Soils of Urban Industrial Traffic
Mining and Military areas

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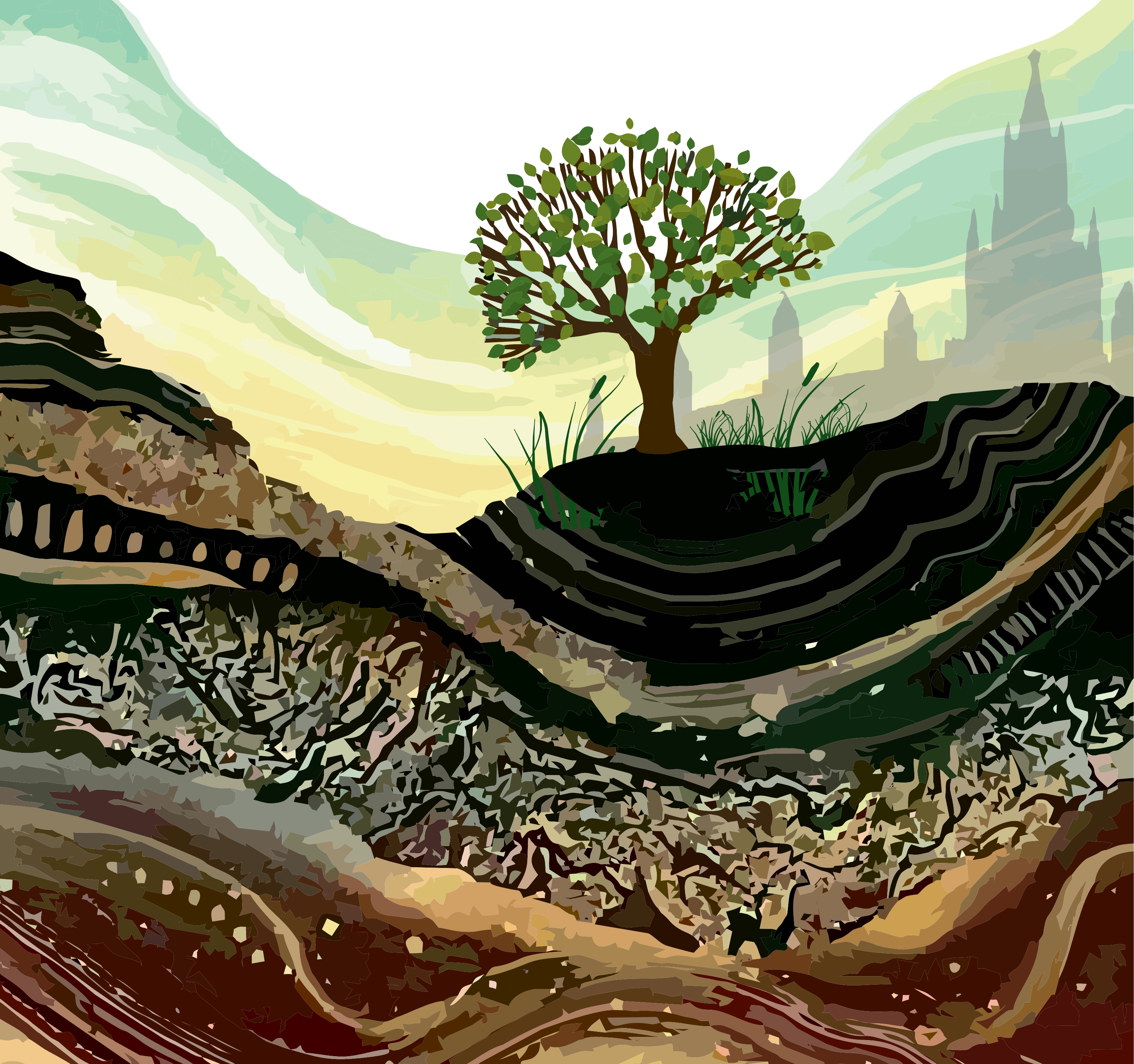
ABSTRACT BOOK



Heavy Metals and Metalloids in Soil Catenas of Mining Areas

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Introduction. A considerable part of heavy metals and metalloids (HMMs) is redistributed in soil catenas, dependent on local landscape-geochemical conditions. There are only few special studies of HMMs' distribution in soil catenas of natural and urban landscapes (Gennadiev and Kasimov 2004; Ruan et al. 2008; Avessalomova 2009). The aim of this study was to determine the features of the HMMs lateral distribution in soil catenas of Dzhida W-Mo (DTMP) and Erdenet Cu-Mo (ECMP) plants influence zones. Particular tasks were as follows: 1) to determine the concentrations of HMMs in soil of conjugate elementary geochemical landscapes of the ore-mining centers; 2) to reveal the major soil and landscape-geochemical factors of the accumulation of HMMs in the catenas and to diagnose lateral geochemical barriers (GBs) according to particular combinations of these factors. GBs are parts of the Earth's crust where intensity of migration of elements decreases sharply within short distances, leading to a concentration of elements (Perel'man and Kasimov 1999; Glazovskaya 2012).

Study objects. Ore-mining centers Erdenet (Mongolia) and Zakamensk (Russia, Buryat Republic) are found in the area of extremely continental climate with cold winter and warm summer. Erdenet territory represents a hilly plain in the zone of expositional forest-steppe with sagebrush-motley grass-grasses plants on haplic kastanozems chromic soils. Gleyic kastanozems chromic soils are common for the floodplains in the narrow strips form. Larch forests are presented at the top of the northern slopes. Zakamensk is located in the mountainous area with a strongly rugged topography, in the taiga zone with larch and birch forests on haplic umbrisols hyperdystric and rendzic leptosols eutric soils. Umbric fluvisols oxyaquic and haplic gleysols dystric soils are common for the lower parts of the smooth slopes and river valleys under the meadow and meadow-marsh vegetation.

The natural soils were anthropogenically modified in the ore-mining centers. The upper soil horizon contains construction and household wastes. Technogenic impact has led to acidification and increase of the content of the physical sand in Zakamensk soil profile and the clay in Erdenet. Artiindustrat and toxicindustrat are formed in the tailings and surrounding areas. Profile of these anthropogenic soils consists of the artificial bulk horizons of toxic and non-toxic materials.

Technogenic impact. Mining plants are developing hydrothermal sulfide deposits. The ECMP was put into operation in 1976. Waste products are stored in the tailing which occupies more than 1500 ha in the Zuna-Gol valley. The DTMP operated from 1934 to 2001. In Zakamensk, 44.5 million tons of waste are stored in Dzhida (filled) and Barun–Naryn (sludge pond) tailings and in the emergency tailing.

Materials and methods. The soil-geochemical survey of Erdenet was performed in summer 2012. We studied six soil catenas with eighteen profiles. The soil pits along the catenas excavated in places characterizing four different landscape-geochemical positions (Perel'man and Kasimov 1999). The soil-geochemical survey of Zakamensk was performed in summer of 2013. Seven catenas with thirty-one soil profile were examined.

The total content of 54 HMMs in the soil samples were identified by mass spectrometry and by atomic emission spectrometry with inductively coupled plasma (ICP-MS and ICP-AES) in the Fedorovskii Institute of Mineral Ores on Elan-6100 and Optima-4300 devices. For the detailed analysis, 16 priority pollutants belonging to the first (Zn, As, Pb, Cd), second (Cr, Co, Ni, Cu, Mo, Sb), and third (V, Sr, Ba, W) hazard classes (GOST 17.4.1.02–83 2008) were selected, as well as Sn and Bi. The properties identified: actual acidity (*pH*), organic carbon content (method of I.V. Tyurin), soil texture (method of laser diffraction, Analysette 22 device).

The obtained data on HMMs concentrations in the background samples C_b were grouped according to their position in the catenas and compared to the elemental percentage abundance (Kasimov and Vlasov 2015) in the lithosphere C via calculation of their relative amounts (clarkes of concentration) $CC = C_b/C$ and reciprocal (clarkes of dispersion) values $CD = C/C_b$. Distribution of HMMs in the catenas and degree of its contrast were characterized by the coefficients of lateral differentiation *L* equal to the ratio of the concentration of a given pollutant in the considered landscape position to its concentration in the autonomous landscape. Location of accumulation zone determines the type of lateral-migratory differentiation HMMs (Gennadiev and Zhidkin 2012): (1) non-accumulative – without significant differences between the element concentrations in the subordinate landscapes, (2) footslope – characterized by the concentration of the elements in the soils of geochemically subordinate landscapes, (3) midslope – showing accumulation of HMMs in the middle part of the catenas; and (4) summit – characterized by the lower element concentrations in the subordinate landscapes in comparison with the autonomous landscapes.

Natural and anthropogenic factors of the accumulation of HMMs in the surface soil horizon and in the soil profile were represented by both quantitative and qualitative variables determined by the method of regression trees using SPLUS software (MathSoft 1999). Mechanisms of developing of the accumulation zones of pollutants can be studied on the basis of the theory of GBs (Saet et al. 1990; Perel'man and Kasimov 1999). Lateral GBs were diagnosed according to the criteria suggested in the study of Perel'man and Kasimov (1999).

Results and discussion. Soil background catenas near Zakamensk and Erdenet have acidic, slightly acidic (*pH*=4.9) and slightly alkaline, alkaline (7.2-9.2) reaction, respectively; organic carbon content 0.2-7% and 0.8-4.1%; light loamy composition with clay fraction 2-2.8% and 2.8-3.5%. The geochemical specialization of soils is greatly affected by the widespread distribution of the volcanic rocks. In the autonomous and subordinate positions, the soils contain increased concentrations of W, Mo, Cd, Bi, and Sr (CC = 1.5–9.2) near Zakamensk and of V, Co, Sr, and As (1.5–3) near Erdenet. Different types of the lateral distribution of the elements are related to the differentiation of the physicochemical properties and the proximity of parent rocks occurrence. In the background catenas HMMs have different types of lateral-migratory differentiation: for the summit accumulative near Zakamensk – Cu, As, Sb, Mo, Pb, V, Co, Ni, Ba, Cd, Sn are common, while V, Cr, Co, Ni are common for those near Erdenet; for the non-accumulative – Bi, Cr, W and Cu, Zn, Sr, Mo, Cd, Sn, W, Ba, Pb, respectively; for the mid-accumulative – Sr, Zn near Zakamensk and footslope-accumulative – As, Sb, Bi near Erdenet.

The contrast in the lateral differentiation of HMMs along soil catenas shows tenfold increases in Zakamensk (*L*=6-47) and several-fold (2-8) – in Erdenet. In both ore-mining centers technogenic impacts have transformed the types of lateral-migratory differentiation of Cu, Sb, Mo, Pb, Bi, W along the geochemical catenas: summit and non-accumulative types in the background catenas changed to footslope-accumulative in the urban. Elements Cr, Ni, Sr have the mid-accumulative distribution. The distribution of the remaining HMMs depends on the individual characteristics of the centers: in DTMP influence zone V, Co, Sn have summit-accumulative type, Ba – mid-accumulative, As, Zn, Cd – non-accumulative; in ECMP influence zone Co – mid-accumulative, Zn, As, Cd, Sn, Ba – footslope-accumulative, V – non-accumulative.

Technogenic impact resulted in the formation of natural-technogenic sorption-sedimentation barriers in subordinate landscapes of the ore-mining centers. In the DTMP impact zone this barrier shows as the increased content of sand (up to 95%) derived from the tailings through water and sulfurous erosion. As a result, concentration of HMMs increases relative to background soil for W, Mo, and Bi 80-fold to140-fold, Sb, Pb, and Cd – 19 to 32-fold, Cu and Zn – 6,5 to 7-fold. In ECMP area the amount of clay fraction increases up to 5-6% and the contents of ore elements Mo and Cu – 7-13-fold. The remaining elements in DTMP area are mainly precipitated on the chemisorption diagnosed by the presence of direct dependence of the concentration of V, Co, and Ba on the contents of Fe, Mn, and Al oxides in the soils. The organomineral barrier specifies the accumulation of Sn, which concentration in the soils is directly correlated with the organic matter content. The concentrations of Mo, Cd and Sb are inversely proportional to the contents of Mn and Al oxides – an evidence of the formation of a gley barrier under conditions of the increased soil moistening with the transformation of Mn^{3+} oxides into less mobile Mn^{2+} protoxides.

In Erdenet, the major role belongs to the chemisorption (V, As, Cr, and Ni) and alkaline barriers. The last one is diagnosed by the positive correlation between *pH* and the concentration of the elements, and is most significant for Sr, W and Sn. Concentrations of the chalcophile elements – Zn, Cd, Pb, Bi and Sb – depend on the nature of parent material; they are higher in the soils developed from the Quaternary deposits and from granodiorite and granite of the Permian intrusive complex.

Conclusion. Technogenic impact has transformed the types of the lateral-migratory differentiation of

HMMs along the geochemical catenas: their accumulation in the subordinate landscapes has become more pronounced. Chemisorption and sorption-sedimentation in conjunction with the acidic and alkaline lateral GBs have the greatest distribution in ore-mining centers. In the DTMP impact zone the organomineral GBs form the local area on the slopes of Modonkul' river valley, and gley GBs – an area along the river course in the form of narrow strips.

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