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Soil Pollution with Heavy Metals in the Industrial Cities of Mongolia

Natalia E. Kosheleva[1], Nikolay S. Kasimov[2], Dechingungaa Dorjgotov[2], Sergey N. Bazha[3], Petr D. Gunin[3], Dmitry L. Golovanov[1], Sandag Enkh-Amgalan[2] and Ochirbat Batkhishig[2]

[1]*Faculty of Geography, Moscow State University, Moscow, Russia, e-mail: natalk@mail.ru*
[2]*Institute of Geography, Mongolian Academy of Sciences, Ulaanbaatar*
[3]*Institute for Ecology and Evolution, Russian Academy of Sciences, Moscow, Russia, e-mail: sbazha@inbox.ru, pgunin@online.ru*

Abstract

The technogenic anomalies in heavy metal patterns in the soils of Ulaanbaatar, Darkhan, and Erdenet cities are characterized both qualitatively and quantitatively. These data permitted to evaluate the background geochemical situation in the study area, and the technogenic specialization of the cities. The geochemical properties of urban soils were shown to display a spatial variability associated with certain functional zones. The ecological status of polluted urban soils was assessed basing on regulatory heavy metal values accepted in Mongolia.

Key words: Heavy metals, urban soils, functional zones, technogenic anomalies, pollution, Mongolia

Introduction

For the recent ten years, the industrial development of Mongolia and growth of the urban population appear to be a basic reason of growing ecological problems on the territory of the large cities. The aggravation of technogenic pressure on the environment was accompanied by air and water pollution, accumulation of pollutants in soil cover, which cause deterioration of life conditions of the urban population. Social-economical and medico-ecological parameters of the environment in Ulaanbaatar determined at the beginning of 1990s have been changed considerably. Thus, goal of this work is to establish qualitative and quantitative characteristics of man-induced geochemical anomalies of the heavy metals (HM), which are dominant pollutants in the soils of three large industrial centers of Mongolia – Ulaanbaatar, Erdenet and Darkhan.

Cities are situated in the intermountain valleys and depressions of Khentei mountainous region within the basin of Selenge river. Ulaanbaatar is the capital city with various industries; Erdenet is the big centre of mining, concentration and primary processing of the copper and molybdenum ore, and in Darkhan ferrous metallurgy, dressing of leather, production of chemical compounds and building constructions were concentrated.

The research included:

– characterization of geochemical composition of background soils in the study region, including geochemical anomaly of natural ore deposit in Erdenet city;

– evaluation of man-induced geochemical transformation of soils in urban environment as a whole and in different functional zones;

– assessment of ecological status of polluted urban soils on the basis of the regulatory HM values accepted in Mongolia.

To address these problems the environmental-geochemical conception was used. It is based on the analysis of concentrations of chemical elements and their compounds in depositing media of urban landscapes (in soils, snow and vegetation cover), which rather exactly reflect process of air pollution and their impact on the environment (Glazovskaya, 1988; Saet *et al.*, 1990; Kasimov, 1995).

Material and Methods

This work was based on the materials of Joint Russian-Mongolian Complex Biological Expedition. Soil sampling was carried out in December 2007 on the territory of Ulaanbaatar (99 samples), Darkhan (46 samples) and Erdenet (50 samples) cities. The mixed soil samples

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have been taken according to the method of "envelope" from topsoil (0-10 sm) with intervals of 500-800 m. Coal samples were collected from three brown coal deposits nearby Ulaanbaatar city – Nalaikh, Baganuur, Chuluut; the ashes of thermal power station TPS-3 were received from the committee for air control at the Ministry of Nature, Environment and Tourism of Mongolia.

Bulk content of Cu, Zn, Pb, Ni, Co, Cr, V, W, Sn, Ga, Ge, Ti, Mn, Y,Zr, Sn, Ba in soil samples was determined using semi-quantitative spectral method at spectrograph DPHS-465C in the laboratory of Alexandrov Geology-geochemical expedition of Institute of Mineralogy, Geochemistry and Cristalchemistry of Rare Elements (Russia). The Hg concentration was determined using methods of nonplasmic atomic absorption at instrument PA-915. Basic physico-chemical properties of soils were studied with routine methods (Orlov, 1985). To evaluate accuracy of semi-quantitative spectral method, part of the soil samples, as well as samples of brown coals and ashes of TPS were analyzed using mass-spectral and atomic-emissive methods with inductively-coupled plasma (ICP-MS) in Research Institute of Mineral Resources with instruments Elan-6100 and Optima-4300 DV ("Perkin Elmer", USA). Both methods gave similar results for studied heavy metals.

Analytical data received was grouped in relation to functional zones and processed statistically using STATISTICA 7 package (Mathsoft, 2004). The stable associations of elements in soils were discovered with method of cluster analysis (algorithm Complete Linkage), the similarity in metal patterns was characterized with correlation coefficients.

Concentration (CC) or dispersion (CD) coefficients of metals in background soils were calculated compared to their global clarkes defined by A. P. Vinogradov (1962), as they occupy intermediate position between Greenwood & Ernsho's (2008) and Bowen's estimations (Bowen, 1979). Coefficients of concentration (Cc) or dispersion (Cd) of heavy metals in urban soils were calculated in relation to background soils. Technogenic-geochemical specialization of urban soils was determined by formula, which included metals with Kc > 1, values of Kc were pointed out in low cases. The ecological-geochemical assessment of urban soils was received on the basis of bulk pollution coefficients *Zc*:

$$Zc = \sum_{i=1}^{n} Cc - (n-1),$$

where, n is a number of metals with Cc > 1 (Saet *et al.*, 1990). In Darkhan and Erdenet, the soils of recreation zones were used as background ones, in Ulaanbaatar they were in the Bogdkhan mountain and recreation zones. To reveal prior pollutants their content in the urban soils was compared with maximum permissible concentrations (MPC) accepted by Mongolian National Center of Standardization (Dotjgotov *et al.*, 2008).

Study area

The territory of Ulaanbaatar city is located in wide intermountain depression of Khentei mountain region at 1300-1500 m above sea level. On the north-west side to it Orkhon-Selenge plateau is situated, which is characterized by the altitudes lowering to North-East direction, soft forms of relief, wide intermountain depressions with bottom 700-1200 m high, where Darkhan and Erdenet cities are located. The climate of this region is sharply continental with significant annual and daily variation of the air temperature.

In the river valleys and intermountain depressions main soil-forming rocks appear to be quaternary sediments with low content of most microelements (CD=1.2-1.5). In intermountain depressions they are represented by alluvial-proluvial sediments of loamy and sandy-loam composition with inclusions of rubble, gravel and pebbles. At some places paleogene–neogene sediments which concentrate Fe, Mn and Co (CC=1.5-2.6) come to the earth's surface. Among the parent rocks granosyenites dominate which enriched with complex of lithophilous elements, as well as metamorphic effusive-sedimentary Devonian and Carboniferous rocks with near-clarke content of Pb, Mo, V and high content of Fe, Ti, Cu, Ni, Cr (CC=1.7-2.8) in relation to their world clarkes (Batkhishig, 1999).

The region belongs to ecotone zone of south Siberia and Central Asia, where unique type of landscapes, the mountain exposition forest-steppe occurs (Khudyakov, 2009). It is presented by forest and sometimes typical taiga on the northern exposition slopes, which are more cool and humid, and where seasonally-frozen soils of turf mountain-forests are forming. The southern warmer slopes are occupied with vegetation of shrubby-dry steppes and meadow-steppe. On the plain, it is changed to dry steppe with mountain chernozems and chestnut soils. Most soils have low content of humus (< 4 %), significant gravelly and stoniness of all soil horizons (Nogina *et al.*, 1984). River valleys are occupied by alluvial soddy stony-pebbly soils with meadow communities, willow-beds and sometimes poplar-larch forests. In meander lakes meadow-boggy soils are forming.

Ulaanbaatar is the largest industrial centre in Mongolia, today the capital has over one million of population. The number of population in Darkhan and Erdenet reached 87 and 80 thousand, respectively. During recent ten years, the population of Ulaanbaatar city has been increased by 1.6 times and car park is about double. Along with industries and traffic, thermal power stations and individual stoves in private houses (gers – traditional round dwelling), which combust brown coal are one of the main sources of air pollution in all the cities (Gunin *et al.*, 2003).

Negative effect of urbanization of the study area is displayed in destruction of natural vegetation, increase of water and wind erosion, which enhances content of dust in the atmosphere. Due to windless anticyclone weather regime in winter stable temperature inversions dominates. They cause increased concentrations of many toxic elements, which are slowly accumulating in snow cover and upper horizon of soils. Thus, in the cities dangerous ecological situation appears.

Results

Regional soil-geochemical background and its transformation in the large industrial centers. To assess technogenic-geochemical transformation of the urban soils chemical composition of background dark-chestnut soils and soils of recreation landscapes was determined and their geochemical spectra were built (Fig. 1a). Background content of the most of metals in the three cities is similar, it is near the world clarkes for Zn, Mn, V, Ti, Cr, Zr, Hg, Ba, and lower for Ge, Co, Y, Ni (CD=1.7-8.4). In the vicinity of Ulaanbaatar, only a high level

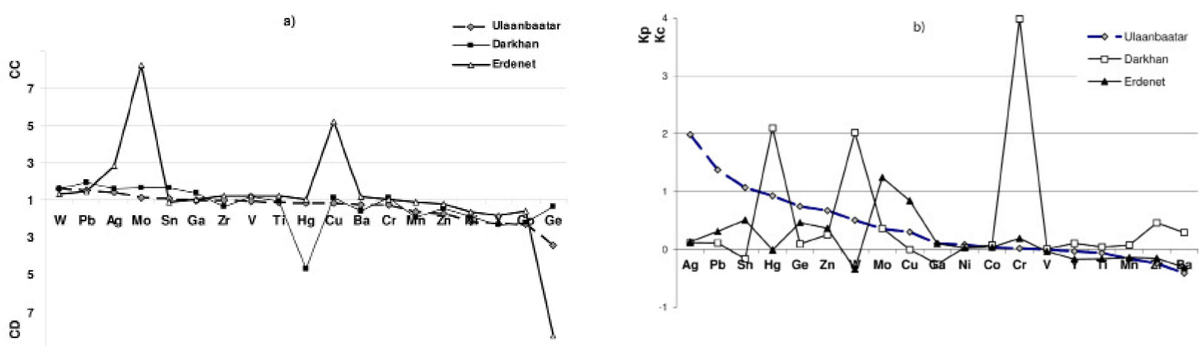

Figure 1. Background geochemical specialization of the region soils (a) and man-caused geochemical specialization of urban soils (b). *Concentration (CC) or dispersion (CD) coefficients of metals in background soils were calculated compared to their global clarkes defined by A. P. Vinogradov (1962), coefficients Cc and Cd – relation to background soils.*

of W (CC=1.5) was found, and in Darkhan it is inherent in Pb, Sn, Mo, Ag and W (CC=1.9-1.5). The region of copper-molybdenum ore deposit in Erdenet is characterized by high content of Mo, Cu, Ag (CC=8.2-2.8).

The urban soils are accumulating HMs incoming from technogenic sources (Fig. 1b). In Ulaanbaatar city, multi-elemental geochemical anomaly of $Ag_{3,0}Pb_{2,4}Sn_{2,1}Hg_{1,9}Ge_{1,7}Zn_{1,7}W_{1,5}$ with relatively low concentration factors has been formed. Its appearance is associated with various industries functioning in the city for a long period and gushing out various pollutants. The soil pollution in Darkhan with $Cr_{5,0}Hg_{3,1}W_{3,0}$ indicates its industrial specialization, which is defined by tanning industry, gold mining and heat-and-power engineering using brown coal. Soils of Erdenet accumulate $Mo_{2,2}Cu_{1,8}Sn_{1,5}Ge_{1,5}$. The source of these elements appeared to be the dump sludge of mining and processing enterprises enriched of Cu and Mo, as well as products of brown coals combustion with high content of Sn and Ge, which spread by wind.

Spatial geochemical heterogeneity of the urban soils. The geochemical heterogeneity of soils in the cities is caused by functional structure of their territories. It includes traffic zone, ger zone, many-storeyed residential blocks, industrial and recreation zones. For each zone, average concentrations of HMs and parameters of their variability were calculated, associations of elements were determined and geochemical spectra were plotted (Table 1).

In Ulaanbaatar, the highest level of pollutant accumulation in soils has been observed near highways and within many-storeyed residential blocks in the central old part of the city, where Pb, Hg, Ag, Zn, Mo, Cu have enhanced concentrations (Cc=3-1.5). In industrial zone, Cc was lower at 0.5 because of large area where industrial emissions incoming from pipes disperse in the atmosphere at considerable height. The weak pollution was found on ger areas situated in suburbs of the city. Despite the fact that these quarters are relatively young Pb and Ge have been accumulated there. The main source of these elements is ash, which forms during incomplete combustion of brown coal used to heat gers.

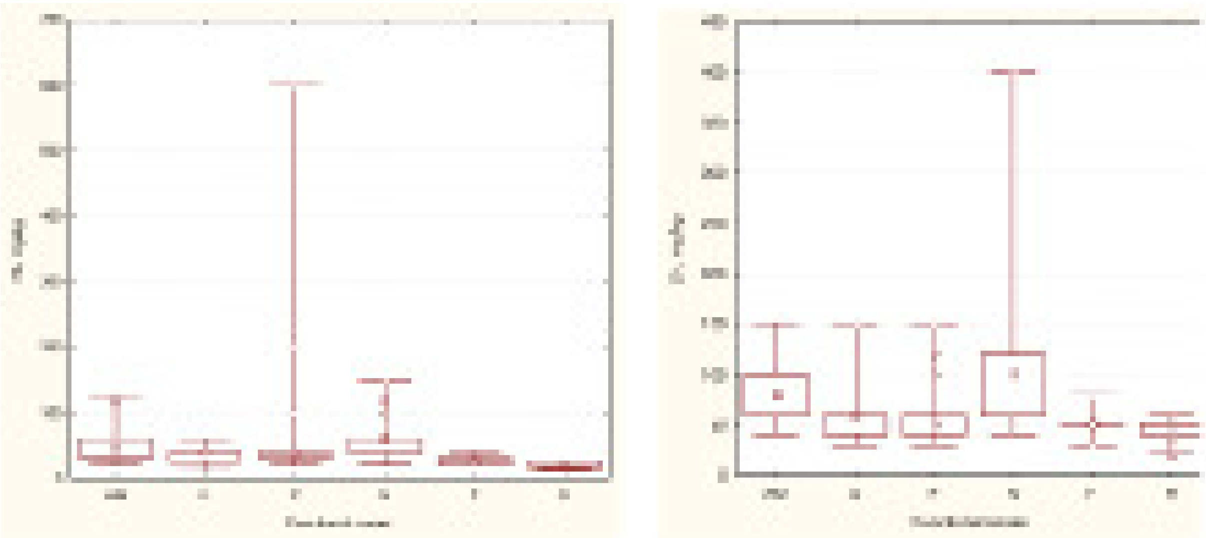

Figure 2. Box-and-Whiskers plots for Zn and Pb content in upper horizon of soils in various functional zones of Ulaanbaatar: *AM – highways; U - ger quarters; P – industrial zones; N – many-storeyed residential quarters; F – background area; R – recreational zones*

Geochemical heterogeneity within the zones is rather high (Fig. 2). It is displayed in increased variability of concentrations of chemical elements and formation of local amonalies with extremely high content of some elements.

Comparison of microelement composition of brown coals and ashes of TPS allowed discovering prior pollutants of urban landscapes in Ulaanbaatar, connected with heat-and-power engineering activities (Table 2). The brown coal of Ulaanbaatar**,** as a most part of sulphureous coals, is enriched with calcophilous elements (Se, Sb, Bi, Pb), as well as W, Be, Mo – elements, which define geochemical specialization of coal-bearing basin. In comparison with coals of the world (Yudovich, Ketris, 2005) coals of Ulaanbaatar have high content of Cu and Pb, and ashes were enriched with W, as well as natural radionuclides, Th and U. The ratio of microelement content in ashes of TPS versus their content in coal showed elements, which transfer to gas phase – Se, Sb, Hg, Te, Bi and possibly, Pb. They do not accumulate in solid phase, spread for a long distance and influence negatively to population health.

The most stable associations of elements, which were found almost in all the functional zones of the city, are: Cu–Zn–Pb; Ni–Co–Ga; Cr–V; Mn–Ti; Ba–Zr. The first association combines elements from technogenic sources, first of all from vehicles. The second and the third associations include the elements, accumulated in fine dust fractions and their concerted variation was associated with heterogeneity of soil texture. The fourth and the fifth associations reflect geochemical features of soil-forming rocks on the territory of city.

Table 1. Average content of heavy metals in upper (0-10sm) horizon of soils in various functional zones of Ulaanbaatar, Darkhan and Erdenet and its maximum permissible concentrations (MPC) (Dotjgotov *et al.*, 2008)

		Elements from different classes of ecological danger (hazard)											
			I				**II**				**III**		
Functional zone	number of samples	***Hg***	***Zn***	***Pb***	***Ni***	***Co***	***Cr***	***Cu***	***Mo***	***W***	***Mn***	***V***	***Sn***
						Ulaanbaatar							
Background	5	0,058	52,0	27,0	29,0	8,40	66,0	42,0	1,20	1,00	660	84,0	2,80
Recreational	**5**	0,080	42,0	19,4	23,0	6,80	60,0	36,0	1,14	3,00	520	78,0	2,40
Traffic	9	0,170	82,2	55,6	31,1	8,44	70,0	60,0	1,96	3,67	544	91,1	4,22
Industrial	23	0,120	60,4	69,1	27,0	7,39	54,4	47,4	1,65	3,17	478	71,7	4,14
Ger areas	23	0,081	59,6	35,2	24,8	7,57	60,4	42,8	1,29	1,35	509	79,1	3,00
Many-storeyed residential quarters	31	0,185	105	59,4	30,6	8,23	72,6	56,5	1,66	3,94	519	85,5	4,17
						Darkhan							
Recreational	3	0,022	50,0	28,3	30,0	8,00	80,0	46,7	1,50	0,50	500	93,3	3,67
Traffic	3	0,083	56,7	40,0	23,3	5,67	80,0	40,0	1,93	3,67	400	80,0	3,00
Industrial	25	0,056	63,6	29,2	32,0	8,92	704	50,8	2,78	7,48	560	104	3,24
Ger areas	7	0,034	91,4	45,8	34,3	10,0	98,6	52,9	2,50	4,57	557	104	4,57
Many-storeyed residential quarters	7	0,058	75,7	34,3	27,1	7,43	98,6	47,1	1,24	4,29	500	100	3,29
						Erdenet							
Recreational	6	0,080	65,0	22,5	34,2	11,0	81,7	243	9,03	1,67	850	107	2,17
Traffic	3	0,037	76,7	21,7	30,0	9,33	60,0	96,7	1,50	1,67	533	103	2,33
Industrial	18	0,101	62,2	24,7	35,0	11,9	113	450	13,6	0,889	822	98,3	2,33
Ger areas	10	0,071	109	30,5	39,0	13,1	88,0	381	13,2	0,50	760	111	5,60
Many-storeyed residential quarters	8	0,062	128	32,5	37,5	10,5	100	95,0	4,31	1,25	625	115	2,75
MPC, sandy soils		0,5	100	70	60	30	60		2	–	–	100	30
MPC, loamy soils		1,0	150	50	100	40	100		3	–	–	130	40
MPC, clay soils		2,0	300	100	150	50	150		5	–	–	150	50

Table 2. Geochemical specialization of Mongolian coal and ashes of heating power station

Sources of pollutants	In relation to clarkes of lithosphere after A.P. Vinogradov (1962)	In relation to average content in coals (a) and ashes (b) of the world (Yudovich, Ketris, 2005)
Coal of Ulaanbaatar (average)	Se333Sb13Bi12W2,1Be2Mo1,8Pb1,6	Pb23Sb16Se4,2Cu3,6Bi2,3Ni1,3 (**a**)
Ashes of HPS	Se128W100Be32Mo13Bi6,5Th6,5As5 Cd4Sb3,7Cu3,7U3,1Sr3Co3Sn1,8Pb1,7	W5Th4,2U2Cu1,7 (b)

In the soils of Darkhan the most wide spectrum of pollutants, $W_{15}Cr_{8,8}Hg_{2,6}Ge_{1,9}Mo_{1,9}Zr_{1,5}$ was determined in the industrial zone. The soils of ger quarters are characterized by the following formula of technogenic-geochemical specialization: $W_{9,1}Zn_{1,8}Mo_{1,7}Hg_{1,5}$. In the soils of many-storey residential blocks significant accumulation of $W_{8,6}Hg_{2,7}Ge_{1,5}Zn_{1,5}$ was revealed. The main features of soil geochemical transformation in Darkhan were displayed in composition of element associations. The most stable are: Cu–Zn–Pb; Mo–W–Ge; Sn–Ga; Zr–Y–Ba; Ni–V; Co–Ti. First three, for fair, are of man-caused origin; moreover, the contamination spreads over large area. The most dangerous/hazardous metals – Cr, Ag, Hg – do not form stable association because of point character of contamination.

In the soils of Erdenet the most contrasting man-made anomaly is in the quarters of gers, where $Sn_{2,6}Ge_{2,4}Zn_{1,7}Cu_{1,6}Mo_{1,5}$ are accumulated. In the soils of the industrial zone $Cu_{1,8}Mo_{1,5}$ are accumulated, in many-storeyed residential blocks – $Ge_{2,2}Zn_{2,0.}$ For traffic zone, pollution was not determined, possibly, because of its transient geochemical position on the slope of river valley. The soil-geochemical heterogeneity of Erdenet is characterized by specific association of elements in each functional zone. Among them the most stable are Cu–Ag–Mo; Mn–Ba–Ti–Y–Zr, reflecting composition of soil-forming rocks, and Pb–Zn, showing man-caused contamination.

Environmental-geochemical assessment of urban soil pollution. The values of bulk soil pollution coefficient Zc for Ulaanbaatar and Erdenet appear to be low in all functional zones. In the first city, Zc varies from 2.5 (ger blocks) to 8.7 (many-storeyed blocks), while in the second one – from 1.3 (highways) to 5.1 (ger blocks) due to high background content of some HMs. The highest Zc values are usual for soils of Darkhan – in residential and traffic zones it varies within 11-14, in industrial zone it achieves 26.7, what corresponds to average level of contamination.

To assess the ecological status of soils in Ulaanbaatar, Darkhan and Erdenet, the concentrations of HM in upper soil horizons were obtained and then compared with regulatory HM values accepted in Mongolia (Dotjgotov *et al.*, 2008), which defined according to granulometric composition of soils (Table 1). Results of comparative estimations indicated that in Ulaanbaatar excess of MPC was fixed only for Cr (MPC excess was found at 25% of the city area), Mo (19 %), Zn (15 %) and Cu (10 %). Portion of man-caused polluted soils is more considerable in two other cities: in Darkhan the most hazardous pollutants are Cr (80 %), V (60), Mo (49), Cu (27), Zn (24), Pb (13), in Erdenet – Cu (82 %), Mo (71), Cr (51), V (24) and Zn (20).

Conclusion

Background geochemical specialization of the region soils displays low or similar HM concentrations compared to their world clarkes. For Ulaanbaatar, exception is W (CC=1.5), in Darkhan – Pb, Sn, Mo, Ag and W (CC=1.9-1.5). A contrasting natural geochemical anomaly was found in soils of Erdenet with high content of Mo (CC=8.2), Cu (5.2), Ag (2.8).

Man-caused geochemical specialization of Ulaanbaatar – $Ag_{3,0}Pb_{2,4}Sn_{2,1}Hg_{1,9}Ge_{1,7}Zn_{1,7}W_{1,5}$ – has been formed under influence of many different sources of soil pollution. Major pollutants of Darkhan soils – $Cr_{5,0}Hg_{3,1}W_{3,0.}$ – were derived from tanning-production, gold mining and heat-and-power engineering. In Erdenet the technogenic accumulation of $Mo_{2,2}Cu_{1,8}Sn_{1,5}Ge_{1,5}$ enhances natural ore anomaly of the first two metals.

Geochemical specialization of functional zones of Ulaanbaatar was shown in wide spectrum of pollutant elements, which present in soils of many-storeyed residential blocks and highways – Hg, Pb, Ag, Zn, W, Ge, Cu, Sn, Mo, Cu. In Darkhan, extremely high level of W and Cr accumulation in soils was observed of the industrial zone and that of W and Hg – in soils of residential and traffic zones. In Erdenet, the most contrasting man-caused anomaly was determined in soils of ger blocks: $Sn_{2,6}Ge_{2,4}Zn_{1,7}Cu_{1,6}Mo_{1,5}$. The soils of industrial zone accumulate $Cu_{1,8}Mo_{1,5}$, many-storeyed blocks – $Ge_{2,2}Zn_{2,0.}$

In Ulaanbaatar soil bulk pollution coefficient Zc changes from 2.5 (ger blocks) to 8.7 (many-storeyed blocks). Maximum values of Zc were determined in soils of Darkhan – 26.7 in the industrial zone, 11-14 in residential and traffic zones. In Erdenet Zc values are not too high – from 1.3 (highways) to 5.1 (ger quarters) – due to high background content of some HMs. Environmental-geochemical assessment of urban soils determined the excess of MPC for four metals (Cr, Mo, Zn, Cu) on 15-25 % of the area of Ulaanbaatar. Ecological situation in two other cities is more hazardous: excess of MPC for Cr, V, Mn was determined on 50-80 % of area of Darkhan and that of Cu, Mo, Cr – in Erdenet city.

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