

Properties, processes and modes characterizing the state of heavy metals in soils

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Abstract. The study proves the expediency of assessing the state of heavy metals in soils by the fractional composition of soil compounds, processes and modes. An informational and energy analysis of the state of heavy metals in soils was carried out. The need for an assessment of the kinetics of their desorption from soils was substantiated. The $\text{CH}_3\text{COONH}_4$ solution displaced 0.3 mg/l Mn from the sod-podzolic soil within 10 minutes, 0.8 mg/l Mn – within 1 hour, 3.3 mg/l Mn – within 1 day, and 12.9 mg/l – within one week; 0.18 mg/L Pb was desorbed within 10 minutes, up to 0.59 mg/l Pb was desorbed within one day. The depositing capacity of soils is an important parameter. Heavy metals in soils are bound into positively and negatively charged systems at pH of 2-10. In the sod-podzolic soil, the content of NiLn^+ was 13.3 mg/l and NiLn^- - 1.9 mg/l. According to the informational assessment, heavy metals in soils are characterized by the relationship with other soil properties and change along the soil profile, which was determined from the equations of pair correlation and multiple regression. According to the energy assessment, heavy metals in soils are characterized by thermal effects of their sorption and desorption and have positively and negatively charged complex compounds and air ions

1 Introduction

Contamination with heavy metals is a serious threat to the agricultural industry and human health [1]. Soil is the main receptor for heavy metals [2,3]. A description of the state of heavy metals in soils is of great agroecological importance. However, despite a significant number of studies, the state of metals has been rarely assessed by the content or ongoing processes and modes.

The study aims at assessing the state of heavy metals in soils by the kinetics factor, the depositing capacity of soils, the content of complex positively and negatively charged

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compounds, taking into account the informational and energy characteristics of soil processes.

The object is sod-podzolic soils and chernozems, arable soils and soils of urban agglomerations [1, 2]. The study aims to determine the bulk and mobile forms of heavy metals in soils, the depositing capacity of soils, the kinetics of sorption and desorption of heavy metals, the content of positively and negatively charged compounds and aeroions [3, 4, 5]. The probability level was $P = 0.95$.

It is promising to assess the state of heavy metals by their displacement from the soil, the depositing capacity of soils to heavy metals, the content of positively and negatively charged complex compounds displaced from the soil by the method of chemical electrolysis-based autography. The influence of heavy metals on the agroecological state of landscape components is determined by the rate of their transition from the soil to the solution. This process is described by the equations of intradiffusion and chemical kinetics of different orders. The higher the rate of transition of heavy metals from the soil to the solution, the greater the inhibitory effect they have on the landscape components, and the lower the MPC values. The kinetics of desorption processes is determined by the absorption capacity of soils, pH, mineralogical and granulometric compositions, humus content, ionic strength of solutions, temperatures, and other parameters. This indicator is typical of some soils and horizons (Table 1).

Table 1. Kinetics of Mn Displacement from Soils (0,1n $\text{CH}_3\text{COONH}_4$), mg/l

Soil	Content in solution at desorption time			
	10 minutes	1 hour	1 day	1 week
sod-podzolic Ap	0,3	0,8	3,3	12,9
B	0,9	1,2	2,2	3,2
chernozem Ap	0,3	2,3	1,0	2,1
AB	0,1	2,2	0,4	0,8

With an increase in the interaction time, the displacement of manganese from soils increases sharply. The degree of an increase in the desorption with an increase in the duration of interaction between the soils and the solution is characteristic of some soils and horizons. In this case, with an increase in the interaction time, different sorption sites are involved in the reaction, and the composition of the equilibrium solution changes. This can decrease the content of the desorbed ion in the solution and increase the duration of desorption, which is typical of chernozem. The kinetics of desorption was also observed for lead whose content was 0.18-0.20 mg/l during the 10-minute desorption, and 0.47-0.59 mg/l – during the one-day interaction of the soil and the solution.

To assess the kinetics of desorption processes, it is promising to calculate the ratio of maximum and minimum concentrations of the displaced ion for long and short interaction periods. With an interaction time of one week and 10 minutes, the ratio of the lead content in the desorbent $\text{CH}_3\text{COONH}_4$ solution was 5.8 for heavy loamy chernozems; 3.6 – for light loamy soils; 2.6 - for sod-podzolic soils; 12.3 - for urban soils of Moscow. For zinc, these indicators were equal to 5.5; 3.0; 1.2 and 1.5, respectively.

The content of elements in the soil and the desorbent is determined by the solubility of their precipitates, effective constants of ion exchange and instability of the complexes. This indicator does not provide complete information on the content of mobile forms of elements in the solid phase of soils. To assess the total content of mobile forms of elements in soils, the depositing capacity of soils is determined when ions are displaced from the solid phase by the successive portions of desorbents. The depositing capacity of soils for Pb in the H_2O extract of 7.5 l/10g was 0.5 mg/100 g for heavy loamy chernozems, and 0.2 mg/100 g for light loamy chernozems; in the lead-contaminated sod-podzolic soil, it was 1.1 mg/100 g;

for Zn, it was 1.2; 0.6 and 2.0, respectively. The soils contain several heavy metals and their hydroxyl complexes.

The content and ratio of positively and negatively charged cation compounds in soils change with the application of organic fertilizers

Heavy metals in soils have different forms and bond strengths, including positively and negatively charged complex compounds with organic ligands (Table 2).

Table 2. Content of positively and negatively charged compounds of iron and nickel systems in sod-podzolic soils after the electrophoretic introduction of nickel, mg/l

Section, horizon	Fe		Ni	
	+	-	+	-
P-1 A	2,4	5,3	13,3	1,9
A ₂	4,0	4,8	6,9	3,5
A ₂ B	2,5	17,3	2,8	4,7
B ₁	3,3	1,9	5,8	3,6
B ₂	2,3	0,9	2,1	4,2
P-2 A	6,9	19,1	7,8	7,7
A ₂	2,5	4,5	5,3	12,3
A ₂ B	3,8	3,5	19,9	6,9
B ₁	1,7	16,4	3,2	5,2
B ₂	3,3	2,4	3,5	3,1

*) 10 g of soil; $\varphi = 12$ v; $t = 10$ min.

The sod-podzolic soils and chernozems contain complex positively and negatively charged compounds Fe, Mn, Ca, Zn, Ni, K, P. Soil saturation with KH_2PO_4 increased the share of positively charged Ca compounds, but decreased the share of positively charged compounds of zinc, iron, and calcium in the soils under study and Ca in the sod-podzolic soil. Soil saturation with nickel increased the share of mobile iron in the soil and slightly increased the share of positively charged iron compounds. Positive and negative compounds of Ca, Mg, Fe, Mn, Zn, Cu, K, Na were found in the leaves of apple trees. At the same time, in Ca, Mg, K, Na, the share of positively charged compounds prevails; in Fe and Mn, negatively charged compounds are dominant. It is necessary to assess the content and ratio of positively and negatively charged cation compounds in the soil-apple tree system in order to identify plant oppression causes.

According to the data obtained, complex compounds of heavy metals have different molecular weights and are characterized by different stability constants of the complexes. The negative logarithm of the instability constants for water-soluble organic soil substances, humic and fulvic soil acids with polyvalent cations pC_H varied from 2 to 20.

The fulvic acids have a higher ability to form complex compounds with heavy metals than the humic acids. The ability of organic ligands depends on the molecular weight of organic substances. With an acidic reaction of the medium, protonation was observed; with an alkaline reaction, the effect of hydrate formation was observed. Thus, in the water extract from the permafrost taiga soils, the Fe content was 2–27 mg/l. During the desorption of iron from the soils 2N HCl ($t = 5$ minutes) before the destruction, 157.7 mg/100 g were displaced from A₁; after the destruction, 796.2 mg/100 g were displaced. During the desorption of iron, 0.1N KCl + 0.01m EDTA were displaced at $pH = 4 - 30$ mg / 100 g, and only 3.7 - at $pH = 8$.

To assess the ability of organic ligands of soil solutions to polyvalent metals, it is promising to determine an increase in the effective solubility of precipitates when the water-soluble organic substance is added to the desorbent.

According to the data obtained, the complexing ability of organic substances in relation to Pb (10-4 m / l) was 18.7 and 16.4 for humic and ulminic acids of the chernozem, respectively; for the humic and ulminic acids of the soddy-podzolic soil, it was 17.3 and

23.2 mg/l, respectively. In relation to Cu, the complexing ability of water-soluble organic substances of the meadow-chernozem and sod-podzolic soils was 2.2 and 2.2 mg/l at the optimal moisture content and 7.8 and 5.8 mg/l - with excess moisture, increasing with the introduction of 30 t/ha hay up to 6-8 mg/l or 175-670 mg/g.

The state of heavy metals in soils is characterized by their content, processes and modes.

In case of contamination, the pH of the environment changes, and the microbiological activity is inhibited with an increase in the share of fungal microflora. This changes the processes of decomposition of plant residues and composition of water-soluble organic substances. The ongoing changes can take over the deeper layers of the soil profile.

The resulting changes in the soil properties change the state of heavy metals. In the leached chernozem, the activity of NO_3 mg/l was $(11.45 \pm 0.9)10^{-4}$ and $(0.83 \pm 0.1)10^{-4}$ within 15 minutes and 3 days, respectively. When Pb (200 mg / kg) was added to the soil, it was $(9.58 \pm 1.89) \cdot 10^{-4}$ and $(0.60 \pm 0.02) \cdot 10^{-4}$, respectively.

The regularities of sequential changes differ for different types and smaller taxonomic units of soils, hydrothermal conditions, and degrees of soil pollution.

In the chernozem, at optimal humidity values, the content of Pb mg/l was 0.01 and 0.09 within 1 day and 3 weeks, respectively; with excess humidity values, it was 0.07 and 0.09; the content of NO_3 mg/l $\cdot 10^{-4}$ was 25.0 and 2.5 at optimum humidity values; with excess humidity values, it was 55.0 and 22.5.

In the sod-podzolic soils containing Pb - 200 mg/kg, the content of NO_3 was $(45.8 \pm 1.9) 10^{-4}$ mg/l within 15 minutes, $(12.6 \pm 2.6) \cdot 10^{-4}$ - within one day, $(0.8 \pm 0.1) \cdot 10^{-4}$ mg/l - within three days. The pH value was 7.7; 8.1 and 8.3 within 15 minutes, three days and six days, respectively; Eh was 473, 459 and 405 mV.

The content of heavy metals changes in the seasonal and long-term dynamics and depends on the level of water and air contamination with heavy metals. In the sod-podzolic soils of the Forest Experimental Dacha located 30 km away from the road, for 80-90 days, the lead content increased from 6 to 104 mg/kg, the zinc content increased from 11.6 to 153.0 mg/kg; the cadmium content increased from 0.04 to 0.74 mg/kg. In the snow cover, the Pb content was 0.26 mg/l, the Mn content was 0.28 mg/l, the Fe content was 13.8 mg/l; the Pb content was 0.52 mg/l, the Mn content was 2.7 mg/l; the Fe content was 32.2 mg/l.

In ordinary chernozems of Krasnodar region, the linear character of long-term trends is described by the following equations: $\text{Pb} = 0.14t + 1.42$; $R^2 = 0.63$; $\text{Cd} = 0.003t + 0.003$; $R^2 = 0.90$; $\text{Co} = 0.15t + 0.499$; $R^2 = 0.71$.

During the growing season, the content of gross and mobile forms changed to a much lesser extent. For mobile forms of Pb, it changed from 4.2 to 4.4 mg/kg; for Cd - from 0.07 to 0.08 mg/kg; for Ni - from 6.5 to 7.1 mg/kg; for Co - from 3.3 to 3.8 mg/kg. The content of Mn changed from 212 to 241 mg/kg.

Under the anthropogenic contamination, the gross content of heavy metals in soils decreases along the soil profile. This dependence is more pronounced for accumulative relief elements. For ordinary chernozems (on plateaus and in accumulative relief elements), the change in the nickel content can be described by the equation: $Y = 54.6 - 0.04H$ cm, $r = -0.75$ and $Y = 71.2 - 0.43H$ cm; $r = -0.90$; for Pb - $Y = 20.1 - 0.02N$ cm, $r = -0.72$ and $Y = 27.4 - 0.14N$ cm; $r = -0.86$; for Zn - $Y = 76.9 - 0.09 N$ cm; $r = -0.93$ and $Y = 94.3 - 0.58N$ cm; $r = -0.87$.

The content of mobile forms of heavy metals in soils depends on the distance of sampling points from the source of contamination. In the center of the Forest Dacha of Moscow Agricultural Academy, the lead content was 62-86 mg/kg; near the mainline, it was 114-139 mg/kg. At the same time, soil contamination with heavy metals depends on the wind rose, wind speed, and air permeability of tree plantations.

The degree of contamination is different for different tree plantations. In the center of the forest park, under the pine-birch phytocenosis, the zinc content was 96 mg/100g; at the border with the city, it was 211 mg/100 g. The degree of contamination does not always depend on the distance from the source of contamination. It increases in granulometric soils and low relief elements with an increase in the intensity of the soddy process of soil formation, compaction, and gleying.

With an increase in the content of heavy metals in soils, they turn into evaporation products from soils and transpiration products from plants. The content of heavy metals in the products of evaporation from soils was as follows: Pb - 0.1-0.2 mg/l; Fe - 0.2-0.8 mg/l; Zn - 0.04-0.10 mg/l; Cu - 0.04-0.10 mg/l. Near the highway, the lead content in the evaporation products from the soil increased from 0.11 to 0.18 mg/l ; under heavy contamination, it increased up to 1.1 mg/l. In transpiration products from plants, the Pb content was 0.11-0.28 mg/l; the Cu content was 0.02-0.20 mg/l ; the Pb content was up to 0.25 mg/l ; the Cu content increased up to 0.25 mg/l.

The content of heavy metals in surface waters and rivers depends on the amount of precipitation, the seasonal dynamics of agricultural practices and changes in the soil properties and the state of heavy metals in soils. In the summer period, the content of heavy metals in the river water (mg/dm³) at a distance of one km in front of and behind the village was as follows: Zn - 0.017 and 0.03; Mn 0.086 and 0.126; Pb - 0.006 and 0.008. In summer, the concentration of heavy metals in water increased: Co - from 0.002 to 0.004 mg/dm³; Zn - from 0.012 to 0.024; Cu - from 0.004 to 0.007; Mn - from 0.09 to 0.15; Pb - from 0.007 to 0.009. Of great agroecological importance is the content of mobile forms of heavy metals and their assimilable forms, which depends on a combination of soil properties, sorption properties of the root systems of plants and hydrothermal conditions. The correlation of mobile forms of heavy metals with humus was $+ 0.84 \pm 0.08$ for Co; $+ 0.59 \pm 0.12$ for Zn; $+ 0.71 \pm 0.11$ for Cu; $+ 0.79 \pm 0.09$ for Mn; 0.64 ± 0.11 for Pb; $+ 0.74 \pm 0.10$ for Cd; $+ 0.80 \pm 0.9$ for Ni. The correlation of the mobile forms of heavy metals with the content of mobile forms of phosphates was significant. It amounted to 0.65 ± 0.1 for Co; 0.55 ± 0.12 for Zn; 0.73 ± 0.10 for Cu; 0.67 ± 0.11 for Mn; 0.57 ± 0.12 for Pb; 0.45 ± 0.13 for Cd; 0.59 ± 0.12 for Ni. At the same time, the correlation of the content of mobile forms of heavy metals with pH was negative. It was 0.29-0.28 for Co, Zn, Cu; for 0.20 Mn; 0.40-0.46 for Pb, Cd, Ni. Information is also provided by the regression models of dependences of the concentrations of mobile forms of metals on soil properties. The dependence on the humus content for chernozems was described by the following equations: Pb = $1.47 + 0.92G$; $R^2 = 0.92$; Cd = $0.01 + 0.01G$; $R^2 = 0.90$; Co = $0.26 + 0.9G$; $R^2 = 0.93$; Ni = $1.6 + 1.16G$; $R^2 = 0.93$ (metal content in mg/kg, humus, %).

The content of water-soluble forms of heavy metals (X_1) often correlates with the content of their mobile forms (X_2) and does not always correlate with the content of acid-soluble forms (X_3) and gross content. The following regression equations were obtained for the soils of the megalopolis park: for Ni, $X_1 = 0.006X_2 - 0.001X_3 + 0.077$; for Pb $X_1 = 0.026X_2 - 0.000X_3 + 0.107$. With a certain degree of approximation, the sorption of heavy metals by soils and their desorption from the soils were described by the Freundlich equation: $\lg Pb = \lg K + 1/n \lg X$ with several different stages of sorption and desorption.

The dependences of the content of mobile forms of heavy metals on the soil properties differ for soils located in different relief elements. The dependence of the content of mobile forms of heavy metals on soil properties was described by the following equations (humus - X_1 , <0.01 mm - X_2 , NO₃ - X_3 , NH₄ - X_4 , P₂O₅ - X_5). As can be seen from Table 3, the relationship between the content of mobile lead compounds and soil properties differs for different elements of the catena. In the gully soils, the dependence of the content of mobile lead compounds on the content of humus ($-0.3X_2$), NO₃ ($+ 0.5X_3$), NH₄ ($-0.3X_4$) is greater than in other relief elements. All the soils are characterized by a positive

relationship between the content of mobile forms of lead and the content of mobile phosphates.

Table 3. The dependence of the content of mobile lead in ordinary chernozems in different elements of the mesorelief on the soil properties

Relief element	Regression equation	r	F
southern watershed	$Pb = -2,8 + 0,8X_1 + 0,05X_2 - 0,3X_3 + 0,3X_4 + 0,1X_5$	0,85	2,2
northern watershed	$Pb = 6,2 + 0,2X_1 - 0,04X_2 - 0,02X_3 - 0,01X_4 + 0,03X_5$	0,96	9,5
south slope	$Pb = 6,4 - 0,2X_1 - 0,02X_2 - 0,02X_3 - 0,04X_4 + 0,1X_5$	0,68	6,6
north slope	$Pb = 1,6 + 0,1X_1 + 0,04X_2 - 0,06X_3 - 0,03X_4 + 0,06X_5$	0,90	3,5
beam	$Pb = 24,9 - 0,2X_1 - 0,3X_2 + 0,5X_3 - 0,3X_4 + 0,01X_5$	0,99	138,4

As can be seen from Table 4, in chernozems, due to the intensive development of the sod process, the content of heavy metals decreases more sharply in the 60-80 cm layer as compared to the 0-20 cm layer. The distribution of heavy metals along the soil profile is determined by soil-forming processes (Table 4).

Table 4. Gross content of heavy metals along the soil profile of Tuva, mg/kg

Soil layer	Cu	Zn	Cd	Pb
chernozem 0-20	21,2	41,7	0,58	20,2
60-80	18,4	31,5	0,42	14,1
Light brown 0-20	11,3	34,5	0,23	10,7
60-80	12,5	30,1	0,21	8,9

According to L.V. Mosina, in the soils of the Forest experimental dacha, the entire root layer to a depth of one m contains a significant amount of heavy metals (2.6-4 times higher than Clarke). The first maximum accumulation of heavy metals was observed in A₁ layer, the second - in B horizon. Even at a depth of 70-100 cm, the lead content varied from 12 to 42 mg/kg. To assess this, dry soil sifting was carried out, and the content of HMs in different layers was determined (after freezing and removing the layers or after successive removal of layers with an adhesive tape). Soil grinding and coagulation with water-soluble organic substances of plant residues + Ca, Mg help to create a soil structure.

The energy state of heavy metals in soils is characterized by thermal effects of their sorption by different types of soils and horizons. The difference in soil temperatures during the absorption of H₂O and 0.1 n Pb (NO₃)₂ was +0.60 for the arable layer of sod-podzolic soils, and +1.10 - for ordinary chernozems. For different soil horizons, it changed from - 0.20 to + 0.2-1.10. The energy state of heavy metals in soil vapor was determined by the content of air ions. The content of positively and negatively charged air ions in the vapor from ordinary chernozems was as follows: positively charged ions - 0.09·10⁻³, negatively charged ions - 0.17·10⁻³; in the soil contaminated with lead, the content of positively and negatively charged air ions was 0.16·10⁻³ and 0.05·10⁻³, respectively. In the degraded chernozems and the soil contaminated with lead, the content was as follows : positively charged ions - 0.14 ± 0.04 and 0.06 ± 0.01; negatively charged ions - 0.13 ± 0.04 and 0.07 ± 0.01 (a·10⁻³). The unipolarity coefficients for uncontaminated and lead-contaminated chernozems were 2.0 ± 0.4 and 4.5 ± 1.3, respectively.

Thus, the study has shown the feasibility of assessing the state of heavy metals in soils by their properties, ongoing processes and modes, by transformation, migration and accumulation of substances, energy and information. The change in the state of heavy metals in soils is interrelated with their state in water and air, plants and microorganisms. An assessment of the state of heavy metals in soils by the rate of transition from the soil to the desorbent solution, the depositing ability of soils, the content of positively and

negatively charged complex compounds, the mathematical laws of relationships with soil properties and their changes in time and space was carried out.

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