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The role of soil's particle-size fractions in the adsorption of heavy metals

Saglara Mandzhieva [a,*], Tatiana Minkina [a], David Pinskiy [b], Tatiana Bauer [a], Svetlana Sushkova [a]

[a] Southern Federal University, Rostov-on-Don, Russia
[b] Institute of Physicochemistry and Biological Problems of Soil Sciences, Moscow oblast, Pushino, Russia

Abstract

The parameters of adsorption of Cu^{2+}, Pb^{2+}, and Zn^{2+} cations by southern chernozem and their particle-size fractions were studied. The adsorption of metals by soils and the strength of their fixation on the surface of soil particles under both mono- and poly-element contamination decreased with the decreasing proportion of fine fractions in the soil. The aim of this work was to study the effect of the particle-size distribution and the silt and physical clay fractions on the adsorption of copper, lead, and zinc by chernozems. The objects of study included the upper humus horizons of different southern chernozems of the Rostov oblast. To study the ion-exchange adsorption of the Cu^{2+}, Pb^{2+}, and Zn^{2+} cations, the soil in the natural ionic form was disaggregated using a pestle with a rubber head and sieved through a 1mm sieve. The soil samples were treated with solutions of Cu^{2+}, Pb^{2+}, and Zn^{2+} nitrates and acetates at the separate and simultaneous presence of heavy metals (HMs). In the solutions with the simultaneous presence of HMs, their molar concentrations were similar. The concentrations of the initial solutions varied in the range from 0.05 to 1 mM/l. The soil: solution ratio was 1:10. The contents of HMs in the filtrates were determined by atomic absorption spectrophotometry. The contents of adsorbed HM cations were calculated from the difference between the metal concentrations in the initial and equilibrium solutions. The increase in the degree of dispersion of the particle-size fractions in similar soils resulted not only in an increase in the content of adsorbed HMs but also in an enhancement of their fixation on the surface of the fine particles. Therefore, the adsorption capacity of the Lower Don soils for Cu^{2+}, Pb^{2+}, and Zn^{2+} decreased in the following sequence: clay loamy southern chernozem > loamy southern chernozem > loamy sandy southern chernozem. This was related to the qualitative differences in the mineralogy and chemistry of the separated fractions and the significant effect of their composition and properties on the parameters of the HMs adsorption.

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Introduction

Highly dispersive soil particles play an essential role in all the interphase interactions in soils: ion-exchange adsorption, water retention capacity, structuring, plant nutrition, immobilization of heavy metals (HMs) etc. Therefore, the assessment of the effect of the particle-size distribution on the adsorption properties of soils is a vital task. In spite of the somewhat arbitrary nature of the methods for the analysis of the soil particle-size distribution and the boundaries of the particle-size fractions, they at large reflect the existing differences in the composition and properties of their particles (Aslanov and Ryzhov, 1969).

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[*] Corresponding author.
Southern Federal University, 194/1 Stachki Ave, Rostov-on-Don, 344090 Russia
Tel.: +79034316269
E-mail address: msaglara@mail.ru

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In the study of the soil's dispersion, attention is focused on the content of physical clay and physical sand, because these data are used for the classification of soils according to their particle-size distribution. The physical sand includes the particles larger than 10 μm. It mainly consists of quartz and small amounts of amphiboles and feldspars. These components play the role of a mechanical diluter for the substances mainly concentrated in the fractions <10 μm (Kryshchenko et al., 2008). The mineral components of the physical sand fraction are relatively inactive. Perelomov (2001, 2003) found that the changes in the physicochemical properties of soils at the addition of 50 wt % washed sand under soil contamination with zinc significantly affected the fractional composition of the metal and increased its biological availability. As a result, the percentage of the exchangeable zinc fraction increased, and that of its residual fraction decreased. This was related to the fact that the surface of SiO_2 particles is a stronger Lewis base compared to soil particles covered with iron hydroxide and organic matter shells and less strongly retains Zn^{2+} (McBride, 1989).

The silt (<1 μm) and dust (1-10 μm) fractions are the most dynamic and active soil components. The silt fraction mainly contains secondary mineral components: clay minerals, coagels, iron and aluminum oxides, allophones, mono- and polysilicic acids, and organic and organomineral compounds. It is characterized by a high adsorption capacity for HMs and exogenic organic substances. According to the sorption capacities of the iron and clay minerals in the silt fractions, the HM cations form the following sequence: $Cd^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+}$ (Ladonin and Plyaskina, 2004). According to the strength of the ion retention by the silt fraction's surface, these elements form a different sequence: $Pb^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$.

The aim of this work was to study the effect of the particle-size distribution and the silt and physical clay (< 10 μm) fractions on the adsorption of copper, lead, and zinc by chernozems of Rostov oblast..

Material and Methods

The objects of study included the upper humus horizons of a medium deep clay loamy calcareous southern chernozem on yellow brown structural clays, a medium deep loamy southern chernozem on yellow brown loess-like loams, and a medium deep loamy sandy southern chernozem on sands from Rostov oblast (Table 1).

Table 1. Physical and chemical properties of the southern chernozems studied (0- to 20-cm Ap horizon)

Parameter	Clay loamy	Loamy	Loamy sandy
Physical clay, %	48,1	48,1	48,1
Silt, %	28,6	28,6	28,6
Humus, %	4,2 /59	4,2 /59	4,2 /59
pH	7,3	7,3	7,3
$CaCO_3$, %	0,12	-	-
P_2O_5, mg/100 g	1,6	1,6	1,6
K_2O, mg/100 g	22,8	22,8	22,8
$Ca^{2+}+Mg^{2+}$, meq/100 g	35	35	35
CEC, meq/100 g	36	36	36

The content of humus was determined by the Tyurin method modified by Simakov, the cation exchange capacity (CEC) was determined by the Bobko–Askinazi method, the available phosphorus and exchangeable potassium were determined by the Machigin method, the pH was determined by potentiometry, and the carbonates were determined by the Kudrin method (Agrochemical Methods..., 1975). The exchangeable cations were determined by the Shaimukhametov method (Shaimukhametov, 1993). The analysis of the particle-size distribution and the separation of the silt (<1 μm) and physical clay (< 10 μm) fractions were performed by the pipette method after the pyrophosphate treatment of the samples (Vadyunina and Korchagina, 1986).

To study the ion exchange adsorption of the Cu^{2+}, Pb^{2+}, and Zn^{2+} cations, the soil in the natural ionic form was disaggregated using a pestle with a rubber head and sieved through a 1 mm sieve. The soil samples were treated with solutions of Cu^{2+}, Pb^{2+}, and Zn^{2+} nitrates and acetates at the separate and simultaneous presence of HMs. In the solutions with the simultaneous presence of HMs, their molar concentrations were similar. The concentrations of the initial solutions varied in the range from 0.05 to 1 mM/l. The soil : solution ratio was 1 : 10. The suspensions were shaken for 1 h, left to stand to 24 h, and filtered. The contents of HMs in the filtrates were determined by atomic absorption spectrophotometry. The contents of adsorbed HM cations were calculated from the difference between the metal concentrations in the initial and equilibrium solutions.

Each point of the experimental isotherms was found in triplicate. The approximation of the experimental isotherms by the Langmuir equation was performed using the SigmaPlot 2001 statistics package at a confidence probability of 0.95.

Results and Discussion

The isotherms of the HM adsorption by the southern chernozems are shown in Figure 1; the parameters of the Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption by the soils studied are given in Table 2.

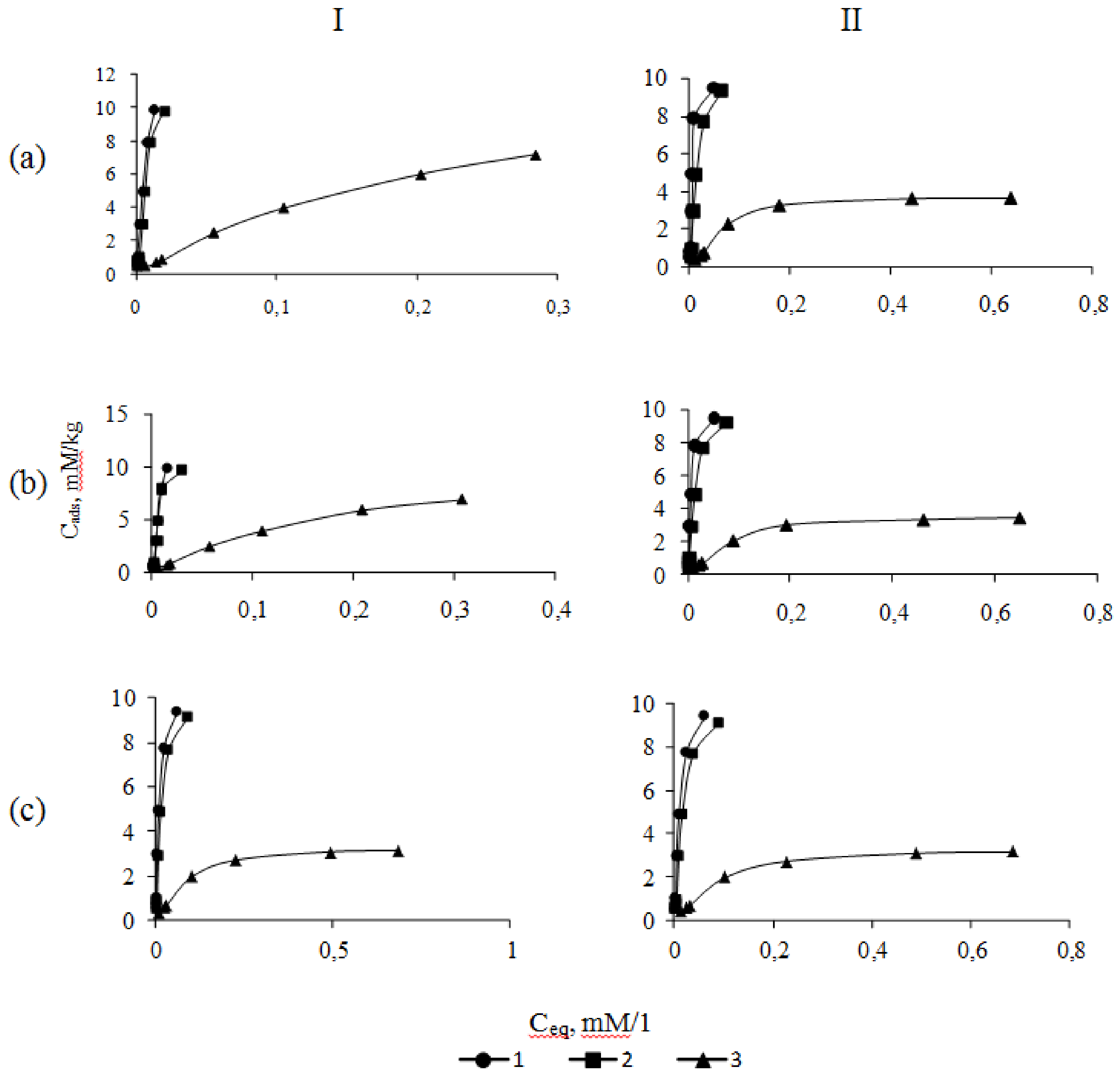

Figure 1. Isotherms of adsorption of (1) Cu^{2+}, (2) Pb^{2+}, and (3) Zn^{2+} by the (a) clay loamy, (b) loamy, and (c) loamy sandy southern chernozems under the (I) mono- and (II) polyelement contamination of the soils.

Table 2. Parameters of the Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption by southern chernozems with different particle-size distributions at the mono- (above the line) and polyelement (under the line) contamination of soils

Adsorption parameters	Cu^{2+}	Pb^{2+}	Zn^{2+}
Clay loamy southern chernozem			
$C\mathrm{max}$, mM/kg	23,66±3,54 13,59±1,19	21,15±5,90 12,88±1,62	13,48±0,48 4,33±0,32
k, l/mM	58,25±13,20 115,90±35,71	47,13±17,11 50,08±8,73	4,09±0,35 11,34±2,77
R^2	0,99 0,93	0,96 0,99	0,99 0,97
Loamy southern chernozem			
$C\mathrm{max}$, mM/kg	20,59±9,16 13,05±1,97	16,57±5,39 12,82±1,22	12,55±0,59 4,19±0,26
k, l/mM	54,54±21,92 84,65±17,00	34,80±12,73 40,18±8,70	3,95±0,25 9,94±1,99
R^2	0,98 0,95	0,88 0,98	0,99 0,98
Loamy sandy southern chernozem			
$C\mathrm{max}$, mM/kg	19,01±1,02 12,35±1,66	14,65±1,19 11,60±1,54	11,05±0,93 3,78±0,18
k, l/mM	25,90±2,36 48,40±11,48	21,83±3,44 31,31±7,94	2,63±0,34 8,27±1,43
R^2	0,99 0,95	0,99 0,97	0,99 0,99

The isotherms had a form described by the following Langmuir equation:

$$C_{\mathrm{ads}} = C_{\mathrm{max}}kC/(1 + kC), \tag{1}$$

where C_{ads} is the content of the adsorbed cations; C_{max} is the maximum adsorption of the HM, mM/100 g of soil; k is the constant of the affinity; and C is the HM concentration in the equilibrium solution, mM/l.

The analysis of the obtained data showed for the southern chernozems that a tendency toward a decrease in the maximum adsorption C_{max} and the metal adsorption constants k was observed when going from the clay loamy to loamy sandy soils (Figure 1). The tendency was more pronounced for the adsorption of Cu^{2+} and Pb^{2+} ions. The decrease in C_{max} at the change of the particle-size distribution in similar soils is related to the known relationship between the specific surface and the adsorption capacity of the soils. For the southern chernozems, it varied in the following sequence: clay loamy > loamy > loamy sandy.

The tendencies toward regular changes in the parameters of the ion exchange adsorption of the HM cations by the soils with different particle-size distributions can be due to the actual differences in the chemistry and mineralogy of the corresponding fractions of the studied soils and the ability of HMs to specifically interact with specific groups of exchangeable sites (Pinsky et al., 2013). Wong et al. (2007) studied the sorption of zinc by soils differing in acidity and particle-size. By the ability to sorb zinc cations, they formed the following sequence: calcareous clayey soil > calcareous sandy soil > acid sandy laterite soil. This sequence indicated an important role of the particle-size distribution and the soil solution's pH during the sorption of metals.

The important role of organic matter in metal adsorption was noted in the works of Karpukhin and Sychev (2003) and Minkina et al. (2006). Data obtained by Plyaskina and Ladonin (2005) indicated that more than 50% of the copper and zinc in all the particle-size fractions of a leached chernozem was bound to organic matter, and the remaining portion was strongly bound to the mineral soil components, including iron minerals. For zinc, the interaction with organic matter was less typical (Putilina et al., 2009; Samokhin et al., 2003). At the same time, a significant part of the surface of chernozem particles is covered with humus films. They have a complex effect on the adsorption capacity of the soil particles. They can hamper the contact of HM ions with reactive sites located on the surfaces of mineral soil components and in their medium and small pores and hydrophobize some surface areas, which resulted in a decrease in the exchange capacity of soils (Pinskii and Kurochkina, 2006). At the same time, new reactive sites can appear due to the functional groups of adsorbed organic molecules. However, the ratio between these two processes in real soils is almost not studied, and no definite quantitative conclusions can be drawn about their effect on the ion exchange adsorption capacity of soils.

The reliable decrease in the value of *k* with the decreasing content of the fine fractions in soils cannot be explained only by the change in the specific surface of the soil particles. The constants characterize the energy of the cations interaction with the active sites on the surfaces and are mainly related to the qualitative composition of the particles. Thus, the change in the adsorption constants with the variation in the particle-size distribution clearly indicates a difference in the qualitative composition of the fine fractions of the soils studied. Moreover, the *k* values depend more on the content of the fine fractions than the C_{max} values. The polyelement adsorption of HMs by soils is characterized by their mutual competition for the exchangeable sites. This competition changes not only the shape of the isotherms but also the adsorption parameters (Figure 1 and Table 2).

In general, the isotherms of the polyelement adsorption of HMs by the studied soils follow the Langmuir equation. The mutual competition of ions eliminates the differences manifested at the monoelement adsorption. According to the constants of the adsorption on the clay loamy and loamy southern chernozems, the cations of the studied HMs form the following sequence: $Cu^{2+} > Pb^{2+} >> Zn^{2+}$. On loamy sandy southern chernozem, they form the following sequence: $Cu^{2+} \geq Pb^{2+} > Zn^{2+}$. Hence, the relative affinities of all the soils for Cu^{2+} and Pb^{2+} ions are again significantly higher than for Zn^{2+}, as is confirmed by the isotherm shapes.

When the studied soils are ranked according to the HM adsorption parameters, the following sequence is observed for the adsorption constants: clay loamy southern chernozem > loamy southern chernozem > loamy sandy southern chernozem. The values of C_{max} for the adsorption of copper and lead little vary with the changes in the soils' particle-size distribution. However, the tendency toward a decrease in this parameter with decreasing contents of physical clay and silt is clearly traced. Thus, in this case too, the extensive adsorption parameter - the maximum adsorption - is less sensitive to changes in the particle-size distribution than the intensive parameter of the process - the constant of the adsorption equilibrium.

The simultaneous participation of three HM cations in the process resulted in their redistribution among the sorption sites with the highest relative affinities for these cations because of the cations mutual competition (Ladonin and Plyaskina, 2003). Correspondingly, the individual values of the maximum adsorption for each of them (Cu^{2+}, Pb^{2+}, and Zn^{2+}) decreased, and the constants characterizing the energy of their interaction with the sorption sites on the surface of the soil particles increased (Table 2). These changes were most noticeable and statistically reliable for zinc, because it was the least competitive element compared to copper and lead (Minkina et al., 2014; Pinskii et al., 2013).

The physical clay, which includes the silt and fine dust (1-10 μm) fractions, is the main carrier of the soil's adsorption properties; therefore, given the quantitative and qualitative compositions of the soil, the further behavior of the HMs can be predicted. Therefore, the direct study of the HM adsorption by the separate soil particle-size fractions is of significant interest.

The separation of the particle-size fractions by the pipette method after the pyrophosphate treatment of the samples disturbs the natural composition of the exchangeable cations; therefore, the samples should be converted into the same state. For this purpose, the soil and its particle-size fractions were converted into the monoionic Ca form. The original soil sieved through a 1 mm sieve and the separated particle-size fractions were converted into the monoionic Ca forms by tenfold treatment with a 0.25 M $Ca(NO_3)_2$ solution. Then, the soil was washed from excess salt with distilled water, air dried, and homogenized. Samples of the soils and fractions were treated with tenfold volumes of solutions containing different amounts of HM nitrates with the addition of calcium nitrate to maintain a constant ionic strength of 0.01 mol/l. The further procedures were similar to those described above for the study of the HM adsorption by soils.

The general shapes of the isotherms of the Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption by the silt and physical clay fractions from the southern chernozem were analogous to those of the HM adsorption by the entire soil: the adsorption was of limited character and followed the Langmuir equation (Figure 2). Copper and lead were more intensively adsorbed by the particle-size fractions than the zinc.

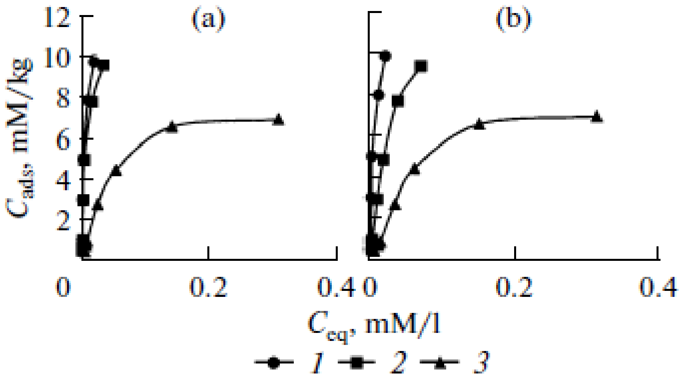

Figure 2. Isotherms of adsorption of (1) Cu^{2+}, (2) Pb^{2+}, and (3) Zn^{2+} by the (a) silt and (b) physical clay fractions of the clay loamy southern chernozem under monoelement contamination.

In the particle-size fractions separated from the soils, the concentrations of copper, lead, and zinc decreased with the decreasing particle-size. The values of *k* and C_{max} characterizing the adsorption of HMs by the southern chernozem and its particle-size fractions formed the following sequence: silt > physical clay > entire soil (Table 3).

Table 3. Parameters of the Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption by a clay loamy southern chernozem and its particle-size fractions

Adsorption parameters	Cu^{2+}	Pb^{2+}	Zn^{2+}
Silt			
*C*max, mM/kg	28.45 ± 0.46	25.20 ± 0.59	17.90 ± 0.47
k, l/mM	80.20 ± 20.29	65.90 ± 16.14	18.65 ± 3.00
R^2	0.99	0.99	0.99
Physical clay			
*C*max, mM/kg	22.15 ± 1.22	20.40 ± 2.15	12.50 ± 1.96
k, l/mM	58.20 ± 14.54	49.26 ± 13.35	12.07 ± 3.12
R^2	0.92	± 0.98	± 0.98
Soil			
*C*max, mM/kg	17.58 ± 3.03	14.54 ± 2.97	8.99 ± 1.90
k, l/mM	38.80 ± 12.33	30.45 ± 11.96	4.94 ± 0.63
R^2	0.95	± 0.96 ±	0.94

The works of some authors (Baidina, 2001; Derkham, 2009; Zhuravleva, 1985; Zyrin et al., 1986; Zyrin and Chebotareva, 1989; Panin and Siromlya, 2005; Plyaskina and Ladonin, 2005; Sadovnikova and Ladonin, 2000; Titova et al., 1996; Travnikova et al., 2000) carried out with different soil types showed that the saturation of the fine HM fractions decreased in the following sequence: silt > fine dust > medium dust. The dust fraction contained 14.6% Cu^{2+}, 16.6% Pb^{2+}, and 12.6% Zn^{2+} on the average for all the soils (Zyrin and Chebotareva, 1989). On the average for all the soils but the krasnozem, the concentrations of Cu^{2+}, Pb^{2+}, and Zn^{2+} in the silt fractions were found to be 52, 38, and 162 mg/kg, respectively. Higher contents of HMs in these fractions were reported by Titova et al. (1996). It was noted that the dust and silt fractions of the soils accumulated 25–65% of the Cu^{2+}, 35–95% of the Pb^{2+}, and 53–89% of the Zn^{2+}. The maximum concentration of Cu^{2+} was found in the dust fractions lower than 1.8 g/cm^3 in density; that of Pb^{2+} was most frequently observed in the silt.

The differences in the parameters of the Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption by the studied soils and their particle-size fractions are determined not only by the specific surfaces of the adsorbents but also by their composition and properties. The silt fraction mainly consists of secondary clay minerals, coagels of iron hydroxides and silicic acid, crystallized iron hydroxides, amorphous compounds of different compositions, and humic substances of lower degrees of condensation. These compounds usually have a large exchange capacity and high affinity for HMs. The fine dust fraction, which also enters in the physical clay fraction, contains more primary minerals (quartz and amphiboles), as well as mica and iron hydroxides.

The data obtained by Kryshchenko and Kuznetsov (2003) showed that the silt fractions of the southern chernozem contain four groups of clay minerals: kaolinite, chlorite, mica, and smectite. In the dust fraction of the soils, the content of hydromicas increases by 10–19% compared to the silt fraction, and that of smectites decreases. The content of humus in the dust fraction increases by the same factor. The content of clay minerals in the silt and dust fractions is higher than that in the entire soil. On the other hand, the higher the content of secondary minerals in the fraction, the higher its adsorption capacity.

The role of organic matter in the adsorption of HMs by the soils and the particle-size fractions is ambiguous. The soil organic matter has a high exchange capacity. However, in the soils and especially in the fine fractions, it is usually bound to the mineral soil components. Highly condensed humus blocks the medium and fine pores, which significantly reduces the adsorption capacity. Organic molecules are strongly sorbed at these positions because of their high activity (Kaiser and Guggenberger, 2003). Kurochkina and Pinskii (2002) showed that carboxyls containing organic molecules are most strongly sorbed on positively charged surface ites, primarily on the apices and edges of crystals and various surface defects, including medium and fine pore throats.

To assess the role of humus in the adsorption of HM cations by the soils and their particle-size fractions, the coefficients of correlation (R) between the content of the sorbed Cu^{2+}, Pb^{2+}, and Zn^{2+}; the contents of the silt and physical clay fractions in the soils; and the humus under mono- and polyelement contamination were calculated. The closest correlations were found between the content of the adsorbed HMs and the contents of the silt and physical clay in the soils under the monoelement contamination. A looser correlation was observed between the content of the adsorbed HMs and the content of humus in the studied soils.

Conclusion

- The increase in the degree of dispersion of the particle-size fractions in similar soils resulted not only in an increase in the content of adsorbed HMs but also in an enhancement of their fixation on the surface of the fine particles. Therefore, the adsorption capacity of the Lower Don southern chernozems for Cu^{2+}, Pb^{2+}, and Zn^{2+} decreased in the following sequence: clay loamy southern chernozem > loamy southern chernozem > loamy sandy southern chernozem.
- The isotherms of the Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption were described by the Langmuir equation in all the cases. In the case of the polylement adsorption of HMs on the soils and their particle-size fractions, the mutual competition of the cations for the exchangeable sites affected the isotherm's shape and the adsorption parameters. The Cmax values of the individual ions decreased and the k values increased compared to the corresponding data for the monoelement adsorption. This indicated an increase in the adsorption selectivity (specificity) of each competing cation. The changes in the adsorption parameters were the most pronounced for zinc and less pronounced (manifested as tendencies) for lead.
- According to the values of the adsorption parameters (C_{max} and k) for the different particle-size fractions, the HM cations formed a sequence analogous to that obtained for the entire soils: $Cu^{2+} \geq Pb^{2+} > Zn^{2+}$.
- The parameters of the HM adsorption by the same particle-size fractions isolated from the different soils decreased in the following sequence: clay loamy chernozem > loamy chernozem > loamy sandy chernozem. This was related to the qualitative differences in the mineralogy and chemistry of the separated fractions and the significant effect of their composition and properties on the parameters of the HM adsorption.
- The analysis of the changes in the parameters of the Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption by the studied soils and their particle-size fractions showed that the extensive adsorption characteristic - the maximum adsorption (C_{max}) - is a less sensitive parameter characterizing the adsorption capacity of the soils than the intensive characteristic of the process - the adsorption equilibrium constant (k).

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