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ENVIRONMENTAL PROTECTION

Soil Cover Geochemistry of Mining Landscapes in the South-East of Transbaikalia (City of Zakamensk)

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Abstract—Presented is a detailed characterization of the present state and pollution of soil cover in the influence area of the Dzhidinskii tungsten-molybdenum plant which takes into consideration the spatial geological inhomogeneity and the functional purpose of urban territories. As part of the investigation, we determined the content levels of heavy metals and metalloids in background soils, and the elements which are the main pollutants of urban soils in the zones of different functional purposes, ascertained the degree of technogenic geochemical transformation of soil cover in the city of Zakamensk, and identified the leading soil- and landscape-geochemical factors for accumulation of heavy metals and metalloids in the urban topsoil (0–10 cm) horizons. An assessment was also made of the ecological hazard of soil pollution by a set of heavy metals and metalloids in the main functional zones of the city. A soil-geochemical survey was carried out, and the ICP-MS method was used to determine the total content levels of 14 heavy metals and metalloids of hazard classes I–III as well as Be, Sn, Cs and Bi. The elements were determined, which are the main pollutants of the soils in Zakamensk: W, Bi, Cd, Pb and Mo. The study revealed a need to take into account the metallogenic specific character and geological inhomogeneity of the area by using the local coefficients of concentration (EF_l) and dispersal (DF_l) which must be calculated not with respect to the average regional background but from the individual (for each parent material) background value in order to more accurately determine the degree of technogenic geochemical transformation of soils, and the ecological hazard of pollution. It is suggested that the ecological hazard should be assessed on the basis of the Integrated Pollution Index (IPI) which is calculated with respect to the world's average concentrations of heavy metals and metalloids in soils and takes into account hazard classes of elements.

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INTRODUCTION

Ore mining has an extensive influence on the state of environment and leads to irreversible changes in soils, waters, vegetation, and in the atmosphere. Mining landscapes constitute special technogenic landscape-geochemical systems with anomalously high contents of elements which, usually, exert an adverse effect on the landscape and which are characterized by a poorly controlled dispersion. Superposition of dispersion patterns and flows on natural geochemical anomalies poses a serious threat to human life; therefore, the ecological consequences of mining activities are studied in many countries of the world.

A large number of publications are devoted to assessing pollution of the environmental components by wastes and discharges from the mining and dressing plants (Russian acronym—GOK) [1–4], the atmospheric transport of pollutants [5, 6], studying their translocation from soils to plants and animal bodies [1, 6–8], and to the spatial and profile distribution of different forms of heavy metals (HM) and metalloids in soils as the main depositing medium [9, 10]. However, the approaches to ecological assessments and zoning of mining territories in conditions of lithological-geochemical inhomogeneity are poorly developed [11, 12]. The leading processes and mechanisms that favor fixing of HM and metalloids in soils are scantily known, which makes their effective remediation and recultivation difficult.

This paper is concerned with the ecological-geochemical characteristics of the surface soil horizons in the city of Zakamensk (Republic of Buryatia). The urban-development enterprise is represented by the Dzhida Tungsten-Molybdenum Plant (DW-MoP) that has been extracting tungsten and molybdenum for 67 years. Geological features were revealed for this territory [13], and a comprehensive ecological-economic assessment was made [14]. After the shutdown of GOK in 2004–

2005, staff members of the Geological Institute SB RAS carried out large-scale investigations of the territory of Zakamensk including the waste disposal sites [15] to characterize the ongoing processes of mineral formation and determine the content levels of HM and the forms of their occurrence [16, 17]. As a result, large-scale maps were compiled for total pollution as well as a number of monoelement geochemical maps for snow and soil cover, and for herbaceous vegetation [17].

A significant body of publications notwithstanding, there remain some outstanding questions for further study. First, the publications cited above use, as the background area, the valley of the Duban brook where only plagiogranites, granodiorites and diorites of the Paleozoic Dzhida complex occur, although it is known that the territory of Zakamensk is characterized by a considerable lithological-geochemical inhomogeneity. Second, the ecological-geochemical assessment is differentiated with respect to the functional zones of the city which differ both in the levels and in the set of priority pollutants. Third, no assessment has been made of the new Zun-Naryn tailing pond and of the state of the northern areas of Zakamensk on the interfluve of the Modonkul’ and Dzhida rivers where the technogenic Modonkul’ deposit emerged as well as of the results of recultivation of the area within the city from 2011 with the purpose of eliminating some of consolidated sands. This measure was undertaken by ZAO Zakamensk as phase I of the program of measures for the elimination of the negative consequences for Zakamensk from the production operations of DW-MoP within the Federal Target Program “The protection of Lake Baikal and Socioeconomic development of the Baikal Natural Territory for the years 2012–2020’. And finally, of considerable theoretical and practical interest is the identification of the leading landscape-geochemical and anthropogenic factors that govern the accumulation of the elements in the main depositing medium, the soils.

In this connection, the objective of this paper is to give a detailed characteristic to the present state of the soil cover in Zakamensk, with due regard for the spatial geological inhomogeneity and the functional purpose of the urban territories, and based on this, to assess the ecological hazard of soil pollution by HM and metalloids; more specifically, to determine the content levels of HM and metalloids in background soils, and the priority pollutant elements in urban soils in the zones of a different functional purpose, ascertain the degree of technogenic geochemical transformation of the soil cover in the city, identify the leading soil- and landscape-geochemical factors for accumulation of HM and metalloids in the surface (0–10 cm) horizons of urban soils, and to assess the ecological hazard of soil pollution by the complex of HM and metalloids in the main functional zones of the city.

OBJECT FOR STUDY

The city of Zakamensk occupies the area of 45 km^2 and lies 460 km to the south-east of Ulan-Ude. The territory belongs in the southern part of the Mongolian-Siberian mountain belt, within the Selenga-Vitim zone, a second-order morphostructure, with a moderate neotectonic activization of the Earth’s crust [18]. The relative altitudes of the dividing crests above the valley thalwegs do not exceed 300–400 m [19].

The city is situated on the boundary of two regional geological structures comprised of Lower-Paleozoic carbonate-terrigenous strata of the Dzhida synclinorium, and by intrusions of granitoids of the Modonkul’ massif.

The climate of the study area is extreme continental, with large amplitudes of diurnal and annual air temperatures, cold (down to –49ºC), long and relatively snow-deficient winters and short warm (the mean July temperature is 15.6°C) summers. According to data from the Tsakir meteostation [19], the annual precipitation amount varies from 250 to 400 mm, and the prevailing wind directions are westerly and south-westerly with the recurrence frequency of 36 and 16%, respectively (Fig. 1). The meteorological conditions are distinguished by frequent inversions, especially in the wintertime, with a large number of days with calm weather [19], which is favorable to atmospheric deposition of dust particles polluted by HM and metalloids and for their subsequent accumulation in depositing media.

In the system of soil regionalization, the territory of Zakamensk refers to the East-Siberian permafrost-taiga zone of the boreal belt of the Eastern-Sayan mountain soil province [20]. In autonomous positions and on steep slopes there occur mountain soddy-taiga and soddy-calcareous soils beneath forest vegetation which comprise *Larix sibirica* and *Betula platyphylla* with the undergrowth consisting of *Rhododendron dauricum*, *Rosa acicularis* and *Vaccinium uliginosum*.

Soddy forest soils occur in the hollows between depressions in the lower parts of gentle slopes and along the valleys of the Modonkul’ and Dzhida rivers beneath the anthropogenically disturbed meadow and meadow-bog vegetation [20], and alluvial meadow soils occur beneath meadow vegetation with sparse willows.

The Modonkul’ (the right tributary of the Dzhida) is the main water artery. Its length is 28 km, and the width of the valley along the dividing boundary is as long as 3 km in the upper reaches and up to 7 km in the lower reaches, and 300–350 m along the riverbed. The valley sides are largely steep, with the erosion incision of up to 2–2.5 m, and the channel width varies from 10 to 30 m. The Modonkul’ receives numerous tributaries: the Barun-Naryn and Zun-Naryn rivers, the Inkur brook, and others which do not function to date; the first two rivers are occupied by the tailing

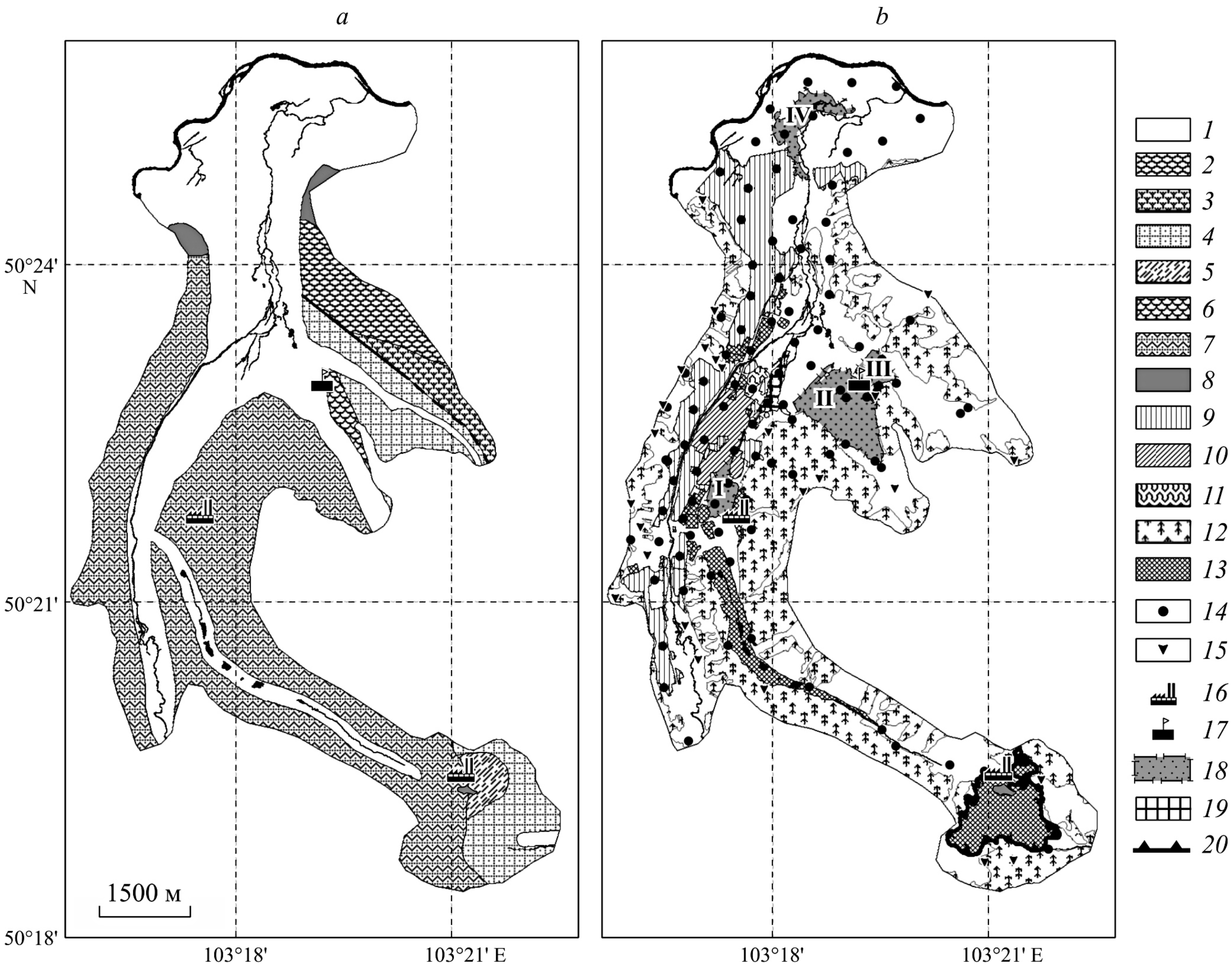

Fig. 1. Geological conditions of Zakamensk (*a*) and its functional zoning with soil sampling points from surface (0–10 cm) horizons (*b*). Geological conditions. Quaternary deposits: *1* – alluvial (shingle, sands, sandy loams, loams). Pre-Quaternary deposits. Formations: *2* – Chernyi-Yar (orthophytes, keratophyres, tuff, tufflavas), *3* – Dzhida (sandstone, aleurites, limestone), *4* – Khokhyurta (basic and neutral vulcanites, limestone, metashale); complexes: *5* – Gudzhir (leucocratic granites, granite porphyries), *6* – Tsakir (serpentinites on dunites and peridotites), *7* – Dzhida (first phase: plagiogranites, granodiorites, diorites), *8* – Dzhida (second phase: granites, granosyenites, syenites). Functional zones: *9* – private buildings, *10* – urban buildings, *11* – recreational, *12* – natural larch forests, *13* – industrial. Sampling points: *14* – urban soils, *15* – background soils. Facilities of industrial zone: *16* – abandoned W-MoP, *17* – dressing plant of ZAO Zakamensk, *18* – tailing ponds (I – Dzhida (leveed), II – Barun-Naryn (hydraulic-mine dump), III – Zun-Naryn, IV – Modonkul' deposit of technogenic sands), *19* – recultivated area, *20* – boundaries of the DW-MoP zones of mining and overburden storage.

ponds, and the Inkur brook was transformed to a cascade of water bodies used for gold-mining.

From 1934 to 2001, the DW-MoP played the role of an urban development enterprise that specialized in mining the stockwork molybdenum (Pervomaiskii) and sulfide-tungsten (Inkur and Kholtoson ore and Inkur and Kholtoson placer) deposits as well as the gold deposits (Myrgensheno and Ivanovka). The proportion of tungsten concentrate made up 73–80% of the total output in the USSR. The ores contain ingredients, i.e. elements of hazard class I–III: Pb, Zn, F, Mo, W, Be, Bi, As, and others [19]; the dressing process used toxic agents which also accumulated in tailing ponds. The operation of the DM-WoP was responsible for 44.5 mil. t of production waste disposed of in the Dzhida (fill dump), Barun-Naryn (hydraulic-mine dump) and emergency tailing ponds (see Fig. 1). In the process of recultivation, 3.5 mil. t of waste were removed from the emergency tailing pond to the upper part of the Barun-Naryn tailing pond.

In 1999, ZAO Zakamensk acquired the Barun-Naryn and Dzhida tailing ponds embarked on the determination of the reserves of metals in technogenic sands as well as searching for the latest technologies of re-extraction of metals. The year 2007 saw the start of the construction of the plant to process (in 2010) the tailings from the DW-MoP (the Barun-Naryn technogenic deposit) so that a new tailing pond emerged in the valley of the Zun-Naryn river.

In addition to having the enterprises specializing in mining mineral resources, the city has facilities for timber harvesting and processing, the production of cast iron, steel and bronze, civil construction, the manufacture of food products, and stone processing.

The following functional zones were identified on the territory of Zakamensk (see Fig. 1): the transport and industrial zones, and two residential zones: the private homestead zone, and the natural-recreational zone (natural forests, urban parks, and recreation zones). The multi-storey residential zone occupies the floodplain positions on the right bank of the Modonkul', while the private homestead zone is situated on the left bank encompassing the lower parts of the slopes of the river valley and a portion of the high floodplain of the Dzhida riverside. The industrial zone includes the Pervomaiskii and Inkur mines, the overburden heaps, DW-MoP, the Liteishchik plant, and the thermoelectric plant; these facilities are all situated south of the urban buildings; the Barun-Naryn, Zun-Naryn and Dzhida tailing ponds are located to the west of the residential zones on the right bank of the Modonkul'. The valley of the Inkur brook is represented by a cascade of water bodies where placer gold and tungsten mining has been resumed. The Modonkul' deposit of technogenic sands was formed on the left bank where the river changes its flow from meridional to sublatitudinal. The background territories include the summits and gentle slopes in the valley of the Modonkul' river.

METHODS AND MATERIALS

A soil-geochemical survey of Zakamensk was carried out in summer 2012. Samples (totaling 129, including background samples) were collected from the surface (0–10 cm) horizon according to a regular network at steps of 450–650 m (see Fig. 1), which provided spatial detailing and a possibility of compiling large-scale geochemical maps of the territory.

Total content levels of 65HM and metalloids in soil samples were determined by the inductively coupled mass spectroscopy method (ICP-MS) in the All-Russian Institute of Mineral Resources. A detailed analysis used 18 priority pollutants belonging in hazard class I (Zn, As, Pb, and Cd), II (Cr, Co, Ni, Cu, Mo, and Sb) and III (V, Sr, Ba, and W), and a number of other elements (Be, Sn, Cs, and Bi).

The values obtained for HM and metalloids in background samples, C_b, were combined in accordance to parent material and compared with the average world values in soils, C, [22] by calculating the global concentration and dispersion coefficients $EF_g = C_b/C$, $DF_g = C/C_b$. The need to compare with the average world values [22] was dictated by the fact that in this paper we consider only the surface horizons where the role of soil organic matter is large.

The geochemical transformation of the urban soils was assessed having regard to the lithological-geochemical inhomogeneity of the territory: the local coefficients of concentration $EF_l = C_u/C_b$ and dispersion $DF_l = C_b/C_u$ of the elements (C_u – concentration of an element in urban samples) were calculated relative to background concentrations belonging in the same parent material. Geochemical spectra of the urban soils were constructed for separate functional zones differing both by the content levels and by the set of elements, the priority pollutants. The set is represented as a formula in which the elements are arranged in decreasing order of the concentration coefficient EF_l, and its values are indicated in the subscript. Ecological-geochemical assessment of urban oils is based on the indicators as developed for correlative ecological-geochemical and sanitary-hygienic investigations of urban environments: maximum and tentative allowable concentrations (MAC/TAC) of the RF [23, 24], and on the exceedance ratio in MAC for separate elements, $HQ_o = C_a/MAC$.

The specific feature of mining landscapes is their occurrence at a metallogenic anomaly with elevated concentrations of ore-related and accompanying elements. Two indicators were therefore used to characterize the total soil pollution by a complex of elements. The degree of geochemical transformation of soil cover under the influence of technogenic sources was determined on the basis of their total pollution indicator, $Z_c = \sum EF_l - (n - 1)$, where n is the number of elements with $EF_l > 1$. The ecological hazard of an increased content level of HM and metalloids in soils was determined by using the integrated pollution index that takes their toxicity into account: $IPI = \sum(p \cdot C_u/C) - (n - 1)$, where n is the number of elements with $C_u > C$, and p is the toxicity coefficient (for the hazard class I elements, p = 1,5; for II, 1.0, and for III, 0.5) [25]. In this case, the average world values of soils [22] rather than the regional background with considerably higher concentrations of HM and metalloids, not infrequently exceeding the sanitary-hygienic standards, were used as a reference. Five classes of Z_c and IPI: were singled out: the low, non-hazardous (< 16), medium, moderately hazardous (16–32), high, hazardous (32–64), very high, very hazardous (64–128) and maximal, extremely hazardous pollution levels (> 128) [26, 27].

A statistical data processing was performed in the Statistica 8 and MS-Excel software packages. For each parent material and each functional zone, we calculated the selective average concentrations of the elements, M, their errors, the standard deviations σ, the variation coefficients ($C_v = \sigma \cdot 100/M$), the maximum and minimum values, and other statistical parameters. The influence of the natural and anthropogenic factors on the spatial distribution of pollutants in soils and technogenic surface formations (TSF) was assessed by the method of regression trees in the S-Plus (MathSoft, 1999) software package thereby permitting the levels of total soil pollution Z_c to be determined for different combinations of the factors, and to assess their significance.

A visualization of soil-geochemical data was carried out by using the method of local interpolation, or kriging, in the MapInfo 11.5 and Surfer 11 software packages. The basis for geochemical maps was provided by a fragment of the national geological map (sheet M-48-51-G, 1997 from [19]), and the city plan compiled from space-acquired images available in the MSU Geoportal system. In order to avoid a too high assessment of pollution of the territory, the data interpolation did not use points with extremely high concentrations of HM and metalloids that exceeded many times the average level in the soils of the city [25] identified by using the three-sigma rule. They are shown on the map as point anomalies.

RESULTS AND DISCUSSION

Geochemical characteristics of background soils. Background soils form on alluvial deposits consisting of shingle, sand, loamy sands and loams; in the first phase of the Paleozoic Dzhida complex: plagiogranites, granodiorites and diorites; the Mid-Permian/Lower-Triassic Chernyi-Yar formation: orthophyres, keratophyres, tuffs and tufflavas, and on the Cambrian complex combining the Dzhida and Khokhyurta formations: sandstone, aleurites and limestone. Ore-enclosing rocks occur in the Dzhida and Cambrian complexes. The soils on these deposits are characterized by different content levels of HM and metalloids (Table 1). It is obvious that all the soils show similar geochemical spectra (Fig. 2, *a*) with the lowest values of Cd (DF_l as low as 2.6) and As (as low as 2.0).

Table 1. Geochemical and statistical indicators of HM and metalloid content in surface (0–10 cm) horizons of background soils

Indicators	Hazard class of elements																	
	Class I				Class II						Class III				not determined			
	As	Cd	Pb	Zn	Co	Cr	Cu	Ni	Mo	Sb	Ba	Sr	V	W	Bi	Be	Cs	Sn
Alluvial deoposits (n = 6)*																		
Average, mg/kg	7.7	0.3	22.8	98.8	14.8	69.3	35.5	40.2	3.6	2.2	506,7	290,0	126.5	7.1	0.5	1.8	16.5	2.9
Min, mg/kg	4.3	0.28	20	78	11	55	28	30	1.9	0.66	440	210	89	4,5	0.38	1.4	3.6	1.9
Max, mg/kg	16	0.38	29	120	18	88	48	55	5.4	5.6	550	390	150	9.9	0.66	2.3	42	3.6
EF_g, (DF_g)**	1.1	(1.3)	(1.2)	1.4	1.3	1.2	(1.1)	1.4	3.2	3.2	1.1	1,7	(1.0)	4.2	1.3	1.4	3.3	1.2
Paleozoic Dzhida complex (n = 15)																		
Average, mg/kg	4.9	0.4	31.7	133.5	22.8	47.8	81.0	34.1	7.8	1.6	698.0	274,0	175.5	34.3	1.3	3.8	10.8	2.6
Min, mg/kg	3	0.23	18	54	11	37	34	20	1.4	0.71	380	130	81	3.1	0.22	1	4.3	1.8
Max, mg/kg	6.7	0.72	100	200	38	67	200	67	48	3.1	1200	480	300	220	9.8	35	54	3.8
EF_g, (DF_g)	(1.4)	(1.1)	1.2	1.9	2.0	(1.2)	2.1	1.2	7.1	2.4	1.5	1,6	1.4	20.2	3.0	2.8	2.1	1.1
Cambrian complex: Khokhyurta and Dzhida formations (n = 4)																		
Average, mg/kg	3.5	0.5	40.5	113.0	13.6	35.4	39.3	27.8	5.1	1.2	587.5	205,0	101.0	31.2	1.1	1.2	5.3	1.7
Min, mg/kg	1	0.23	5.9	37	3.3	8.6	27	11	2.1	0.64	290	150	14	2.1	0.19	0.39	1.1	1.3
Max, mg/kg	5.4	0.89	90	200	18	62	67	48	10	2	1100	320	170	62	2.9	1.8	8.1	2.1
EF_g, (DF_g)	(2.0)	1.1	1.5	1.6	1.2	(1.7)	1.0	(1.0)	4.6	1.8	1.3	1,2	(1.3)	18.3	2.7	(1.1)	1.0	(1.4)
Mid-Permian/Lower Triassic Chernyi-Yar formation (n = 2)																		
Average, mg/kg	6.6	0.2	16.5	81.5	17.0	56.5	29.5	25.5	1.4	2.8	655.0	130,0	185.0	4.9	0.3	1.3	7.9	2.0
Min, mg/kg	4	0.13	15	78	15	41	18	20	0.96	1.9	510	120	180	3.8	0.26	1	5.9	1.7
Max, mg/kg	9.1	0.18	18	85	19	72	41	31	1.8	3.7	800	140	190	6	0.39	1.5	9.8	2.3
EF_g, (DF_g)	(1.0)	(2.6)	(1.6)	1.2	1.5	(1.1)	(1.3)	(1.1)	1.3	4.2	1.4	(1,3)	1.4	2.9	(1.3)	(1.1)	1.6	(1.3)

* n – number of samples.

** The values in brackets correspond to DF_g,.

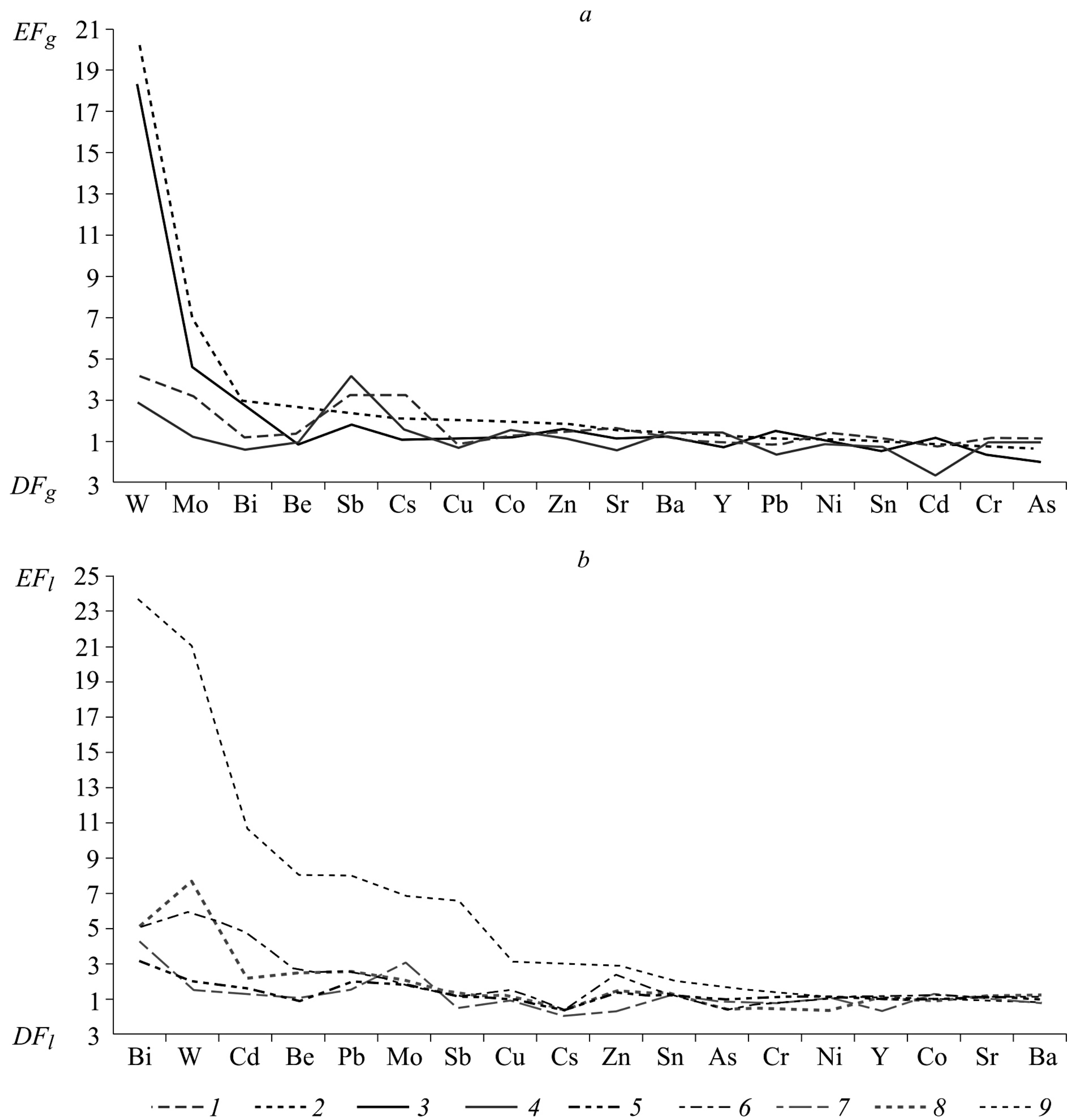

Fig. 2. Geochemical spectra of background (*a*) and urban (*b*) soils in the area of Zakamensk.
Background soils occurring on: *1* – Quaternary alluvial deposits (*n* = 6), *2* – Paleozoic Dzhida complex (*n* = 15), *3* – Cambrian complex (*n* = 4), *4* – Mid-Permian/Lower-Triassic Chernyi-Yar formation (*n* = 2). Urban soils occurring at: *5* – private homesteads (*n* = 24), *6* – urban buildings (*n* = 6), *7* – natural-recreational zone (*n* = 19), *8* – transport zone (*n* = 4), *9* – industrial zone (*n* = 52).

All the background soils have a common group of elements exceeding the average world values: W (EF_g = 2.9–20.2), Mo (1.3–7.1), Bi (2.7–3.7), and Sb (1.8–4.2). The ore elements W and Mo are characterized by the largest values of EF_g. The soils on the Chernyi-Yar formation comprising effusive rocks are depleted in all the elements, except for W, Mo, Sb, Cs, Co, Ba and V.

The soils on the Dzhida complex are distinguished by the highest average concentrations of hazard class I (Be and Zn), II (Co, Cu and Mo) and III (Ba and W) elements. Background spoil samples on alluvial deposits are characterized by the highest average values of As, Cr, Ni, Sr, Bi, Cs and Sn. The lowest average concentrations of almost all elements were recorded in the soils on the Chernyi-Yar formation, and on the Cambrian complex. The sole exception for the former is provided by Sb and V, and for the latter by Cd and Pb.

The priority pollutant elements in urban soils. According to the geochemical spectra of the soils for different functional zones (see Fig. 2, *b*), the industrial zone of the city is most polluted: $Bi_{23.6}W_{21.0}Cd_{10.8}Be_{8.1}Pb_{8.0}Mo_{6.9}Sb_{6.6}$, which is in agreement with data from [17]. The list of elements representing priority pollutants is determined by their entry from several sources: the tailing ponds with high content levels of these substances inherited from the initial ores [17], from the Liteishchik plant, the emissions from which contain W, Sb, Mo, Pb, Cu and Cr [26], and from the boiler oil-burning thermoelectric plant, the mineral components of which include V, Ni, Cr, Mo, Pb and Cu compounds [26, 28].

The residential zone with multi-storey buildings occupies the second place as regards the soil pollution level, because it is surrounded by technogenic sands of the Dzhida tailing pond with an increased degree of aeration and water permeability when compared with rocks. Therefore, this area exhibits active deflation, water erosion, sheet wash and chemical sulfuric weathering, which acts to increase the rate of sulfide oxidation and dissolution of weathering products. Their lateral migration leads to enrichment of the soils of the nearby residential zone with $W_{6.0}Bi_{5.2}Cd_{4.8}Pb_{2.6}Be_{2.5}Zn_{2.4}$.

The soils of the transport zone accumulate $W_{7.6}Bi_{5.1}Be_{2.5}Pb_{2.5}Cd_{2.1}Mo_{2.1}$, and $Bi_{4.3}Mo_{3.0}$ correspond to the natural-recreational zone. The cleanest soils occur in the zone of homesteads, and in the natural-recreational zone which are located mainly on the left bank of the Modonkul' river. The sole exception for the former zone is provided by the ore elements and their satellites: $Bi_{3,1}W_{2,0}Mo_{1,8}$, as well as by the $Pb_{2,0}Zn_{1,3}$ pollutants typical for urban territories. For the other elements in these zones, the values of EF_l are similar to background values, i.e. usually, they do not exceed 1.1–1.3.

Thus the priority pollutants of the soils in Zakamensk are represented by the halcophilic elements W, Bi, Cd, Pb и Mo which mostly occur in the form of sulfide minerals [29]. The cationogenic elements (Bi, Cd and Pb) migrate in acidic waters in the form of true solutions, and in the form of organic high-molecular complexes in weakly acidic-neutral waters [30]. By contrast, the complexing W migrates weakly in strong alkaline waters. Mo is an anionogenic element is deposited with organic matter and Fe and Al hydroxides; it migrates in alkaline conditions [31].

Assessing the degree of technogenic geochemical transformation of urban soils. The consequences of technogenic impacts on the urban soil cover were assessed in terms of the total pollution index Z_c from the complex of HM and metalloids with respect to background soils occurring on the same parent materials. In the influence zone of the DM-WoP, several anomalous zones were revealed (Fig. 3). The most contrasting zone occurs at the recultivated (in 2011) emergency tailing pond with no vegetation cover, and the upper layer is represented by a mixture of the previously buries humus horizon and production wastes. The values of Z_c reach 485–721, exceeding the extremely hazardous level by a factor of 3–5.

Another anomaly arose within the main Barun-Naryn and the new Zun-Naryn tailing ponds with a maximum Z_c of 316 and 292, respectively. The third anomaly encompasses the Modonkul' technogenic deposit on the left bank of the river; its origin is due to the erosion processes, channel transport and subsequent deposition of material from the tailing ponds on the mechanical barrier where the direction of flow changes from meridional to sublatitudinal. The maximum values of the Z_c index reach 200. The fourth anomalous zone emerged within the Dzhida tailing pond (max $Z_c = 258$) and the emergency canal for discharging wastes from the DW-MoP (265) where the values of the total pollution indicator exceed more than twice the extremely hazardous level. The emergence of the fifth anomaly in the south-easternmost part is due to deluvial wash-out of material from the overburden heaps.

The most severe technogenic impact corresponds to the soils in the DW-MoP waste storage areas occupied by the multistory residential buildings with the highest population density, children's institutions and other infrastructures as well as by the floodplain and terraces of the Modonkul', Barun-Naryn and Zun-Naryn rivers, the Inkur brook and the overburden storage areas. The highest soil pollution level ($Z_c > 128$) was recorded in 25% of the urban territory. Such an extensive area of extremely polluted soils is due to a wide range of uses of production wastes containing toxic elements of hazard class I–III: in preparing concrete mixes for the construction of houses and other buildings, creating children's sandboxes, covering roads, filling pits, etc. With such total contents of HM, there is taking place an increase of the sickness rate of the population as regards the respiration organs and the musculoskeletal system [32].

A weak technogenic geochemical transformation ($Z_c < 16$) is characteristic for the soils occupied by 'dachas' (country-cottages) and the natural-recreational zone in the outskirts of the city, on the banks of the Modonkul' river in its upper reaches, and on its left bank in the middle and lower reaches, and in the upper reaches of the Zun-Naryn and Barun-Naryn rivers. The total area of these tracts constitutes 35%.

An average degree of soil geochemical disturbance ($16 < Z_c < 32$) was revealed around the places of waste storage in the downstream section of the Inkur brook valley, on the recultivated emergency tailing pond, on

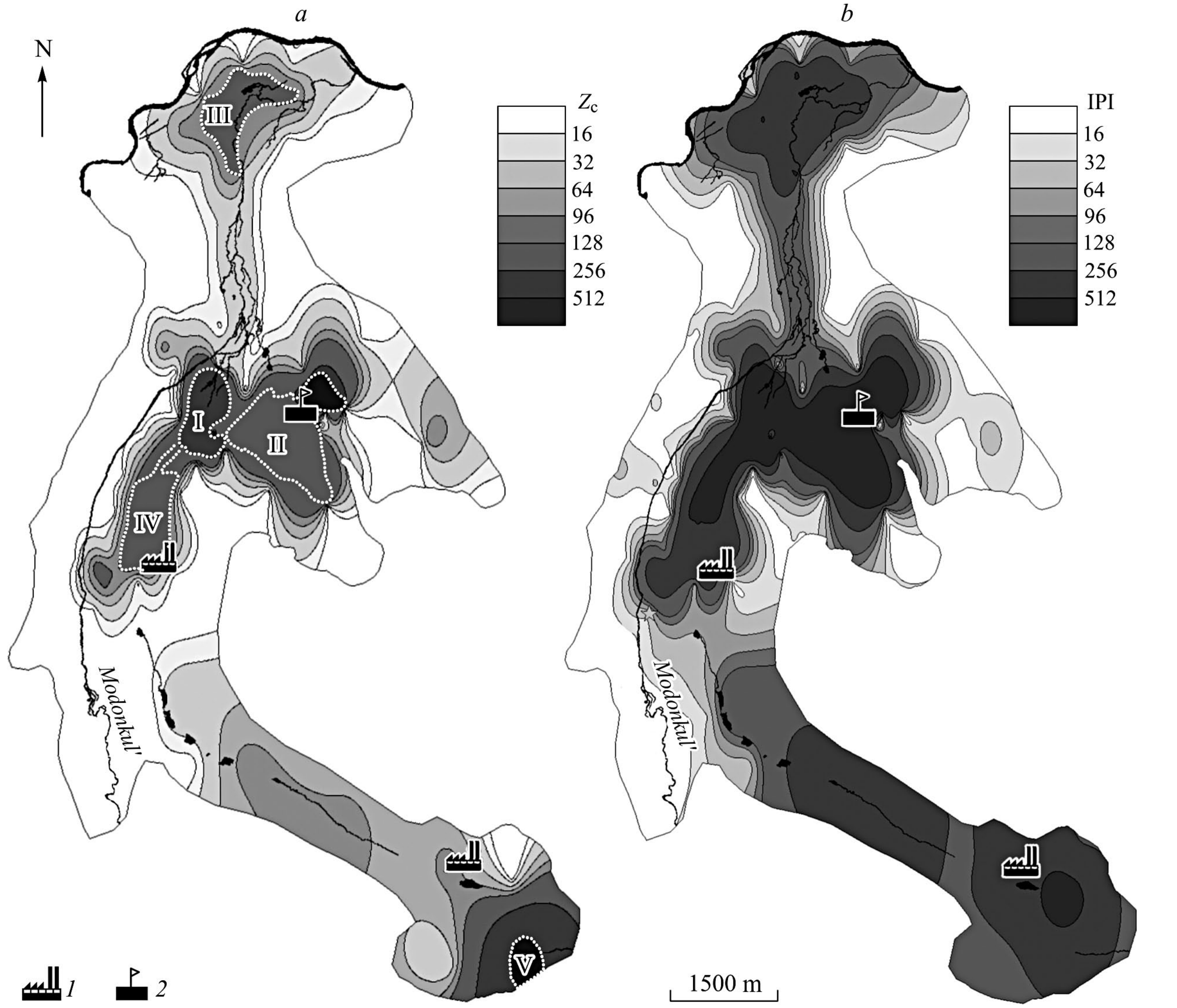

Fig. 3. Distribution of the total (*a*) and integral (*b*) pollution indicators in the surface (0–10 cm) soil horizon and TSF of Zakamensk. Facilities of the industrial zone: *1* – abandoned DM-WoP, *2* – dressing plant of ZAO Zakamensk. The numbers correspond to the accumulation zones of HM and metalloids.

the urban refuse disposal site east of the city, and along 3.5 km of the valley of the Modonkul' river between the Barun-Naryn tailing pond and the Modonkul' technogenic deposit. The area of these tracts makes up 12%. A moderate and a high level of anthropogenic load ($32 < Z_c < 128$) was observed around the main zones of accumulation, i.e. the tailing ponds, as well as along the brook valley. The total area constitutes 28%.

The differentiation factors for urban soils according to content of HM and metalloids. The role played by the natural and anthropogenic factors that are responsible for the spatial differences in the total accumulation of HM and metalloids in urban soils was ascertained through multidimensional regression analysis. We examined the influence of the functional purpose of the territories, i.e. the nature and level of anthropogenic impact on the landscape; parent materials that determine the natural geochemical inhomogeneity of the soils; absolute terrain elevations characterizing the geochemical position of an elementary landscape or its occurrence at artificial accumulative forms (tailing ponds, overburden heaps, etc.) in the industrial zone, and the physicochemical properties of the soils determining the migration capacity of the elements: response of the medium, humus content, the Al_2O_3, Fe_2O_3 and MnO oxides, and the particle-size composition (the amount of physical sand and clay fraction).

It is found that the value of the total soil pollution indicator, Z_c, is determined by the nature and level of anthropogenic impact (Fig. 4). A further differentiation of soil pollution depends on content of clay fraction (particulate matter less than 0.001mm in diameter),

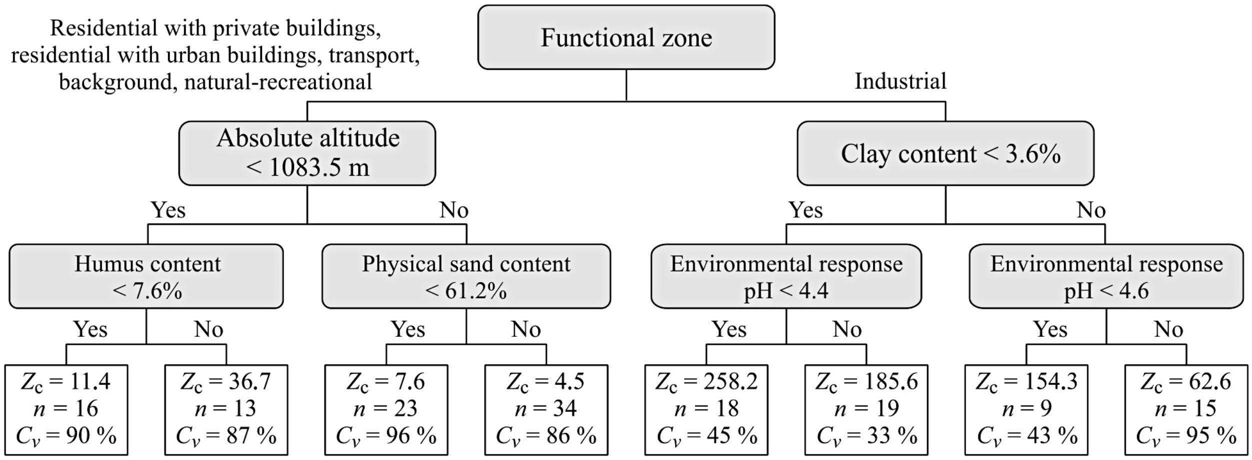

Fig. 4. Differentiation of the total soil pollution indicator Z_c of Zakamensk versus anthropogenic and natural factors. The mean value of Z_c, the number of sampling points n and the variation coefficient C_v. are given for each end node.

and on alkaline-acid conditions. The two factors are determined by mining technology and geochemical characteristics of ore bodies. Clay fraction is produced due to crushing of W-Mo-containing material to particulates as small as 0.07 mm. Acidulation is caused by various acids used in the ore dressing process, and by chemical sulfuric weathering of material that is extracted and accumulates in spoil heaps of the sulfide-tungsten deposits (Inkur and Kholtoson); in this case, ore minerals are liberated, and the rate of sulfide oxidation and the rate of dilution of weathering products are increased.

The territories where the content of clay fraction in soils and TSF exceeds 3.6% constitute natural landscapes that underwent technogenic acidulation. Soils of the highest acidity (pH < 4.6) with a critical pollution level (Z_c = 154) occur in the vicinities to the open cast, spoil heaps (within the 200-m zone) and in the valley of the Gudzhirka river draining them as well as in the production area of DW-MoP. A high soil pollution level in the industrial zone (the average Z_c = 62.4) was observed on the territories occupied by the thermoelectric plant, the pollution control facilities, and the urban and unauthorized waste disposal sites in the lower reaches of the Modonkul' river as well as the area between the Barun-Naryn and emergency tailing ponds.

In the other functional zones, the leading factors for soil pollution are represented by the geochemical position (abs. alt., m), and by humus content. The largest average value of Z_c = 36.7 was revealed in subordinate landscapes at abs. alt. < 1082 m, on the floodplain and on the first terrace above floodplain of the Modonkul' river where alluvial soils occur, with high content of organic matter (> 7.7%). The lowest pollution (Z_c = 4.5–7.6) is typical for autonomous and transit (valley slopes) positions as well as for the upper reaches of the Modonkul'.

Assessing the ecological-geochemical state of soil cover in Zakamensk. The ecological hazard of soil pollution was assessed by comparing the contents of HM and metalloids with the current normative of the RF [23, 24]. Most of the elements lack any legislatively approved MAC/TAC; therefore, the hazard coefficients (or, according to GOST, the exceedance ratios in MAC) $HQ_o = C_a/MAC$ were calculated only for V, Pb, As, Cd, Cu, Ni, Zn and Sb; a more stringent normative was used where both MAC and TAC were available for an element.

In all zones, the most severe ecological hazard comes from Pb, Sb, Cd and As, the content levels of which in the soil cover are determined by technogenic factors (Table 2). In the industrial zone, HQ_o of these elements is 7.8, 3.6, 2.1 and 1.7, respectively, and in the residential multistory zone, it is 1.8, 0.5, 0.8 and 1.0. In the soils of the transport zone, the values of HQ_o are lower for all substances, except for Pb, Zn and Sb which are present in exhaust emissions. The main sources of HM in all zones are represented by wastes from DW-MoP, because the payable ores from the Pervomaiskii stockwork and the Inkur and Kholtoson deposits contain, in addition to the elements (W, and Mo) extracted, contain high concentrations of Pb, from 400 to 5600 mg/kg, and Zn, 380–3800 mg/kg [19]. The soils in the background areas are distinguished by an exceedance in MAC: As (HQ_o = 1.1), and V (1.1).

The hazard of polyelement pollution of the surface soil horizons in Zakamensk was assessed from the IPI index which was more contrasting than the Z_c index, with the spread of values from 1.5 to 1737, averaging 93, which indicates a very hazardous ecological situation.

The zone of ecological disaster (*IPI* > 128) includes almost half the city, 49%. A critical state of

Table 2. Hazard quotients HQ K_o of HM in soils in the functional soils of Zakamensk

Functional zone	Exceedance ratio in MAC, HQ_o		
	> 2	2–1	< 1
Industrial	$Pb_{7.8}Sb_{3.6}Cd_{2.1}$*	$As_{1.7}Zn_{1.7}Cu_{1.2}V_{1.0}$	$Ni_{0.5}$
Residential with urban buildings		$Pb_{1.8}Zn_{1.1}As_{1.0}V_{1.0}$	$Cd_{0.8}Sb_{0.5}Ni_{0.5}Cu_{0.4}$
Residential with private buildings		$Pb_{1.6}As_{1.2}Cd_{1.1}V_{1.0}$	$Zn_{0.7}Sb_{0.5}Ni_{0.5}Cu_{0.4}$
Natural-recreational		$Pb_{1.8}As_{1.0}$	$V_{0.9}Zn_{0.7}Sb_{0.6}Cd_{0.3}Cu_{0.3}Ni_{0.3}$
Transport		$Pb_{1.8}As_{1.0}$	$V_{0.9}Zn_{0.7}Sb_{0.6}Cd_{0.3}Cu_{0.3}Ni_{0.3}$
Background		$As_{1.1}V_{1.1}$	$Pb_{0.9}Zn_{0.5}Cu_{0.5}Ni_{0.5}Sb_{0.4}Cd_{0.2}$

* subscript – value of K_o.

environment has influence on the adaptive responses of the population. There are taking place changes of thickness rates in children and adolescents accompanied by a decrease in human body resistivity to pathogenic factors [33]. A hazardous (*IPI* 32–64) and a very hazardous (64–128) pollution levels were recorded in 9 and 11% of the urban area, respectively, and only 20% of the area showed an allowable level (*IPI* < 16) which has no negative effect on human health.

Hence, two-third of the city's territory is currently faced with a critical ecological situation characterized by a very hazardous and exceptionally hazardous soil pollution. Among the priority measures for the bettering of thee ecological situation would be recultivation of the Dzhida, Barun-Naryn and Zun-Naryn tailing ponds as well as the Modonkul' deposit with isolation or phytoremediation of wastes from DW-MoP. Isolation could use methods of consolidating dry sands with bitumen emulsion, liquid glass, resins and other binding materials in order to prevent deflation and eluviation of toxic metals [34]. Phytoremediation implies planting vegetation where plants serve as "hyperaccumulators" which, first, prevent deflation and deluvial removal of material from the decaying dam and from the surface of the Barun-Naryn and other tailing ponds, and, second, extract HM from the soil and concentrate them in terrestrial organs [35]. By removing the phytomass, it would be possible to gradually decrease the hazardous concentrations of pollutants in soils. To keep track of the accumulation of HM and metalloids, it would be appropriate to establish an ecological monitoring of the new Zun-Naryn tailing pond and the adjacent territories.

CONCLUSIONS

Mining landscapes are characterized by high contents of ore-bearing and satellite elements in soils. This is the result of technogenic changes in natural environment caused by the extraction of concentrated clusters of useful components. It is exhibited by a change in directedness and intensity of morphogenetic processes, a change in the balance of erosion-accumulation processes as well as by involving in migration flows a large amount of HM and metalloids supplied to landscapes. As a result, the upper soil horizons develop stable polyelement associations of pollutant elements, the set of which is largely linked to the petrochemical features of the study territories. In the influence area of DW-MoP there emerged an anomalous zone of a large group of chalcophile elements: W, Bi, Cd, Pb, and Mo. The soils of the industrial zone and the adjacent residential multistory zone are experiencing the strongest technogenic load.

Experience of soil-geochemical investigations showed a need to take into account the geological inhomogeneity and metallogenic specificity of mining centers. The local coefficients EF_l / DF_l must be calculated not with respect to the average regional background but with respect to the individual (for each parent material) background value, which would permit a more accurate determination of the degree of technogenic geochemical transformation of soils. For assessing the ecological hazard of polyelement contamination in conditions of an increased geochemical background, it is suggested that the IPI index should be used; it is calculated in accordance with the world-average concentrations of HM and metalloids in soils and takes the toxicity of elements into account. Multidimensional regression analysis can be sued to determine the role played by the natural and anthropogenic factors that are responsible for the spatial differences in the total accumulation of HM and metalloids. An important characteristic of this technique involves taking into consideration not only quantitative but also qualitative indicators, such as the functional zone, parent material, etc. In this analysis, the number of the indicators used can be increased.

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