54.6	9.2	8.2	13.7	46.6	35.7	0.9	84.7	11.8	0.1	0.6	0.7	12.3	213.5	57.9	21.0	2.4
EF_g (DF_g)	1.4	(1.2)	2.0	1.2	2.1	1.9	(1.4)	1.6	7.1	(1.1)	1.1	2.4	2.1	1.5	20.2	1.2	3.0

Table 2 continued

Parameter	V	Cr	Co	Ni	Cu	Zn	As	Sr	Mo	Cd	Sn	Sb	Cs	Ba	W	Pb	Bi
Soils on the Cambrian complex: Khokhyurt and Dzhida series ($n = 4$)																	
Mean	101.0	35.4	13.6	27.8	39.3	113.0	3.5	205.0	5.1	0.5	1.7	1.2	5.3	587.5	31.2	40.5	1.1
σ	66.6	23.4	6.9	18.6	18.8	67.6	1.9	77.7	3.5	0.3	0.4	0.6	3.3	360.8	30.7	37.2	1.2
EF_g (DF_g)	(1.3)	(1.7)	1.2	(1.0)	1.0	1.6	(2.0)	1.2	4.6	1.1	(1.4)	1.8	1.0	1.3	18.3	1.5	2.7
Soils on the Middle Permian – Lower Triassic Cherny Yar series ($n = 2$)																	
Mean	185.0	56.5	17.0	25.5	29.5	81.5	6.6	130.0	1.4	0.2	2.0	2.8	7.9	655.0	4.9	16.5	0.3
σ	7.1	21.9	2.8	7.8	16.3	4.9	3.6	14.1	0.6	0.04	0.4	1.3	2.8	205.1	1.6	2.1	0.1
EF_g (DF_g)	1.4	(1.1)	1.5	(1.1)	(1.3)	1.2	(1.0)	(1.3)	1.3	(2.6)	(1.3)	4.2	1.6	1.4	2.9	(1.6)	(1.3)

* n is the number of samples; ** enrichment factors EF_g are given against the global background C_g; dispersion factors DF_g are given in parentheses

values), because it is confined to the deposit, whose primary and secondary ores are enriched with these elements (Gavrilova et al. 2010), and the grinding of the extracted ore enhances the aerogenic pollution of the study area. Another set of priority pollutants is found in the impact zone of the Dzhida tungsten–molybdenum plant: $Bi_{23.6}W_{21.0}Cd_{10.8}Pb_{8.0}Mo_{6.9}Sb_{6.6}$, which agrees with the reported data (Smirnova and Plyusnin 2013). In contrast to Erdenet, in Zakamensk, the list of pollutants depends on their input from several sources: tailings with high concentrations of these elements inherited from the original ores (Khodanovich et al. 2002); emissions from the Liteishchik plant, which contain W, Sb, Mo, Pb, Cu, and Cr (Saet et al. 1990); and emissions from the thermal power plant fuelled by heating oil, whose mineral components include V, Ni, Cr, Mo, Pb, and Cu compounds (Novoselov 1983; Saet et al. 1990).

In Erdenet, the soils of the residential zone with multistory houses accumulate Bi, Cu, and Mo. Their presence is related to the petrochemical features of soil-forming rocks. The minimum concentrations of all the analyzed HMs and metalloids are confined to the ger house zone due to its remote location west of the ore deposit and the predominance of western and southwestern winds. The geochemical differences between the urban and background soils in the concentrations of other elements are usually insignificant.

The residential zone with multistory houses in Zakamensk is second in the level of soil pollution. Technogenic sands of the Dzhida tailing dump approach the residential area. The sands have no plant cover on their surface; they are characterized by higher air and water permeability than hard rocks. Therefore, active deflation, water erosion, sheet wash, and chemical (sulfuric) weathering are observed, enhancing the oxidation of sulfides and the dissolution of weathering products. Their lateral migration results in the enrichment of soils in the residential zone adjacent to the technogenic sands with $W_{6.0}Bi_{5.2}Cd_{4.8}Pb_{2.6}Zn_{2.4}$. In farmland (dacha) and natural recreation zones, which are predominantly located on the Modonkul left bank, soil pollution is insignificant, owing to the absence of tailing dumps with production waste. Exceptions for the former zone are ore elements and their accessories $Bi_{3.1}W_{2.0}Mo_{1.8}$, as well as $Pb_{2.0}Zn_{1.3}$, the most typical pollutants for urban areas.
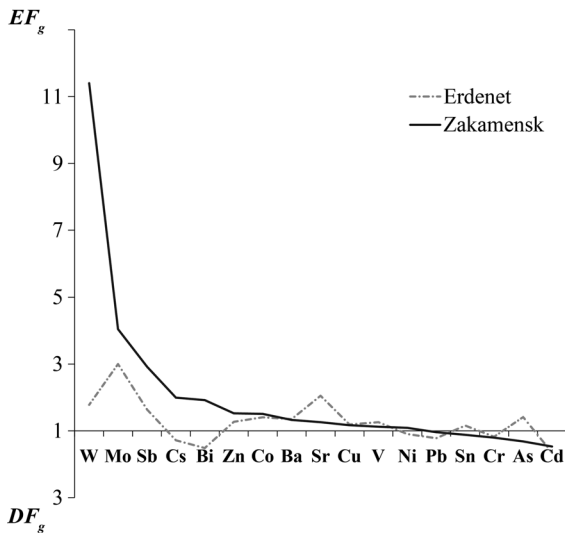
Fig. 2 Geochemical spectra of background soils near the cities of Erdenet and Zakamensk

The content of all other elements in these zones is close to background levels.

In general, the urban soils of Erdenet are characterized by elevated mean concentrations of ore elements Mo and Cu, while a wide array of elements against the local background, Bi–W–Cd–Pb–Mo–Sb–Zn–Cu, is accumulated in soils of Zakamensk (Fig. 3).

Thus, technogenic transformation of urban soils in both mining centers is manifested in the accumulation

of chalcophilic elements: W, Bi, Cd, Pb, and Mo for Zakamensk and ore elements Cu and Mo for Erdenet. Cationogenic elements (Bi, Cd, Pb, and Cu) migrate in the form of true solutions in acidic waters and in the form of high molecular weight organic complexes in neutral waters (Udachin et al. 2003). In contrast, W is a complexing agent, which slightly migrates in strongly alkaline (sodic) waters. Mo is an anionogenic element, which precipitates with organics and Fe and Al hydroxides, and migrates under alkaline conditions (Kabata-Pendias 2011).

Ecological–geochemical assessment

To assess the environmental hazard of the pollution of urban soils in Erdenet, concentrations of HMs and metalloids in their upper horizons were compared to the sanitary–hygienic norms for V, Cr, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, and Pb adopted in Mongolia (MNS 5850:2008), which are determined depending on the soil texture; for Zakamensk, they were compared to the norms of the Russian Federation (GN 2.1.7.2041-06, GN 2.1.7.2042-06), which are established only for V, Pb, As, Cd, Cu, Ni, Zn, and Sb. The particle-size analysis of soil samples showed that the soils in Erdenet mainly have a loam texture; an exception is the tailing dump composed of loamy sandy techno-genic surface formations.

Table 3 Accumulation levels of HMs and metalloids in the surface (0- to 10-cm) soil horizons of mining landscapes

| Functional zone	Local enrichment factor EF_l				
	>20	20–10	10–5	5–1.5	<1.5
Erdenet					
Multi-story houses (19)*				Bi, Cu, Mo	As, Ba, Bi, Cd, Co, Cr, Ni, Pb, Sb, Sn, V, W, Zn
Single-story hoses (40)					As, Ba, Cd, Co, Cr, Cs, Cu, Mo, Ni, Pb, Sn, Sr, V, W, Zn
Industrial (51)		Cu, Mo		As, Sb, W	Ba, Bi, Cd, Cr, Ni, Pb, Sr
Transport (16)				Cu, Mo	As, Ba, Bi, Cd, Cr, Cs, Ni, Pb, Sn, W
Pastures (68)				Cu, Mo	Ba, Bi, Cd, Cr, Cs, Ni, Pb, Sn, W
Zakamensk					
Multi-story houses (6)			Bi, W	Cd, Cu, Mo, Pb, Zn	Ba, Co, Ni, Sb, Sn, Sr, V,
Single-story houses (24)				Bi, Cd, Mo, Pb, W	Cr, Ni, Sb, Sn, Sr, Zn
Industrial (52)	Bi, W	Cd,	Mo, Pb, Sb	As, Cs, Cu, Sn, Zn	Co, Cr, Ni, V
Transport (4)			Bi, W	Cd, Mo, Pb,	Ba, Cu, Sb, Sn, Sr, V, Zn
Natural recreation (19)				Bi, Mo, W	Cd, Co, Ni, Pb, Sn, Sr,

* *n* is the number of samples
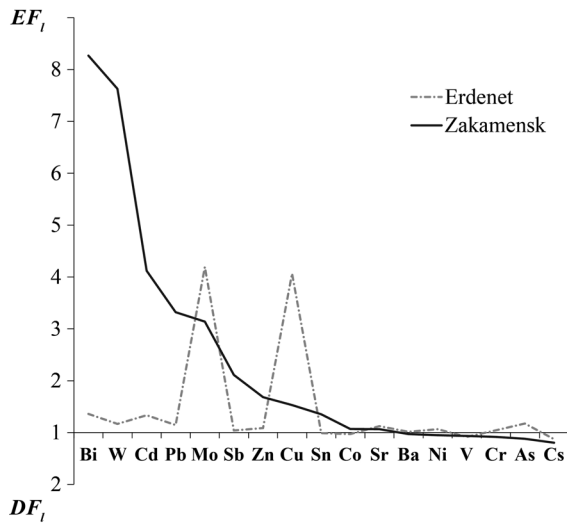
Fig. 3 Geochemical spectra of urban soils in the cities of Erdenet and Zakamensk

In Erdenet, the most significant excess of MPC for Mo, Cu, and As with mean K_o values of 8.6, 5.7, and 3.8, respectively, was found in soils of the industrial zone (Fig. 4a). A point maximum is found on the territory of the Erdenet plant, where the values of K_o are 525 for Cu, 218 for As, and 290 for Mo. Elevated concentrations of As with K_o 2.6–3.0 are recorded in all land-use zones. The distribution of Mo and Cu varies with type of land use: the highest mean values of

K_o (3.4 and 1.9, respectively) are found in the residential zone with multistory houses, and the minimum values (1.0 and 0.62, respectively) are observed in the ger house zone. Zn, Cr, Sr, Pb, Co, Ni, Cd, and Sn pose no environmental risk, and their concentrations do not exceed the MPCs established by the Mongolian legislation; the K_o values make up 7–77 % of the norms.

In all land-use zones of Zakamensk, Pb, Sb, Cd, and As pose the highest hazard; their distributions in the soil cover are determined by the level of technogenic load and the distance from tailing dumps (Fig. 4b). The values of K_o for these elements are 7.8, 3.6, 2.1, and 1.7, respectively, in the industrial zone and 1.8, 0.5, 0.8, and 1.0, respectively, in the multistory residential zone. Their main sources are waste from the Dzhida tungsten–molybdenum plant, as the commercial ores from the Pervomaiskoe stockwork and the Inkur and Kholtoson deposits contain, along with the extracted elements (W, Mo), high concentrations of elements of hazard classes I–III (Pb, Zn, As, Cd, Be, Bi, etc.). Waste is widely used in the construction of buildings, playgrounds, and roads. Cd and Pb are also present in the sulfide sewage from the ore-dressing plant (Smirnova and Plyusnin 2013).

The soils of the Zakamensk traffic zone, in contrast to the analogous zone of Erdenet, contain values of K_o lower than 1 for all elements, except for Pb. This is
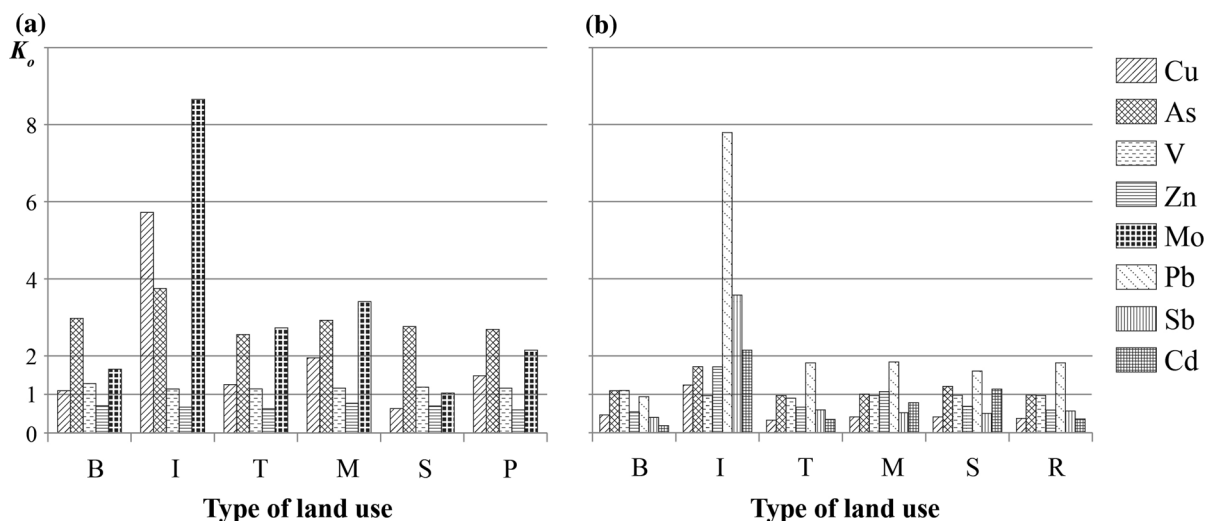

Fig. 4 Distribution of the coefficients of MPC exceedance (K_o) in soils of various land-use zones in the cities of Erdenet (**a**) and Zakamensk (**b**). Land-use zones: *B* background, *I* industrial, *T* traffic, *M* multi-story houses, *S* single-story houses (ger houses in Erdenet and dachas in Zakamensk), *P* pastures (Erdenet), *R* recreation (Zakamensk)

related to the fact that the population of Zakamensk is 8 times smaller and the city area is 4 times smaller than Erdenet. As a result, there is significantly less motor vehicles and no transit vehicles in Zakamensk. In Erdenet, along with the cars of local inhabitants, there are numerous load carriers, which are related to the presence of a railroad station, to which products, construction wares, and other goods necessary for adjacent settlements are brought.

To assess the multielemental pollution of urban soils, the integrated index of risk, IIR, was calculated (Fig. 5a, b). In Erdenet, its variation range was from 0.4 to 2102, with an average value of 45. In Zakamensk, its variation range was narrower (1.5–1737), but the average value is 2 times higher, indicating a very hazardous environmental situation created by the Dzhida tungsten–molybdenum plant.

In the impact zone of the Erdenet MPP, 39 % of the area in the ger house zone and on pastures (Figs. 5a, 6a) is characterized by low danger of soil pollution (IIR < 16). In the multistory residential zone, which occupies 26 % of the city area, the IIR values of 16–32 correspond to medium pollution level, and the region of high pollution (15 %) with IIR of 32–64 covers the Erdenetii-Gol valley, between the Erdenet MPP and the tailing dump, as well as the areas around the overburdened dumps. The maximum level of environmental hazard (IIR > 128) was established in 14 % of the area, including 12 % occupied by the tailing dump, where visitors are very rare, and only 2 % of the area is occupied by the working site of the Erdenet MPP (IIR = 2102).

Several anomalous zones are revealed within the city of Zakamensk: a hazardous tailing dump on the Modonkul right bank (IIR = 1738) remediated in 2011; the Zun-Naryn and Barun-Naryn tailing dumps and the Modonkul technogenic deposit

(IIR = 512–1024); the impounded Inkur River valley; middle course of Modonkul River valley and the Dzhida tailing dump (IIR = 256–512). Areas with slightly polluted soils (IIR < 16) occur in the southern, southwestern, and western regions of the city with private single-story houses.

The Dzhida tungsten–molybdenum plant had a strong negative effect on the state of natural landscapes; therefore, almost 50 % of the city area has an extremely dangerous level of soil pollution (Fig. 6b). This results in an increase in the morbidity rate of children and teenagers, which is accompanied by a decrease in their resistance to pathogenic factors (Prusakov et al. 2005). Dangerous and very dangerous pollution levels are recorded in 9 and 11 % of the city area, respectively; only in 20 % of this area (9 km²) the level of pollution is permissible, which does not affect the health of citizens.

Thus, a seventh of the area of Erdenet and half the area of Zakamensk can be included in the zone of ecological disaster, requiring urgent measures. In the former city, special attention should be given to the working area of the Erdenet MPP, where many local inhabitants work. In the latter city, remediation of the areas of the Dzhida, Barun-Naryn, and Zun-Naryn tailing dumps and the Modonkul deposit with the removal or phytoremediation of waste from the Dzhida tungsten–molybdenum plant should be planned.

Microelemental composition of bottom sediments

The concentrations of HMs and metalloids in the background samples of bottom sediments collected in the heads of the studied rivers were compared with their mean concentrations in the background soils. No differences were revealed in Erdenet, with ratios

Fig. 5 Integrated index of risk (IIR) in the cities of Erdenet (**a**) and Zakamensk (**b**)

(a) 14% 6% 15% 26% 39%

permissible (Z_{eh} <16)
moderately dangerous (*16-32*)
dangerous (*32-64*)
very dangerous (*64-128*)
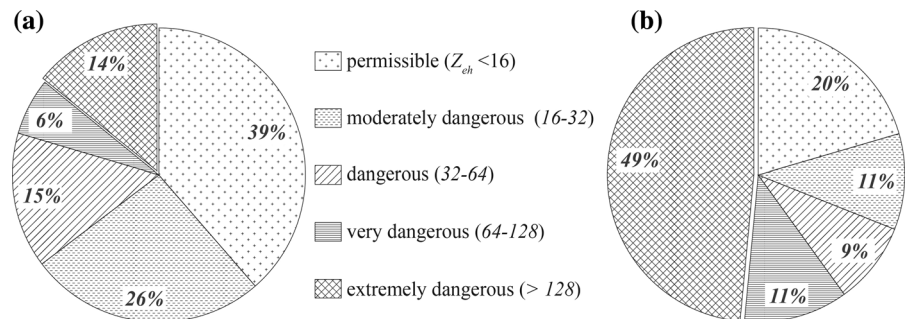extremely dangerous (*> 128*)

(b) 20% 49% 11% 9% 11%

Table 4 Geochemical characterization of bottom sediments in the rivers Erdenetii-Gol and Modonkul upstream of the cities of Erdenet and Zakamensk

Background conditions	Accumulation		Dispersion		
	1.0–1.5	>1.5	1.3–5	5–20	>20
Erdenet, Erdenetii-Gol River	V, Cr, Co, Ni, Zn, As, Sr, Cd, Sb, Ba, W	Bi			Mo
Zakamensk, Modonkul River		Sb	V, Cr, Co, Ni, Cu, Zn, Cs, Sn, Ba, As, Sr	Mo, Pb	$Bi_{46}W_{39}$
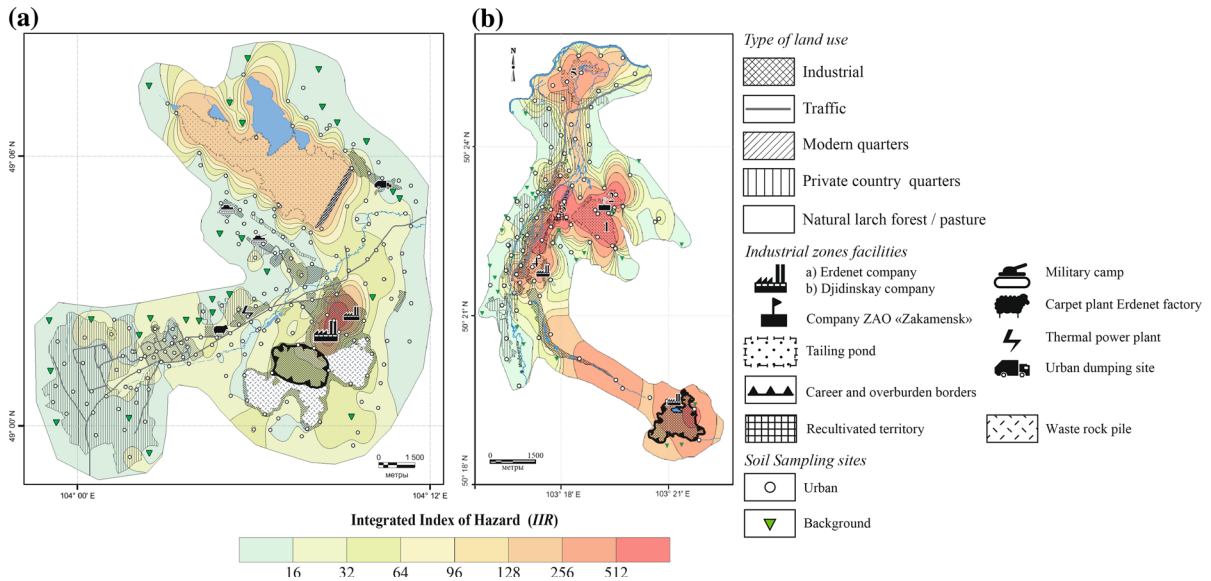
Fig. 6 Areas with different IIR levels in the cities of Erdenet (**a**) and Zakamensk (**b**)

varying from 1 to 1.5 in favor of either accumulation or dispersion (Table 4). Exceptions are Mo, which is more intensively leached from bottom sediments than from soils, and Bi, which, on the contrary, is characterized by higher concentrations in bottom sediments.

A different situation is observed in Zakamensk: The concentrations of most elements in the bottom sediments of the River Modonkul are lower than in the background soils by 1.5–5 times. The largest dispersion is typical for the chalcophilic elements: ore W–Mo (DF_l = 39 and 19, respectively) and their accessories Bi–Pb (46 and 6). This can be due to several reasons: first, the Modonkul head is located beyond the ore-enclosing rocks; second, water has a weakly acid or neutral reaction, which is favorable for the migration of these elements in the form of high molecular weight organic complexes (Udachin et al. 2003) and compounds with Fe and Al hydroxides. As, Sr, and Cs

(EF_l and DF_l < 1.5) are characterized by near-background values.

The pollution of aquatic landscapes in city areas was assessed from the local enrichment/dispersion factors calculated against the background conditions in the riverheads. In Erdenet, the values of EF_l and DF_l are in the range of 1.0–1.6 for all elements, except the ore metals Cu and Mo. An abrupt increase in the concentrations of Cu and Mo (EF_l = 30 and 13, respectively) is observed in the region of the MPP. The sources of Cu and Mo include atmospheric precipitation and solid fallouts enriched with these elements owing to wind and water erosion of overburdened dumps and losses of concentrate during transportation by the adjacent railroad. At the exit of the city, bottom sediments are also enriched with ore elements; however, the values of local enrichment factors are 1.5 times lower (18.5 and 8.1, respectively). This is related

Fig. 7 Accumulation of HMs in bottom sediments of the Modonkul River downstream of the Western adit (*1*), the Barun-Naryn and Zun-Naryn tailing dumps (*2*), and the Dzhida River at 2 km (*3*) and 30 km (*4*) downstream the Modonkul junction
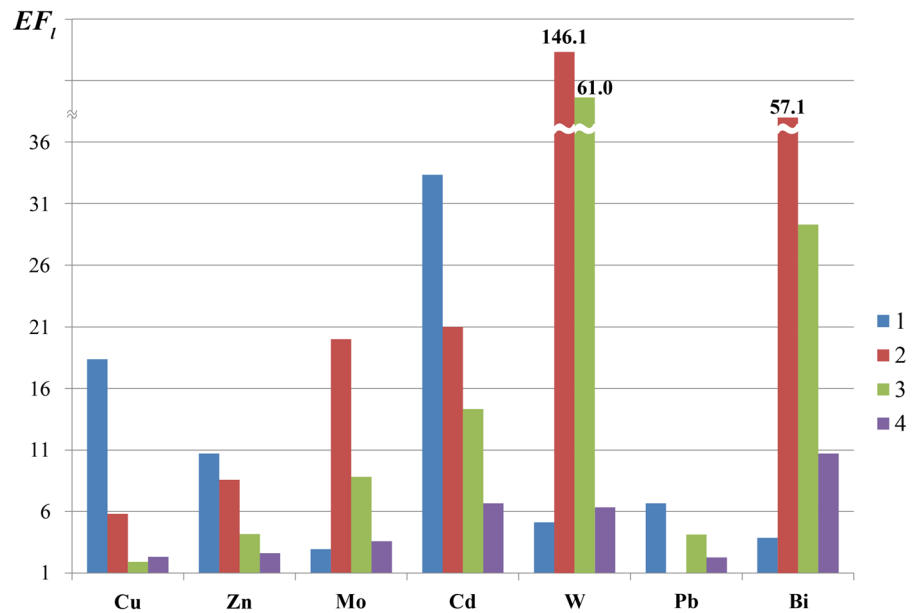
to the construction of a small dam, where particles enriched with Cu and Mo are precipitated on the sedimentation barrier due to abrupt decrease in river velocity.

The bottom sediments in Zakamensk are under the effect of tailing dumps and the Western adit, which was used for the development of the Inkur tungsten sulfide deposit. A sharp increase in the concentrations of major chalcophilic elements is observed in the Modonkul bottom sediments at 1.5 km from the confluence of the brook effluent from the adit with a strongly acidic reaction (pH = 3.5–4.0): Cd, by 33.3 times; Cu, by 18.4 times; Zn, by 10.7 times; Pb, by 6.7 times; W, by 5.1 times; and Bi, by 3.9 times. All elements, except W, are cationogenic; i.e., they are most mobile under acidic conditions.

Downstream of the tailing dumps of the Dzhida tungsten–molybdenum plant, the concentrations of ore and other cationogenic and chalcophilic elements in bottom sediments abruptly increase compared to the background values—$W_{146}Bi_{57}Cd_{21}Mo_{20}Zn_{8.6}Pb_{7.3}$-$Cu_{5.8}$ (Fig. 7). This is due to erosion and sheet wash of particles less than 0.07 mm in size from the surface of the tailing dump, as the technology of mineral extraction involves the disintegration of rock to this size.

After the confluence of the Modonkul and the Dzhida, the concentrations of HMs and metalloids decrease appreciably. This is caused by the sedimentation barrier at the site of the abrupt turn of the

Modonkul course from meridional to sublatitudinal, where the technogenic Modonkul deposit was formed. This accumulation zone is mainly composed by finely grained sands and consists of thin seasonal bands reflecting periodical inundations (Khodanovich 1999; Khodanovich et al. 2002). Downstream, in 30 km, a gradual decrease in the concentrations of HMs and metalloids occurs due to the deposition of transported material from the Modonkul River.

Conclusions

1. The high concentration of ore and accessory elements in soils is a specific feature of the studied mining landscapes. The changes of direction and intensity of relief formation and the balance of erosion–accumulation processes cause the involvement of large amounts of arriving HMs and metalloids in migration fluxes. Therefore, the upper soil horizons in the analyzed mining centers are characterized by high concentrations of chalcophilic elements: $Mo_{4.3}Cu_{4.1}$ in Erdenet and $Bi_{8.3}W_{7.6}Cd_{4.1}Pb_{3.3}Mo_{3.1}$ in Zakamensk. The set of priority pollutant elements directly depends on the character and level of anthropogenic load. In both cities, the topsoils in industrial zone are strongly disturbed and enriched with $Mo_{10.7}$-$Cu_{10.6}As_{1.6}Sb_{1.5}W_{1.5}$ in Erdenet and

$Bi_{23.6}W_{21.0}Cd_{10.8}Be_{8.1}Pb_{8.0}$ $Mo_{6.9}Sb_{6.6}$ in Zakamensk. In the Erdenet industrial zone, the maximum values of danger coefficients K_o are 8.6 and 5.7 for the ore elements Cu and Mo, respectively, and 3.8 for As. In Zakamensk the maximum risk is associated not with ore elements (for which there are no official norms), but with Pb, Sb, Cd, and As; their K_o reach 7.8, 3.6, 2.1, and 1.7, respectively. The minimum concentrations of the analyzed HMs and metalloids are confined to single-story residential zones: the ger house zone in Erdenet ($Cr_{1.2}Ni_{1.2}Zn_{1.2}$) and farmland (dacha) zone in Zakamensk ($Bi_{3.2}Pb_{2.0}W_{2.0}Mo_{1.8}$). The reasons are the large distance from major sources of contamination, i.e., from the industrial zones and motor roads, and predominating wind direction.

2. The ecological situation in the cities is caused by intensive multielemental pollution of the soil cover. The maximum values of IIR are confined to the emergency tailing in the impact zone of the working area of the Erdenet MPP and the Dzhida tungsten–molybdenum plant; they exceed the extremely dangerous level (128) by 16 and 14 times, respectively. Although the Erdenet MPP still actively produces nonferrous metals and processes about 27 million tons of ore annually, it controls the distribution and storage of waste products, which significantly reduces the modern impact zone and the concentrations of HMs and metalloids in the soils of this zone. The Dzhida tungsten–molybdenum plant was closed 15 years ago; however, a vast zone of ecological disaster with IIR >128 has formed in the city because of the ill-advised distribution of tailings. The zone occupies about half the city area, and deterioration of the geochemical state of soils was observed during the last decade.

3. The effect of the mining centers on the state of the river system is local and does not spread to the Selenga River, the main waterway in the region. Downstream from Erdenet, the local enrichment factors of HMs and metalloids in the bottom sediments of the Erdenetii-Gol River are 33 % lower than within the city, owing to artificial pool which forms sedimentation barrier. By contrast, the Dzhida tungsten–molybdenum plant radically transformed the geochemistry of bottom sediments in the Modonkul River. Maximum geochemical changes occur downstream from the tailing dumps, where the concentrations of the ore elements W and Mo and their accessories Bi and Cd exceed the background values by 146, 20, 57, and 21 times, respectively.

4. The ecogeochemical survey of the state and pollution of mining landscapes showed that geological heterogeneity and metallogenic specificity of their territories should be taken into consideration. The local coefficients EF_l/DF_l should be calculated against the individual background values for each parent rock, rather than against the mean background level, for more accurate assessment of the anthropogenic geochemical transformation of soils. To evaluate the environmental hazard of multielemental pollution in the area with high natural content of trace elements, the integrated pollution index (IIR) is proposed, which is calculated against the mean global concentrations of HMs and metalloids in soils with consideration for the toxicity of the elements.

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