Mobile fractions of heavy metals in the soils of Kuzbass (Western Siberia)

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Abstract. Kuzbass is an industrial conglomerate of the Western Siberia with a developed coal mining industry, which creates a powerful techno-genic impact on the components of the environment, in particular, on the soil cover. This study considers the ecological state of soil ecosystems (natural and techno-genic), associated with the coal industries facilities in the Kuzbass. Comparative characteristics of the content of mobile fractions of heavy metals (HM) (Pb, Cd, Cu, Zn, Mn, Ni, Co, Cr) in soils of natural and man-made landscapes are given. It has been established that the degree of the mobile fractions of heavy metals in soils of the natural ecosystems is determined by coarseness of grading, oxidation reduction potential (ORP), acid-base properties, organic matter content. Unlike natural soils, the abiotic conditions of soil formation (mineralogical composition, the ratio of coarse earth and fine earth in the soil mass) and the degree of severity of organic-accumulative processes are main factors that determine level content of the mobile fractions of heavy metals in the soils of the techno-genic systems. A comparative assessment of the inactivating ability of soils with respect to pollutants was carried out. It is established that the soils of the natural and techno-genic ecosystems with respect to heavy metals are characterized by different buffer capacity. The soils of techno-genic landscapes have smaller indicators of inactivating ability. Among the techno-genic soils, the minimum values of the buffer capacity are noted for the initial embryo earth. The information obtained can be used in the monitoring research to monitor the level of the man-caused impact on soil ecosystems in Kuzbass and to prevent negative processes in land use.

1. Introduction
Kuzbass is the largest coal basin in Russia today, which accounts for almost 40% of total production and more than 70% of coking coal production. One of the main components of the natural complex, which is subjected to a more intensive influence of techno-genesis in the operation of coal mining enterprises, is the soil ecosystem. When coal is extracted by open pit mining or underground method, dispossession of soils and their specific degradation takes place not only in the areas of the mountain outcrops, but also in adjacent natural landscapes as a result of aero techno-genic flux of toxicants with coal and industrial dust [1-6]. The purpose of the work is to analyze the content of mobile fractions of heavy metals and to identify factors and conditions affecting their behavior in soils of the natural and techno-genic landscapes, located near the coal industry objects within the Kuzbass, as well as the establishment of immobilization activity of the investigated soils in relation to pollutants.
2. Objects and methods of research

The soils of the natural and techno-genic ecosystems of Kuzbass served as the objects of research. Soils of the natural ecosystems are represented according to the soil classification of Russia [7], sodpodzolic gleys, gray, dark gray, clay-illuvial chernozem. According to the World reference base (WRB) classification system [8], the soil data can be attributed to the reference soil group (RSG) of albeluvisols and phaeozems. The soils of techno-genic ecosystems, in accordance with the classification [9], are represented by the following types of embryo earth: initial, organic accumulative, humus, humus accumulative. According to WRB, the soil data can be classified as regosol, and anthrosols. Soil samples were taken at the boundaries of the sanitary protection zones of industrial facilities. The mobile fractions of HM were displaced by acetate-ammonium buffer with pH 4.8, followed by their determination by atomic absorption method on an AS-3 spectrophotometer. To evaluate the buffer capacity of soils [10], the results of analyzes of their humus-accumulative horizons were used.

3. Discussion of results

3.1. Soil of natural landscapes

It is established that the properties of soils and their chemical nature have a significant effect on the mobility of microelements. The heavy coarseness of grading of the studied soils of the natural ecosystems, in particular, the high content of physical clay (43.0-54.6%) and alluvion (16.4-30.5%) largely determine the content and mobility of 1-1M. The maximum concentration of mobile fractions of heavy metals is observed in illuvial horizons, which are heavier in terms of the grain size, acting as sorption geochemical barriers to the migration of metals (Pb, Cu, Co), associated with soluble forms of humic acids.

Occurrence form of HM and their valence, ability to migrate in landscapes and in the soil profile, assimilated by plants and carried out with natural waters is determined by the reaction of medium and ORP. The investigated soils of natural landscapes are confined to the eluvial landscape of the foreststeppe type with pH of solution from 5.5 to 7.5, therefore, under conditions of the oxidizing environment, two HM associations can be distinguished: sluggish (Pb, Cd, Ni, Cu, Co, Cr, Mn) and mobile (Zn). The influence of the alkaline barrier in the fayoseme, appearing on the sites of a sharp increase of pH of the medium in a weakly acidic geochemical environment, has been revealed. As the pH value increases in the carbonate horizons, cationic chemical elements accumulating actively migrate in acidic and slightly acidic media (Cr, Mn, Co, Ni, Cu, Zn, Cd).

Along with the alkaline barrier, humic horizons can also act as a geochemical barrier to the migration of elements due to the complexation processes. Since fulvic acids predominate in the qualitative composition of the humus of the albeluvisols, it is in these soils, that formation of the fulvative complexes with HM with increased migratory capacity is observed. The predominance of humic acids in the group composition of humus fayoseme promotes the formation of complex heteropolar salts with the heavy metal ions (Pb, Cd, Cu, Mn, Co) [11], that accumulate biogenically in the upper part of the soil profiles.

3.2. Soils of techno-genic landscapes

In the process of extracting minerals in the territory of Kuzbass, significant amounts of stripping soils are carried to the daylight surface, as the result of which, new techno-genic landscapes are emerging, which are characterized by specific conditions of soil formation, which lead to the formation of a peculiar soil cover with set of young soils - embryozem [12], different from soils of natural biogeocenoses.

From the analysis of the data (Table 1), it follows that there is no intensive accumulation of HM in soils of techno-genic ecosystems. Their concentrations do not exceed the values of maximum allowable concentration (MAC), which is due to the low content of fine earth (6-17%) in the
composition of soil mass, low cation exchange capacity (9.2-39.5 mg*eq/100 g) and weak expression of humus-accumulative processes.

Table 1. The content of mobile fractions of heavy metals in embryozems, mg/kg

| Horizon          | Pb  | Cd  | Cu  | Zn  | Mn  | Ni  | Co  | Cr  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Initial embryozem (regosols) |     |     | 2.23 | 0.13 | 2.30 | 12.5 | 25.2 | 0.51 | 0.24 | 0.71 |
| Organic-accumulative embryozem (anthrosols) |     |     |     |     |     |     |     |     |
| A0               |     |     |     |     |     |     |     |     |
| C1               | 11.6 | 0.04 | 0.08 | 0.11 | 0.73 | 0.11 | 0.40 | 0.25 |
| C2               | 0.78 | 0.01 | 0.07 | 0.05 | 0.81 | 0.49 | 0.52 | 0.85 |
| Humus embryozem (anthrosols) |     |     |     |     |     |     |     |     |
| Ad               | 0.88 | 0.03 | 0.09 | 1.54 | 38.6 | 0.24 | 0.90 | 0.63 |
| C1               | 2.43 | 0.04 | 0.08 | 1.45 | 38.0 | 0.47 | 1.22 | 0.73 |
| C2               | 1.75 | 0.06 | 0.07 | 0.82 | 27.7 | 0.69 | 1.53 | 0.61 |
| Humic accumulative embryozem (anthrosols) |     |     |     |     |     |     |     |     |
| Ad               | 1.89 | 0.08 | 0.06 | 1.06 | 34.1 | 0.31 | 0.04 | 0.68 |
| A1               | 1.15 | 0.04 | 0.07 | 0.75 | 28.1 | 0.30 | 0.07 | 0.26 |
| C                | 0.77 | 0.05 | 0.07 | 0.18 | 37.1 | 0.40 | 0.67 | 0.19 |
| MAC of mobile fractions of HM in the soils, mg/kg | 6.0 | 1.0 | 3.0 | 23.0 | 100-140 | 4.0 | 5.0 | 6.0 |

3.3. Buffer capacity of the investigated soils

Based on the data on the inactivating effect of soil properties and composition, an assessment of the index of ecological and geochemical status of soil ecosystems — immobilization activity of soils in relation HM, expressed in points (Table 2).

Table 2. Buffer capacity of soils of natural and techno-genic landscapes in relation to heavy metals

| Soils                              | Sum of points | Degree of buffering | Sum of points | Degree of buffering |
|------------------------------------|---------------|---------------------|---------------|---------------------|
| sod-podzolic gley (albeluvisols)   | 22.5          | medium              | 30            | medium              |
| gray (phaeozems)                   | 33            | advanced            | 35.5          | advanced            |
| dark gray (phaeozems)              | 33.5          | advanced            | 41            | high                |
| clay illuvial chernozem (phaeozems)| 36            | advanced            | 38.5          | advanced            |
| embryozems                         |               |                     |               |                     |
| initial (regosols)                 | 20            | low                 | 27.5          | medium              |
| organic accumulative (anthrosols)  | 24            | medium              | 31.5          | advanced            |
| humus (anthrosols)                 | 20.5          | medium              | 33            | advanced            |
| humic accumulative (anthrosols)    | 21.5          | medium              | 34            | advanced            |

This parameter makes it possible to assess the ability of soils to act as a buffer in the migration path of pollutants in both the radial and lateral directions. On the basis of the calculated data, taking into account the coarseness of grading of soils, the amount of organic substance, acidity of the soil
solution, the content of sesquioxides and carbonates, it can be concluded that the investigated soils of the Kuzbass natural ecosystems have an essential enhanced ability to withstand pollution of 1-1M. The degree of buffering to elements mobile in alkaline medium varies in the range from the medium in sod-podzolic gley soil up to high in dark gray. The indices of resistance to pollution for elements, mobile in the acidic medium, increase in a row from podzolic type soils to chernozems and vary in the range from 22.5 to 36 points.

Under conditions of technogenic, soils act as a powerful buffer system that restrains the anthropogenic imbalance of chemical elements in the biosphere [13, 14]. The ecological potential of soils, on the one hand, provides the necessary reserve of nutrients, and on the other hand, contributes to the preservation by inactivating the incoming pollutants, of the necessary ecological environment. The buffer capacity of the soils of the man-made ecosystems (Table 2) increases in the direction from initial embryozem to humus accumulative, which is due to the increased contribution of fine earth and organic components in this evolutionary series. Inactivating ability of soils of the man-made landscapes in comparison with natural soils is estimated by lower indicators.

4. Conclusions
Based on the ecological and geochemical analysis of soils of natural systems of Kuzbass, it can be concluded that mobility degree of heavy metals is determined by the coarseness of grading, ORP, acid base properties, organic matter content. Unlike natural soils, the abiotic conditions of soil formation (mineralogical composition, the ratio of coarse earth and fine earth in the soil mass), the technogenic phase of the formation of the dumps and the degree of severity of organic accumulative processes are the main factors of content of mobile fractions of heavy metals in the soils of the man-made ecosystems.

Soils of natural and technogenic ecosystems have different buffer capacity in relation to 1-1M. It has been established that a smaller inactivating ability is peculiar for soils of technogenic landscapes. In the series of technogenic soils, the minimum values of the buffer capacity are noted for the initial embryozems.

Reference
[1] Ovsyannikova S V and Seredina V P 2014 Regional monitoring of the Kuznetsk coal field soils on the accumulation of the heavy metal mobile forms Vestnic KrasGAU 11 (98) 100-5 (In Russian)
[2] Seredina V P, Shaykhutdinova A N and Ovsyannikova S V 2015 Features of behavior of mobile forms of heavy metals in the soils of the Kuzbass Materials of the 141 AllRussian Scientific and Practical Conference “Problems of the Southern Urals” (Orenburg: Orenburg State University) 10 (185) 236-9 (In Russian)
[3] Guisti L 2011 Initial screening for contaminated land Journal of Soils and Sediments Heavy metals in urban soils of Bristol (UK) 11 1385-98
[4] Brian J A 2013 Heavy metals in soils: trace metals and metalloids in soils and their bioavailability (Imprint: Springer) p 613
[5] Khan T 0 2014 Soil degradation, conservation and remediation (Imprint: Springer) p 237
[6] Shirkin L A, Trifonova T A, Selivanova N V and Gruzdkov D 2007 The heavy metals migration from industrial wastes in soils The International Conf. on Soils Urban Industrial, Traffic and Mining Areas (Nanjing, China) 18-27
[7] Shishov L L, Tonkonogov V D, Lebedeva I I and Gerasimova M 2004 Classification and diagnostics of soils in Russia (Smolensk: Oykumen) 342 (In Russian)
[8] World reference base for soil resources 2006 World Soil Resources Reports 103 (FAO, Rome) 141
[9] Kurachev V M and Androkhanov V A 2002 Contemporary Problems of Ecolog. Classification of soils of technogenous landscapes 3 255-62 (In Russian)
[10] Ilyin V B 1995 Agrochemistry Evaluation of soil buffering with respect to heavy metals 10 109-13. In Russian
[11] Gillet S and Ponge J F 2002 European Journal of Soil Science Humus forms and metal pollution in soil 53 (4) 529-39
[12] Alekseeva T P, Burmistrova T I, Sysoeva L N, Trunova N M and Seredina V P 2016 Ecology and Industry of Russia A study of initial process of soil remediation at coal dump using peat preparations 20 (11) 39-43 (In Russian)
[13] Brown G E, Foster A L and Ostergren J D 1999 Proc. Natl. Acad. Sci. USA Mineral surface and bioavailability of heavy metals: A molecular scale perspective 96 (7) 3388-95
[14] Villen-Guzman M, Paz-Garcia J M, Amaya-Santos G, Rodriguez-Maroto J M, Vereda-Alonso C and Gomez-Lahoz C 2015 Chemosphere Effects of the buffering capacity of the soil on the mobilization of heavy metals Equilibrium and kinetics 131 78-84