ECOLOGICAL AND GEOCHEMICAL FEATURES OF THE DISTRIBUTION OF TRACE ELEMENTS IN VIRGIN AND ARABLE CHERNOZEMS

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ABSTRACT

The distribution of manganese and zinc in virgin and arable chernozems located near technogenic objects of the mining enterprise was analyzed. Soil sampling was carried out from soil sections. The analysis of soil elemental composition was carried out by x-ray fluorescence method. Mathematical processing of the results included the use of standard software packages for statistical calculations. It was ascertained that Zn belongs to the elements of concentration and Mn – to the elements of the dispersion. Exceedings in relation to the maximum permissible or approximate permissible concentrations were not detected, but the concentration of manganese was above the background. The coefficients of radial differentiation in the upper horizons of soils for zinc are higher than for manganese and they are higher on virgin land than on arable. Concentrations of the studied elements in the upper layers of soils are weakly connected with the impact of dumps and tailings. The acid-basic property of soils is the significant factor influencing the distribution of the studied elements. Humus content and the amount of silt in soils have the weak influence.

Keywords: Kursk magnetic anomaly (KMA), maximum permissible concentration (MPC), soil clark, regional background concentration, coefficient of radial differentiation

INTRODUCTION

Belgorod oblast is located in the KMA region and is known by the powerful development of the mining industry. However, there are also valuable protected objects: «Yamskaya steppe» is the only in the world preserved area of the southern variant of meadow steppes in combination with oak forests on deep chernozems. Preservation of natural soil diversity of the protected area is an objective basis for evaluation the reference virgin soils and changes in their properties under the influence of anthropogenic factors. However, the protected area is exposed by the impact of the mining company, as there are dumps and tailings near it. Dusting, typical for such technogenic objects, can lead to a change in the geochemical properties of virgin chernozems, whereby they cease to perform the reference function. The aspects of the state of soil cover in the vicinity of mining enterprises are widely observed in publications. First of all, it concerns the size of the direct destruction of soil cover due to

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quarry-dump activities and identifying the degree and nature of soil pollution in the vicinity of the mining enterprises, especially by heavy metals [1,2]. The literature indicates that Cd, Pb, Cu, Zn, Hg, As and Ni are the priorities for the control of heavy metals in mining areas [3]. In the Russian Federation, the gross content of nine heavy metals in soils is controlled, while for some metals – V, Mn, Pb – maximum permissible concentrations (MPC) are accepted, for others – Cd, Cu, Ni, Zn – approximately permissible concentrations (APC) are introduced [4].

As noted in [5], several landscape-functional zones of technogenic transformation of natural complexes are distinguished in mining regions. First, themselves the mining and quarry-dump mining landscapes with almost complete degradation of soil and vegetation cover, with high concentrations of heavy metals in dust, technogenic sediments, waters and plants. The second zone consists of the mining landscapes that are directly exposed to the influence of quarries and other objects, in 2-3 km against which the content of soil dust and heavy metals in the air exceeds 10 and more times the maximum permissible concentration. The outer borders of this zone are quite difficult to distinguish, especially in areas with dense ravine-beam-valley network. Metallurgical plants impact on the environment in radius of 5-10 km. In this zone, the association of pollutants is reduced, and the most extensive haloes are often formed by Zn and Pb. This is the third zone with the rather strong pollution of soils. Background landscapes are usually located no closer than 15-20 km from the sources of pollution – this is the fourth zone in which there is moderate area pollution, depending on the terrain and climate.

We have previously considered the geochemical features of soils in the industrial zone of the mining complex [6]. The elements observed in this article – manganese and zinc-were chosen on the basis of their important biological role in ecosystems and organisms.

On the territory of the Belgorod oblast, the continuous agrochemical survey was conducted, during which the regularities of distribution of microelements in soils were ascertained. According to published information [7], the average content of the gross manganese in the arable layer of the chernozems in the Belgorod oblast is 416 mg/kg, zinc – 44 mg/kg, which is lower than the MPC for manganese and APC for zinc.

To determine the degree of anthropogenic pressure, it is necessary not only to determine the content of hazardous metals in soils, but also to substantiate the permissible rate of such pressure taking into account the regional background and provincial climatic conditions. After analyzing the various methods of determining the degree of soil pollution by heavy metals, Okolelova A.A. et al [8] consider that is appropriate for accounting the processes of soil formation to calculate the coefficient of radial differentiation relative to the parent rock – R.

The aim of the study was to identify the changes of the geochemical properties of chernozems of the reserved area in connection with the close location of mining enterprise.

DATA AND METHODS

In 2016, the VII Congress of the Society of soil scientists after V. V. Dokuchaev was held in Belgorod. For the organization of the soil excursions soil sections on the territory of protected area «Yamskaya steppe» were laid (virgin chernozem, section 1), and arable land near the border of the reserve (arable chernozem, section 2). The scheme of the placement of soil sections is shown in Figure 1. Section 2 is 50 m closer to technogenic objects, so it could be expected that the soil pollution on the arable land should be either equal or higher than on the virgin site, depending on the wind direction.

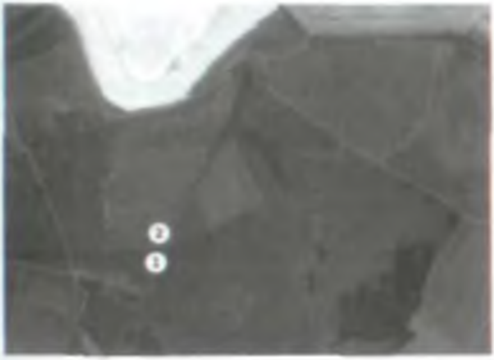

Fig.1. Position of soil sections on the space image of the study area:

1-virgin chernozem (protected area «Yamskaya steppe»),

2-arable chernozem (agricultural land)

Three series of samples were selected near the sections. Both soils were referred to chernozems typical carbonate rummaged by heavy-loamy chernozem on loess-like loam. At the same time, virgin chernozem is powerful and arable one - medium. Sampling was carried out till the depth of 60 cm with the interval of 10 cm, below (to the depth of 200 cm) - with the interval of 20 cm. The analysis of the elemental composition was carried out on the x – ray fluorescence spectrometer SPECTROSCAN MAX-GV.

To determine the clarks concentration (Cc) or dispersion of elements (Cd) the ratios of the content of the elements in the soil to soil clark by A.P. Vinogradov) were calculated. To determine the degree of soil pollution, the concentrations of elements were compared with MPC and APC, as well as with the regional background concentration. The coefficient of radial differentiation-R relatively to the parent rock was calculated by the formula:

$$R = Ci / Cc\ ,$$

where *Ci* and *Cc*, respectively, the concentration of the element in the concrete horizon and rock.

Mathematical processing of the results included the use of standard software packages for statistical calculations.

RESULTS AND DISCUSSION

Manganese is an element, the geochemistry of which is called «paradoxical», because the processes of its concentration, scattering, oxidation and regeneration are seemingly contrary to the rules of thermodynamics [9]. It is characterized by accumulation in the upper soil layer due to fixation by organic matter. In the Belgorod oblast, the distribution of the element over the soil profile has the equal character [10].

Zinc is very dangerous element (hazard class 1); many of its compounds are toxic. It has a high migration capacity, especially in acidic environment. At the same time, it is an important trace element that is actively involved in many biochemical processes. In the Belgorod oblast the zinc content in arable soils is 44 mg/kg, which is 6 mg/kg lower than clark.

Table 1 shows the indicators that characterize the accumulation of the studied elements in the upper part of the humus layer of virgin soil or in the arable horizon of chernozem on arable land.

Table 1. Indicators characterizing the accumulation of the studied elements in the upper / arable horizon

Area	Clark, mg/kg	Background, mg/kg	MPC or APC, mg/kg	Cc	Cd	Background exceeding	Exceeding MPC or APC
Mn							
Virgin	800	416	1500	0.88	1.14	1.69	0.47
Arable	800	416	1500	0.79	1.26	1.52	0.42
Zn							
Virgin	50	74	220	1.55	0.64	1.05	0.35
Arable	50	74	220	1.44	0.70	0.97	0.33

Determination of clarks of concentrations is of applied importance, as it allows to determine the direction of the migration of elements in soils. It is ascertained that Zn belongs to the elements of concentration and Mn – K elements of the dispersion. The similar pattern for zinc was observed by us earlier.

Evaluation of the degree of pollution with the help of indicator of MPC (APC) shows the favorable picture: for Zn the ratio is 0.33-0.35; for Mn – 0.42-0.47. At the same time, MPC norms do not take into account partial natural genesis of pollutants, whereby, on the territory of positive geochemical anomaly the danger is overestimated, and in the area of negative – understated, so to detect the degree of soil pollution it is necessary to take into account the regional background and provincial natural conditions [8]. In this regard, the evaluation of the excess of background regional concentration was conducted. It is ascertained that Zn concentrations in the studied soils are actually equal to the background – the excess is 0.97-1.05 times, but for Mn there is the clear excess of the regional background – 1.52-1.69 times. It should be noted that for arable land, these exceedings are lower than for virgin lands. This fact allows proving that the stated above hypothesis about income of the called elements from dumps and the tailings storage facility is not confirmed. Therefore, the active income on the surface of the soil Mn and Zn from technogenic objects was not observed.

The reason for this may be the direction of prevailing winds in the study area: it is more often western or south-western, and the polluter object is in the northern direction (see Fig. 1). At the same time, the results of studies also showed that the spatial distribution of heavy metals in soils has no direct connection with the objects of at the objects of open mining of iron ores of KMA; the authors did not reveal the concentrations near quarries, dumps, tailings and in the direction of prevailing winds, but skeleton maps of the total index of soil pollution by heavy metals show the confinedness of the main pollution zones to industrial centers.

Figure 2 shows the curves of the profile distribution of the studied trace elements.

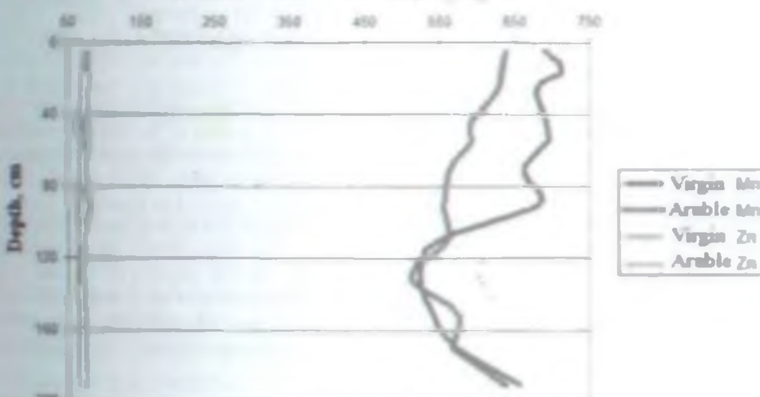

Fig.2. Distribution of Mn and Zn in the profile of the studied soils

In both cases, up to the depth of 1 m, the content of the elements is lower in arable chernozem than in the virgin land. The possible cause of this event may be different species composition of vegetation growing on the plots, and removal of the significant portion of biomass on the arable land during harvesting, so additional research is needed to confirm this hypothesis.

Table 2 shows the coefficients of radial differentiation in soil horizons in comparison with the parent rock. R values for zinc in all horizons are higher than for manganese, and on virgin land for both elements are higher than on arable land. In general, R of the studied elements is close to one, which indicates that there is no significant accumulation of these metals in the upper part of the profile. The values of the coefficient R of the upper horizons are less or equal than in the rock, they indicate about the absence of anthropogenic accumulation of the element – this situation is determined for the arable chernozem. Exceeding the concentration of elements in the soil in comparison with rock indicates about their accumulation – in virgin chernozem weak accumulation is observed.

Table 2. The coefficients of radial differentiation

Virgin	Mn	Zn		Arable	Mn	Zn
Ad0-15	1.07	1.11		Ap0-15	0.99	1.02
A15-75	1.05	1.07		App15-38	0.98	1.01
AB75-85	1.03	1.09		AB38-60	0.93	0.96
Bca85-110	0.94	1.05		Bca60-98	0.88	0.95
BCca110-180	0.83	0.94		BCca98-180	0.87	0.97
Cca180-200	1.00	1.00		Cca180-200	1.00	1.00
Average for humus horizons (A+AB)	1.05	1.09		Average for humus horizons (Ap+App+AB)	0.97	1.00

Thus, the determined regularities of distribution of R again confirm that arable and virgin chernozems differ in the trends of accumulation-hoarding of the studied elements, and the reasons for the weak accumulation of these elements in the upper horizons of virgin chernozem are not related to the nearest technogenic objects.

Evaluation of the close correlation between the content of elements and soil properties showed the close negative relationship with soil pH (for manganese Ccor = -0.83, for zinc Ccor = -0.76), weak positive relationship with humus content (0.63 and 0.57, respectively) and weak negative relationship with the content of silt (-0.48 and -0.59, respectively). Evaluation of determination allows us to conclude that 69% of the variation of manganese and 58 % of the variation of the zinc content in studied soils profiles are due to the variation of pH values.

CONCLUSION

The results of the conducted field and laboratory study, including the evaluation of the degree of pollution by manganese, and zinc based on the comparison with soil clarks MPC/APC and regional background concentrations and calculations of the coefficients of radial differentiation, allow to formulate the following conclusions:

1. For zinc, the previously determined pattern of concentration in the soils of the region in comparison with clark was confirmed, but for manganese, the tendency to dispersion was shown.

2. Evaluation of the degree of pollution by comparing the concentrations of elements with MPC / MPC suggests that pollution by these elements is not observed: for zinc concentrations are 0.33 – 0.35 MPC, for manganese-0.42-0.47 MPC.

3. Comparison with regional background concentrations showed that for Zn concentrations in the studied soils are actually equal to the background – the exceeding

– 0.97-1.05 times; for Mn there is a clear exceeding of the regional background – 1.52-1.69 times.

4. For manganese and zinc till the depth of 1 m the content of the elements is lower in arable chernozem than in virgin land. As arable chernozem is closer to technogenic objects, it can be argued that the hypothesis concerning the intake of these elements from mine dumps and tailings was not confirmed.

5. Evaluation of radial differentiation coefficients showed that arable and virgin chernozems differ in the trends of accumulation-accumulation of the studied elements: in the upper horizons of arable chernozem there is no anthropogenic accumulation of the studied elements, while in virgin chernozem there is the weak accumulation.

6. The presence of close negative relationship between the content of elements with soil pH indicates that 69% of the manganese content variation and 58% of the variation of zinc content in the profiles of the studied soils are due to variation of pH values.

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