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Impact of Geochemical Barriers on the Accumulation of Heavy Metals in Urban Soils

N. E. Kosheleva, Academician N. S. Kasimov, and D. V. Vlasov

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Abstract—Based on multidimensional statistical models that connect the levels of contents of heavy metals and metalloids in the soils of the Eastern Administrative Okrug of Moscow with landscape and anthropogenic factors, a comparative estimation of the capacity of the complex geochemical barriers in the surface layers of urban and background soils is carried out. The share of heavy metals fixed in the urban soils due to the technogenous transformation of their physical and chemical properties, which amounted to 40–50% of the total content for Bi, Pb, Cd, Sb, As, and up to 26–30% for Zn and Cu, is calculated. The growth in the content of Bi, Sb, As, Cu, Pb, and Zn in urban soils is caused by an increase in the quantity of iron and manganese oxides. The increase in the content of Sb, As, and Pb is related to organic matter; and the rise in Bi, Cd, and Cu has resulted from the increasing amounts of the silt and clay particles in the soils, which indicates the leading role of sorption geochemical barriers. Cu, Zn, and Cd also accumulate on alkaline barriers.

Keywords: heavy metals and metalloids, geochemical barriers, ecogeochemistry, urban landscapes, technogeneous transformation, soil properties.

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In urban landscapes the emission of technogeneous dust enriched with pollutants leads to the transformation of natural properties of soils and accumulation of different elements on the peculiar aerotechnogeneous geochemical barrier (GB) in the upper soil layer [3, 7, 9, 13]. The capacity and contrast range of this barrier determine the further behavior of pollutants to a considerable degree. The chemical composition of the emitted particles, which change the properties of the surface layers of soils, vary enormously, depending on their size and origin. They consist of big particles PM10 with a diameter less than 10 μm, fine ones, PM2.5 (less than 2.5), PM1 (less than 1), and very fine particles PM0.1 (less than 0.1 μm). In cities, PM10 concentrate Zn and Pb; to a lesser extent—As, Cr, Sb, Cu, Ni, Sn, Sr, Cd, Mo, and Ag. PM2.5 are enriched with V, Cr, Mn, Zn, Se, Pb, Ni, Cd, Pt, Pd, and Rd [15]. PM2.5 and PM10 have a 40–60% share of biologically available forms of Ag, Co, Mn, Mo, and Sb, 60–80% of Cu, Ni, and Zn, and over 80% of Cd, Pb, and Tl [12].

The emitted carbonate dust increases the pH of the upper soil layers [2, 3]. The fine fractions of dust and humus substances increase the urban soil exchange capacity. The water losses from the distributing networks which cause waterlogging and sealing, i.e., the placement of buildings on the soil surface, asphalting the soils, etc., lead to compaction and decrease soil porosity and a change in their gaseous regime [9]. This results in the formation of alkaline, sorption, gley, oxidation, and complex geochemical barriers. As usual, their capacity and contrast range are much higher than in the natural counterparts [3], which is an important factor of enhancing the formed anomalies of heavy metals (HM) and metalloids.

The purpose of this work is to assess the impact of technogeneous transformation of the physical and chemical properties of soils on HM accumulation. To do this, we calculated the HM content in the surface layers whose properties corresponded to urban and background soils at a fixed aerial load. The calculations were based on multidimensional statistical models that describe accumulation of metals on the complex GBs depending on natural and anthropogenic factors that determine the input and fixation of the HMs in the soil cover.

We solved the stated problem using the example of the Eastern Administrative Okrug (EAO) of Moscow, where the Faculty of Geography, Moscow State University, has been conducting landscape–geochemical studies continuously [5–8, 10]. Moscow is among the top big industrial centers of Russia with respect to pollution levels [10]. This okrug may rightly be considered as an industrial center of the capital: there are large industrial zones on its territory (Sokolinaya gora, Prozhektor, and Perovo), highways (Moscow Ring Road, shosse Entuziastov, Zelenyi prospect, etc.), Heat Electric Generation Plant-11, and the Incinera-

Faculty of Geography, Moscow State University, Moscow, Russia
e-mail: vlasgeo@yandex.ru

Table 1. Content and mobility of heavy metals in the surface (0–15 cm) layers of the background and urban soils

Soils	As	Bi	Cd	Cu	Pb	Sb	Zn
	Total content, mg/kg						
Background	2.0	0.13	0.21	20	14	0.36	37
EAO	7.8	0.61	1.6	59	63	1.71	179
	Exchange and organomineral forms, mg/kg						
Background	0.04	0.004	0.08	4.2	8.5	0.01	1.0
EAO	0.43	0.098	0.28	16	7.4	0.03	22
	Mobility, %						
Background	2.0	3.1	38.1	21.0	60.7	2.8	2.7
EAO	5.5	16.1	17.5	27.1	11.8	1.8	12.3

tion Plant in the industrial zone of Rudnevo. Urbanization strongly altered the soil cover in the okrug. Anthropogenically transformed soils are dominant there: urban soddy podzolic, urbic technosols, ekranic technosols, and technic regosols that are spread on the glacifluvial sands, clay sands, and technogeneous deposits [11].

This work is based on materials of a soil–geochemical survey in the summer of 2010 and 2011 fulfilled in accordance with technique [10] in the southern part of the EAO (districts: Perovo, Novogireyevo, Ivanovskoye, Veshnyaki, Kosino–Ukhtomskii, and Novokosino) with respect to its land-use structure [6]. Along with 73 samples of urban soils 10 background samples were taken from the surface (0–15 cm) soddy–humus layers of the national natural park Meshchera.

The physical and chemical properties of the soils were determined at the Environmental–Geochemical Center of the Faculty of Geography, Lomonosov Moscow State University: the pH of the water extract was obtained by the potentiometric method; particle-size distribution by a laser particle sizer (Fritsch, Germany); and the content of organic carbon using the Tyurin method. The total content of Cd, Pb, Sb, As, Bi, Zn, Cu, MnO, and Fe_2O_3 was analyzed by the mass-spectral and atomic-emission methods with inductively coupled plasma using the Elan-6100 and Optima-4300 devices (PerkinElmer, United States) at the All-Russian Scientific-Research Institute of Mineral Resources (Moscow). The mobile forms of HMs were studied in an extract of an ammonium acetate buffer with ethylenediamintetraacetic acid (AAB with EDTA) on the novAA–400 atomic absorption spectrometer (Analytik–Jena AG, Germany).

The leading factors of HM migration and accumulation in the soils were found by multivariate regression analysis. The dendrograms were plotted by recurrently dividing the initial database into two parts in a SPLUS package (MathSoft, 1999) and observing the resulting features and grouping variables [14]. For each finite node of the regression tree, the average concentration (or mobility[1]) of a metal and the variation coefficient *Cv* were calculated by *n* points of testing. The HM distribution and mobility in the soils of the EAO of Moscow were modeled with respect to the following factors and conditions:

anthropogenic: type of land use that determines the intensity of pollutants emissions and their composition; the dust load; motor vehicle emissions; the structure and density of building; thickness of technogeneous deposits; and sealing of soils;

landscape: type of sediments and geochemical position (a type of elementary landscape) that determines the intensity of lateral migration and the zones of HM accumulation; waterlogging of soils that controls their oxidation–reduction conditions; greenspace of the area; physical and chemical properties of soils: the pH, the content of leading HM–carrier phases (organic matter, Fe and Mn oxides, silt fractions (less than 1 μm), fine (1–5), medium (5–10), coarse (10–50 μm of dust), as well as fine (50–250 μm), medium, and coarse (250–1000 μm) sand.

Types of land use were allocated on the EAO zoning map compiled by the high resolution images from the QuickBird satellite (Digital Globe, United States) [6]. The specific motor vehicle emissions at each mainline was calculated by V.R. Bityukova using the statistical data, and the dust load at each point was obtained based on the data of [5]. The other anthropogenic and landscape factors were evaluated with the help of the maps [6, 11].

As compared with the background conditions, the technogeneous transformation of properties of urban soils in the EAO is manifested in the growth of Mn and Fe oxide contents by 1.5 and 3.6 times, respectively, and an increase in the pH of the surface layers from an acidic (4.8 on the average) to neutral (7.1) and sometimes alkaline reaction (8.5). The content of soil organic carbon increases from 2.3 to 3.5%, and that of physical clay, from 12 to 16%, which is caused by the emission of technogeneous dust [5, 7, 10], as well as a change in or addition of soil owing to recultivation works. The concentration of total Cd exceeds the background level by 7.6 times; Bi, Sb, Zn, Pb, and As by 4–5 times; and Cu, by about 3 times (Table 1). As a rule, technogenous dust is strongly enriched with mobile forms of elements [12, 13]; therefore, the content of exchange and organomineral forms of Zn and Bi extracted by AAB with EDTA is above the background levels by 36 and 22 times, respectively; and that of As, Sb, Cu, and Cd, by 3–10 times.

The differentiation of the HM total content and mobility is shown by the dendrograms (Fig. 1) that characterize the dependence between the newly formed physical and chemical properties of soils and

[1] Mobility is the percent of mobile forms with respect to the total content of a chemical element.

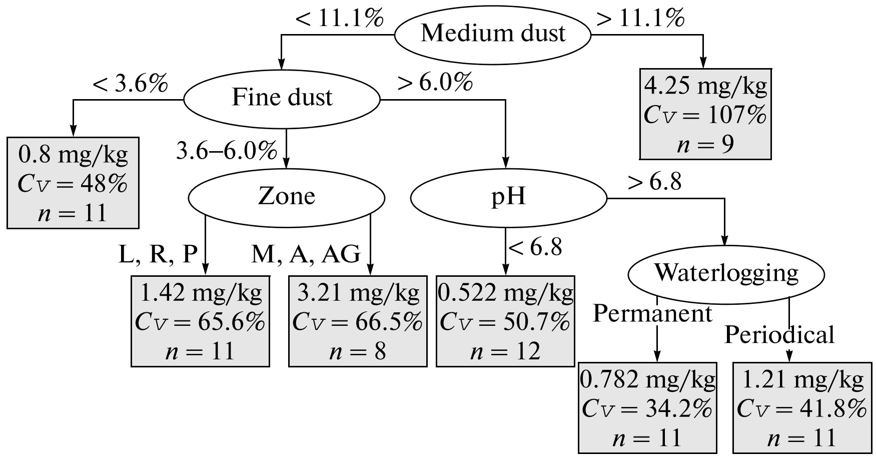

Fig. 1. Total content of Cd in the EAO's soils (in boxes) at various combinations of anthropogenic and landscape factors. *Land-use zones*: M and L are the area of medium-rise and low-rise residential buildings, P is industrial, A is transport, R is recreational, and AG is postagrogenic areas.

fixation of elements at the GBs (Table 2). The total content of HMs in urban soils depends directly on the concentration of Fe and Mn oxides (Bi, Sb, As, Cu, Pb, and Zn), organic matter (Sb, As, Pb), particle-size distribution (Bi, Cd, and Cu), and pH (Cd, Cu, and Zn).

Most HMs enter the surface layers of the EAO from the atmosphere; therefore, the forms and mobility of elements in the emissions are passed to urban soils to a considerable degree. The analysis of HM mobility with respect to particle sizes made it possible to determine the forms of elements as parts of the particular granulometric fractions (Table 2). The dominant input of Pb with medium dust, Cd and Zn with coarse dust, and As with the sandy fraction increases the mobility of these metals in soils due to the great share of mobile forms of elements in the emissions, whereas Cu and As in the medium dust and Sb in the fine dust occur in tightly bound forms that are not extracted by AAB with EDTA. As the Fe oxide content increases, the mobility of Pb, Zn, and Bi decreases. The role of Mn oxides and soil organic matter is displayed in the strong fixation of Bi and strengthening of As mobility. The growth in pH and sealing of soils, which changes their oxidation–reduction potential, decreases Cd mobility.

The sorption barriers play an important role in the accumulation of the majority of the considered HMs in the soils, and Cd, Cu, and Zn are also accumulated on the alkaline barrier (Table 2). The strengthening of the role of sorption barriers is explained by the domination of soils with an increased content of Fe_2O_3, MnO, and dusty particles in the EAO, as compared with the background content, which confirms the data of other researchers [1, 4].

Based on the values at the final nodes of the dendrograms, we determined the total contents of the HMs at the same testing points and with the same factors of the technogenous load but with the physical and chemical parameters of the background soils. For example, at the background value of fine and medium dust in soils, which is less than 11.1% and less than 3.6%, respectively, the content of total Cd is 0.8 mg/kg (Fig. 1). The difference between the actual and calculated concentrations characterizes the quantity of HMs that is fixed in urban soils due to an increase in their absorbing capacity.

As compared with the background soils, change in the characteristics of urban soils leads to an increase in *d* of the average total content of all elements by 33–99% (Table 3; Fig. 2). Here, the share of *p* of fixed Bi, Pb, and Cd is 45–50; that of Sb and As, 40; and Zn, 26%. In the urban soils the mobility of Pb and As decreases and the mobility of Cd and Bi increases; for the remaining elements, it remains the same (Table 3).

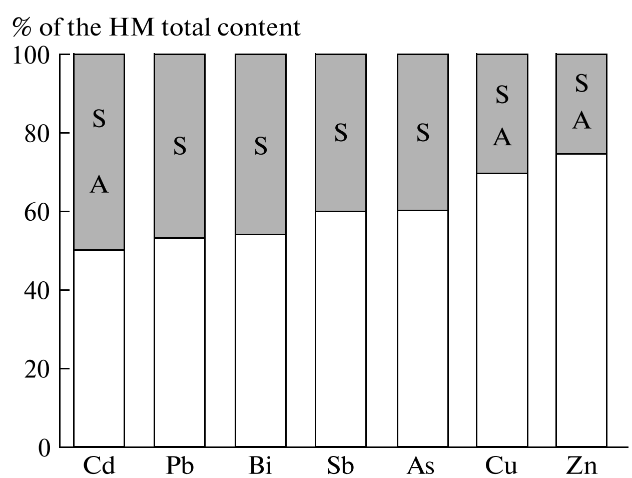

Fig. 2. Accumulation of the HMs in the surface layers of soils in the EAO of Moscow as a result of increased capacity (gray color) of the geochemical barriers: S is a sorption barrier, A is an alkaline barrier.

Table 2. Influence of natural and anthropogenic factors on the distribution and mobility of heavy metals in the surface layer of the soils in the EAO of Moscow

Factors			Total content							Mobility						
			Pb	Cu	Zn	Cd	Bi	Sb	As	Pb	Cu	Zn	Cd	Bi	Sb	As
Landscape	Soil–geochemical properties	pH		2+	2+	3+							2–			
		Content:														
		C_{org}	2+					2, 4+	2+					3–		2+
		Silt	3–									4+				
		Fine dust				2+										
		Medium dust			4+	1+				1+	3–					6–
		Coarse dust		3–			5–					2+	1+			
		Fine sand									4+				2–	5+
		Medium and coarse sands	4+				2+									1+
		Fe_2O_3	2+	1+	1+		1+	3, 5+	1, 3+	5–		3–		2–		
		MnO	3+		5+		3+	4+						3–		
	Type of sediments								3	2		1		1	3	
	Geochemical position		1										1			
	Soil waterlogging					4										
Anthropogenic	Land-use zone			3	3	3	3, 4	1		4, 5	2	5		4	1	4
	Greenspace							5+			3–				3–	
	Soil sealing				3–					4+			3–			
	Dust load			4+							1+					
	Motor vehicle emissions									3+						
	Building-up structure											6				3

The ranks 1–6 show a decrease in the significance of a factor: "+" index growth and "–" index decrease lead to an increase/decrease in the concentration (mobility) of an element; the character of dependence is not established for the quality variables.

Table 3. Average content and mobility of heavy metals in the surface layers of soils in the EAO of Moscow and their change due to an increase in the capacity of the geochemical barriers

Element	Total content of HMs, mg/kg				Mobility, %		
	model (M)	actual (R)	surplus d, %	share of p growth in R	model (M_m)	actual (R_m)	$R_m - M_m$
Cd	0.80	1.59	+99	50	30.3	37.7	+7.4
Pb	33	63	+89	48	14.3	9.7	–4.6
Bi	0.33	0.61	+83	46	9.0	11.7	+2.7
Sb	1.03	1.71	+67	40	1.8	2.1	+0.3
As	4.68	7.76	+66	40	6.0	4.3	–1.7
Cu	41	59	+44	30	23.9	23.2	–0.7
Zn	133	179	+33	26	11.4	12.3	+0.9

M and M_m are the content and mobility of HMs for the background properties of soils, mg/kg; growth $d = (R - M)/M \times 100$, %; $p = (R - M)/R \times 100$ is the share (%) of a fixed element as a result of technogeneous transformation of the physical and chemical properties of urban soils.

Due to the physical and chemical properties of urban soils, the mobile Pb and As that come from the atmosphere are partially neutralized and become less available for plants. The velocity of accumulation of the mobile Cd and Bi exceeds the rates of their total content growth, which leads to an increase in the ecological hazard of polluting urban soils with these elements.

Thus, an increase in the capacity of areal GBs in urban soils at a fixed aerial load depends on the transformation of the physical and chemical properties of surface layers of soils that can fix 33–99% of HMs more as compared with the background counterparts. Transformation of particle-size distribution, accumulation of humus and Fe and Mn oxides, and soil alkalization under urban conditions lead to the formation of complex GBs. To reveal the mechanisms of their functioning at a different technogeneous loads, it is further required to study the ratio of the HM fraction composition in solid–phase emissions from the atmosphere and in soils.

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