Absorption capacity of hydromorphic soils in relation to heavy metal

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Abstract. Comparative studies of ion-exchange adsorption of Zn(II) and Cu(II) cations by hydromorphic soils of southern Russia have been performed. Various equations (Langmuir, Freundlich, and Dubinin-Radushkevich) were used and the adsorption parameters and adsorption energy were calculated to describe the obtained isotherms. A significant decrease of the distribution coefficient (Kd) with an increase of the metal concentration in an equilibrium solution was revealed. It is shown that the Langmuir equation and, to a lesser degree, the Dubinin-Radushkevich and Freundlich equations are the most suitable model to describe the adsorption processes of Zn(II) and Cu(II) by the soils in all experimental variants. The strong correlation between the parameters of the sorption of metals obtained using a particular chosen model was established. The Langmuir equation provides higher strengths of a bond than the Dubinin-Radushkevich equation. In all cases, the sorption capacity of meadow soil in relation to the studied metals is higher than for alluvial soil due to the low buffering capacity of the latter. Both types of soils characterize with higher affinity to Cu(II) than to Zn(II).

1. Introduction
The growth of anthropogenic impact creates potential environmental risks of accumulation of heavy metals (HM) in soils. Due to low biodegradation ability, metals accumulate in the environmental objects and reveal hazardous risks for various trophic links [1]. Thus, studies of the mechanisms of HM fixation by active soil carrier phases preventing the accumulation of inorganic pollutants in plants, ground, and surface waters are relevant.

The processes occurring at the phase interface play an important role in the activity of all soil processes and formation of soil properties. Sorption is the main process responsible for the behavior of HMs in soils therefore the mobility of metals is directly related to their distribution between the solid and liquid phases of soil. At the same time, the amount of adsorbed metal depends on the composition and properties of soil, such as pH of the soil solution, the redox potential, the cation exchange capacity (CEC), the type and amount of clay minerals, soil organic matter, the content of Fe and Mn oxides and carbonates [2–4]. Thus, the HM absorption by soils and their components are studied significantly wide throughout the world [5–10].
The study of the mechanisms of HM absorption by hydromorphic floodplain soils is interesting and associated with both their great national economic and ecological significance. Being a barrier between run-offs of chemical elements into water bodies, these soils accumulate both vital and polluting elements performing a protective function in valley landscapes. A feature of soils of river floodplains is their dependence on frequently changing ecological conditions associated with the relief, hydrological conditions, the dynamics of deposition of alluvial sediments, the variable moisture, and vegetation diversity. The complexity of the pedogenesis, its high dynamism, the specific of water supply, and the significant influence of intrazonal factors are the main reasons for the poor knowledge of the absorption capacity of floodplain soils regards to HMs.

The studies on the absorption of Zn and Cu by hydromorphic soils are especially important due to these are both physiologically active trace elements and HM, whose abundance and deficiency has a negative impact on ecosystems. Copper and zinc are highly technophilic and used in various industries. According to the International Copper Study Group (ICSG), Cu is the second most consumed non-ferrous metal in the world economy after Al with gross production 23 million tons. In addition to industrial sources of Cu that pollute the soil cover, the part of metal in soil with copper-containing pesticides is also high. Copper sulfate (CuSO$_4$·5H$_2$O), being an active ingredient in fungicides, is also used as micronutrient fertilizer to replenish Cu deficiency in soils [11].

Nonferrous and ferrous metallurgy, chemical industry (production of superphosphate fertilizers), solid domestic wastes, and sewage sludge bring a significant contribution to soil pollution with Zn compounds. Zinc ranks third in terms of consumption among all non-ferrous metals after Al and Cu, with a global annual production of about 12 million tons, but at the same time provides only 2% of world production according to the International Lead and Zinc Study Group (ILZSG). The sources of additional Zn to soil are mineral (phosphorite and lime flour, azofoska) and organic fertilizers (manure) used in agriculture. In this regard, Zn compounds are one of the most distributed environmental pollutants at the present time.

The purpose of this study is to compare the pattern and absorption mechanisms of Zn(II) and Cu(II) by alluvial and meadow soils.

2. Materials and methods

The objects of study were the hydromorphic soils of the Lower Don basin (Rostov region, Russia). The soils were classified as meadow heavy loamy soils (Calcric Fluvisols (Loamic)) on alluvial deposits and alluvial sandy soils (Calcric Fluvic Arenosols). Soils of both types were selected in the areas without anthropogenic impact, located in the floodplain of the Seversky Donets River, a large right-bank tributary of the Don River. The absence of high concentrations of HM, including Zn and Cu (table 1) in the natural soils, was shown by our previous studies [12].

The Calcric Fluvisols (N 48° 21′ 06.67″ E 40° 14′ 09.57″) are located in the central part of a floodplain meadow on the left bank of the Seversky Donets River. The Calcric Arenosols (N 48° 20′ 12.91″, E 40° 14′ 10.89″) are located at the edge of the floodplain on the right bank of the Seversky Donets River. The soil samples were taken from the surface layer (0–20 cm), dried at room temperature, ground and sieved (1 mm mesh) to remove residual, such as visible stones and plants, and then stored at 4 °C until further use. The studied soils differ from each other according to physicochemical parameters (table 1).

The specific adsorption of HMs by hydromorphic soils was analyzed by constant weights method (5 g) and variable concentrations (from 0.05 until 1.0 mM/L). Each of the concentrations corresponded to one point on the adsorption isotherm. The investigated metal solutions were prepared from chemically pure salts Zn(NO$_3$)$_2$·6H$_2$O and Cu(NO$_3$)$_2$·3H$_2$O due to their good water solubility. The mass ratio of the liquid and solid phases was 1:10 [8]. The suspensions were filtered through a blue ribbon filter after shaking for an hour, day settling and reaching an equilibrium state. The equilibrium concentrations of HM ions in an aqueous solution were determined by the atomic absorption spectrometry (atomic absorption spectrometer with electrothermal atomization and polarizing Zeeman correction of nonselective absorption by MGA-915MD, Lyumeks, St. Petersburg, Russia).
Table 1. Physicochemical properties of the studied soils.

| Soil         | pH water | $C_{org}$ | CaCO$_3$  | Physical clay (< 0.01 mm) | Clay (< 0.001 mm) | Exchangeable Ca$^{2+}$ + Mg$^{2+}$, cmol(+) / kg | Cu | Zn |
|--------------|----------|-----------|-----------|--------------------------|------------------|-----------------------------------------------|----|----|
| Calcaric Fluvisols | 7.5      | 4.3       | 0.6       | 55.8                     | 32               | 38.1                                           | 37 | 110 |
| Calcaric Arenosols | 7.5      | 0.9       | 0.1       | 2.8                      | 1.6              | 6.6                                            | 15 | 85 |

The amount of metal absorbed by the solid phase was deduced from the difference between the added amount and the concentration measured in the equilibrium solution:

$$C_{ad} = \frac{(C_i - C_{eq}) V}{m},$$

where:

- $C_{ad}$ is the amount of metal adsorbed by a unit sorbent mass, mM·kg$^{-1}$;
- $C_i$ is the initial metal concentration in solution, mM·L$^{-1}$;
- $C_{eq}$ is the equilibrium metal concentration in solution, mM·L$^{-1}$; $V$ is the solution volume, cm$^3$ and $m$ is the air-dry sorbent mass, g.

The obtained data were used to draw the $C_{eq}$–$C_{ad}$ plot, where $C_{eq}$ is the equilibrium concentration of metal added to the solution, mM·L$^{-1}$; and $C_{ad}$ is the specific content of metal in the sorbent phase, mM·kg$^{-1}$.

Coefficients of metal distribution between the solid and liquid phases ($K_d$) and the sorption degree ($S$) were computed according to formulas:

$$K_d = \frac{(C_i - C_{eq}) V}{C_0 m},$$

$$S = \frac{C_i - C_{eq}}{C_i} \times 100\%,$$

where:

- $C_i$ and $C_{eq}$ are, respectively, the initial and equilibrium metal concentration in solution, mM·L$^{-1}$;
- $V$ is the solution volume, cm$^3$;
- $m$ is the sorbent aliquot, g.

The results were statistically processed using the SigmaPlot 12.5 and Excel software packages with confidence coefficient of 0.95. Each experimental isotherm point was fixed after three replications.

To approximate the experimental isotherms, several widespread models were used describing the processes of HM adsorption by soils. Two-parameter sorption models of Langmuir (4), Freundlich (5) and Dubinin-Radushkevich (6) were used:

$$C_{ad} = \frac{C_\infty K_L C_S}{(1+K_L C_S)},$$

$$C_{ad} = C_F C_S^n,$$

$$C_{ad} = C_\infty \exp(-Be^2),$$

where:

- $C_{ad}$ is number of absorbed cations, $C_\infty$ is value of maximum adsorption of HM, mM·kg$^{-1}$;
- $K_L$ is Langmuir constant, mM·L$^{-1}$;
- $C_S$ is concentration of HM in equilibrium solution, mM·L$^{-1}$;
- $K_F$ is Freundlich constant, kg·L$^{-1}$;
- $n$ is empirical exponent in the Freundlich equation;
В is Dubinin-Radushkevich constant characterizing the binding energy; 
ε is Polanyi adsorption potential, ε=RTln(1+1/Cs).

The Langmuir model is based on three main suppositions: all adsorption sites on the sorbent surface are energy equivalent; sorption occurs in some places and interaction between the sorbed ions is lacking. Sorption is characterized by multilayer pattern, and it reaches the maximum when the monolayer is completely filled up containing a finite number of identical sites [3, 13, 14]. The Dubinin-Radushkevich isotherm is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential [15]. It was applied to distinguish between the physical and chemical adsorption [16]. The Freundlich model assumes that first of all sorption centers with a stronger binding capacity are filled up and the bond strength shows inverse correlation with the filling degree. In contrast to the Langmuir and Dubinin-Radushkevich equations, the Freundlich isotherm does not yield the limit value of metal adsorption during saturation [17].

Both models ((4) and (6)), in contrast to the empirical Freundlich equation, allow the comparison of the thermodynamic parameters of the absorption, such as the characteristic energy of adsorption and the value of the maximum adsorption C∞ for different soil types.

To calculate the average value of the binding energy for equation (6), the Hobson’s equation was used [18]:

\[ E = B \cdot \frac{1}{\sqrt{2}} \]  

(7)

The quantity \( K_L \) of equation (4) is related to the Gibbs energy as:

\[ \Delta G = -RT \ln k, \]  

(8)

where:

\( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\));
\( T \) is absolute temperature (K).

3. Results

The calculation results of the \( K_d \) values and the degree of sorption \( S \) of the Zn(II) and Cu(II) ions for Calcaric Fluvisols and Calcaric Arenosols are presented in tables 2 and 3.

| Soil                  | Metal concentration in the initial solution, mM∙L\(^{-1}\) | 0.05 | 0.08 | 0.1 | 0.3 | 0.5 | 0.8 | 1.0 |
|-----------------------|----------------------------------------------------------|------|------|-----|-----|-----|-----|-----|
| Calcaric Fluvisols    | Zn(II)                                                   | 73   | 47   | 46  | 45  | 38  | 29  | 25  |
| Calcaric Arenosols    |                                                          | 40   | 28   | 27  | 27  | 22  | 18  | 14  |
| Calcaric Fluvisols    | Cu(II)                                                   | 1657 | 1394 | 1577| 1569| 1587| 1260| 942 |
| Calcaric Arenosols    |                                                          | 546  | 724  | 784 | 642 | 506 | 333 | 241 |

A significant decrease of the \( K_d \) value with an increase of the metal concentration in the initial and, accordingly, in the equilibrium solution was noted in all investigated samples, which indicates a decrease of the fraction of the absorbed metal and the interaction energy of ions with functional groups located on the surface of the sorbents determining their absorption capacity. The decrease of the absorption capacity is explained by the presence of several types of sorption centers on the surface of soil particles, differing in the magnitude of their affinity and selectivity for various cations, including Zn and Cu. Experimental data on the adsorption of Cu(II) and Zn(II) by soils revealed differences in their adsorption capacity as a result of differences in the chemical properties of the studied elements (the structure of their electronic shells) and significant differences between types of soils (their composition and
properties). In all variants, the sorption capacity of the meadow soil regard to the studied metals is higher than in alluvial soil due to the low buffering capacity of the latter, and the \( K_d \) and \( S \) values for Cu(II) ions for both types of soils are significantly higher than the values for Zn(II) (tables 2 and 3).

**Table 3.** The degree of sorption (\( S \)) of HM ions by hydromorphic soils, %.

| Soil                  | Metal concentration in the initial solution, mM L\(^{-1} \) |
|-----------------------|-------------------------------------------------------------|
|                       | 0.05 | 0.08 | 0.1  | 0.3  | 0.5  | 0.8  | 1.0  |
| Zn(II)                |      |      |      |      |      |      |      |
| Calcaric Fluvisols    | 88.00| 82.50| 82.00| 81.67| 79.00| 74.63| 71.50|
| Calcaric Arenosols    | 80.00| 73.75| 73.00| 68.40| 64.88| 57.90|      |
| Cu(II)                |      |      |      |      |      |      |      |
| Calcaric Fluvisols    | 99.40| 99.29| 99.37| 99.37| 99.37| 99.21| 98.95|
| Calcaric Arenosols    | 98.20| 98.64| 98.74| 98.47| 98.06| 97.09| 96.02|

For a qualitative and quantitative characterization of the interaction of zinc and copper with the soil absorbing complex (SAC) of the studied soils, adsorption isotherms were constructed with their approximation using several models. The isotherms of ion-exchange adsorption of Zn(II) and Cu(II) in meadow and alluvial soils from solutions of nitrate salts are shown in figure 1. Both types of soils characterized by a higher affinity for Cu(II) than for Zn(II) according to the shape of the isotherms and their position in the coordinate system (near the ordinate axis). The adsorption isotherms of Cu(II) and Zn(II) for both types of soils correspond to the L-form according to Dzhails [19] and indicate the uptake of metal either by one mechanism or by several similar mechanisms.

![Figure 1. Adsorption isotherms of the HM by the Calcaric Fluvisols (1) and Calcaric Arenosols (2).](image)

It is shown that the Langmuir equation is the most suitable model for description of the HM adsorption by the all studied soil types, whereas the Dubinin-Radushkevich and Freundlich equations to a lesser extent (table 4). However, in contrast to the empirical Freundlich equation, both models ((4) and (6)) allow the comparison of thermodynamic parameters of the absorption, such as the characteristic adsorption energy and the maximum adsorption \( C_\infty \) for different soil types.

The thermodynamic parameters of cations for equations (4) and (6) were calculated and compared using the statistical program SigmaPlot 12.5 (table 5). The data obtained by the Langmuir equation show that the \( C_\infty (\text{Cu}) > C_\infty (\text{Zn}) \) values, and the \( C_\infty \) values of the meadow soil are higher than the corresponding values for the alluvial soil. The \( K_L \) values characterize the interaction energy of absorbed cations with SAC are also higher for meadow soil than for alluvial soil. The reason of the higher absorptive capacity of meadow soil is the higher content of organic matter, clay, and silt in comparison with the alluvial sandy soil, where the content of \( C_{eqj} \) is 0.9% (table 1). The differences between the \( K_L \) of the cations of Cu(II) and Zn(II) are significantly high (by 17–27 times) depending on the type of soil, which indicates
the important role of the individual characteristics of metals (electronegativity, hydrolysis constants, and softness parameter) during interaction with soil.

**Table 4.** Approximation degree $R^2$ of HM adsorption isotherms by hydromorphic soils using different equations.

| Soil                | Zn(II) Frendlich | Zn(II) Langmuir | Zn(II) Dubinin-Radushkevich | Cu(II) Frendlich | Cu(II) Langmuir | Cu(II) Dubinin-Radushkevich |
|---------------------|------------------|-----------------|----------------------------|------------------|-----------------|----------------------------|
| Calcaric Fluvisols  | 0.994            | 0.999           | 0.962                      | 0.981            | 0.996           | 0.994                     |
| Calcaric Arenosols  | 0.981            | 0.996           | 0.967                      | 0.983            | 0.999           | 0.989                     |

It was found that the calculated values of the Gibbs energy ($\Delta G$) according to equation (4) and the interaction energy of adsorbed cations with SAC (E) in equation (6) were significantly different from each other. Similar differences in the values of these indicators were noted in the work of Dalal [20]. In all cases, the adsorption parameters obtained using the Dubinin-Radushkevich equation were significantly lower (table 5) that resulted in higher values of the binding energy of metals with soil according to the Langmuir model compared with the Dubinin-Radushkevich model and keeping the general trend meadow soil > alluvial soil, Cu > Zn.

**Table 5.** Thermodynamic parameters of the Langmuir and Dubinin-Radushkevich equations for HM adsorption by hydromorphic soils.

| Soil                | Langmuir equation | Dubinin-Radushkevich equation |
|---------------------|-------------------|--------------------------------|
|                     | $C_\infty$, mM/kg$^{-1}$ | $K_d$, L·mM$^{-1}$ | $-\Delta G$, kJ·M$^{-1}$ | $C_\infty$, mM/kg$^{-1}$ | E, kJ·M$^{-1}$ |
| Zn(II)              |                   |                               |                            |                           |                |
| Calcaric Fluvisols  | 13.48             | 3.95                          | 3.49                        | 2.07                      | 0.62            |
| Calcaric Arenosols  | 10.12             | 3.37                          | 3.00                        | 1.84                      | 0.55            |
| Cu(II)              |                   |                               |                            |                           |                |
| Calcaric Fluvisols  | 19.15             | 105.76                        | 12.55                       | 3.84                      | 0.76            |
| Calcaric Arenosols  | 13.75             | 57.09                         | 10.01                       | 3.12                      | 0.66            |

This is related with the fact that the Dubinin-Radushkevich equation better describes weak adsorption interactions between soil and HM ions, caused by molecular (Van der Waals) forces, as well as by the specific calculation of the parameters (theory of multilayer adsorption). Thus, the results obtained using these two equations cannot be compared, since the equations describe different mechanisms for the strength of the interaction of HM ions with soil, and the Dubinin-Radushkevich equation describes less strong interactions of metals with soil.

Thus, it has been established that the parameters of metal sorption are strongly depending on the chosen model. The Langmuir equation provides the higher values of bond strength than the Dubinin-Radushkevich equation.

**4. Conclusion**

The pattern of the absorption of Zn(II) and Cu(II) by hydromorphic soils in the south of Russia were studied, and certain differences in the adsorption capacity of the studied soils regards to metals were revealed. These differences are based on the different chemical properties of the studied elements (the structure of their electronic shells) and the differences between composition and properties of soils. Sorption isotherms of the Calcaric Fluvisols (Loamic) showed a high affinity of the surface of soil particles to the studied metals in comparison with the Calcaric Fluvic Arenosols. This is due to the
higher content of organic matter, clay, and silt in the Fluvisols, compared to the Arenosols. In all cases, Cu(II) showed a greater affinity for adsorption sites than Zn(II).

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