Influence of various factors on parameters of adsorption of Zn$^{2+}$ cations by meadow soil

T V Bauer$^1$, T M Minkina$^2$, D L Pinsky$^3$, F Mikailsoy$^4$, S N Sushkova$^2$ and I P Lobzenko$^2$

$^1$ Federal Research Center Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia
$^2$ South Federal University, Rostov-on-Don, Russia
$^3$ Institute of Physicochemical and Biological Problems of Soil Science, Russian Academy of Sciences, Pushchino, Russia
$^4$ Igdir University, Igdir, Turkey

E-mail: bauer@sfedu.ru

Abstract. The effect of changing the range of introduced metal concentrations, the ratio of solid and liquid phases, and the combined presence of other metal ions in the solution on the absorption of Zn by the meadow soil was studied. As the range of applied concentrations expands and increases (up to 100 mM/L), there is a significant decrease in intensity of metal adsorption and an increase in the soil sorption capacity. It was found that with increasing dilution of the external solution (soil / solution ratio 1:10), the thermodynamic parameters of adsorption with respect to Zn increase. During the joint absorption of Zn with cations of other metals, the dominant process that affects the shape of the isotherm and the parameters of metal adsorption is their mutual competition. Competitive relationships of metal ions lead to their redistribution between different soil reaction centers.

1. Introduction

A study of the nature of soil stability in relation to heavy metals is associated with patterns of absorption of pollutants by soil. The absorption of heavy metals is affected by such natural factors as the concomitant anion, complexation in solutions, and precipitation of poorly soluble metal compounds. In [7, 11], the influence of the Cl$^-$, SO$_4^{2-}$, CH$_3$COO$^-$, and NO$_3^-$ anions on the adsorption value and the interaction mechanisms of the Zn$^{2+}$ cation with solid phases of the soil were studied. It was revealed that CH$_3$COO$^-$ has the greatest influence on the bond strength of a metal with the surface of soil particles, and the NO$_3^-$ anion has the least effect.

The formation of associated forms of metals affects their behavior in the system, including adsorption by the soil absorption complex (SAC) and formation of precipitation of sparingly soluble salts. This influence is carried out through various mechanisms: a change in the form of metals in solution and the transfer of a part of the metal to a different chemical state, which has properties different from free ions [8]; a change in the ionic strength of solutions due to the formation of complexes with a zero charge and the associated change in the thermodynamic activity of cations; a change in the mechanisms of interaction of associated ions with the surface of soil particles.

An important mechanism for the immobilization of heavy metals in soil is the formation of precipitates of sparingly soluble compounds. The probability of such processes is experimentally
shown using the advanced analysis of the fine structure of absorption spectra (EXAFS spectroscopy). Zinc can precipitate in the form of ZnO, ZnCO3, Zn5(OH)6(CO3)2 [9, 13].

In studying TM adsorption by soils, the poly-element nature of pollution is rarely taken into account. Studies show that in areas with developed industries, soil pollution occurs simultaneously with a wide range of pollutants [6, 12]. Cases when monometrical soil contamination occurs are rare.

In case of multi-element pollution of soils, the redistribution of metal cations is difficult to quantify from the standpoint of the theory of ion exchange. The mutual competition of cations for exchange sites, aggravated by specific properties of metals and heterogeneity of the surface of soil particles, makes this problem extremely difficult. At the same time, the need to study the mutual influence of HM ions on soil absorption processes is obvious, since polycation exchange is always carried out under natural conditions. Therefore, an important issue is inclusion of all cations in the system capable of exchange in the sorption process [2].

The quantitative characteristics of the adsorption of metal ions by soils depend on the methods for their determination. In particular, a change in the ratio of the solid phase / solution can affect the aqueous phase of metals [1]. It is known that an increase in the soil / solution ratio due to the evaporation of moisture increases the concentration of all ions in the liquid phase, and this, in turn, increases the absorption of ions with a lower charge due to the concentration-valence effect. However, new problems related to the phase ratio arise [4].

Studies on the patterns of heavy metal absorption by meadow soils are crucial due to the fact that these soils are the most fertile soils used for arable land and pastures.

The purpose of this work is to study the effect of the experimental methodological conditions and the presence of other metal ions on the adsorption parameters of Zn$^{2+}$ cations by the meadow soil of Rostov Region.

2. Materials and Methods

The research object is the upper humus horizon (0–20 cm) of meadow heavy loamy soils. It is characterized by the following physical and chemical properties: $C_{org}$ – 4.3 %, pH – 7.5; EKO – 40.3 cM (+) / kg; exchange cations (Ca$^{2+}$, Mg$^{2+}$) – 38.1 cM (+) / kg; CaCO$_3$ – 0.6 %; the content of physical clay is 55.8 %, sludge is 32.0 %.

The adsorption of Zn$^{2+}$ cations was studied on the soil in its natural ionic form. Ten-fold (by weight) quantities of solutions of Cu nitrate salts in the concentration range of 0.05–1.0 mM/L and 0.05–100 mM/L were poured onto the samples of soil passed through a sieve with a mesh diameter of 1 mm to determine the influence of the concentrations on the parameters of ion-exchange metal adsorption.

The suspensions were shaken for an hour and left for a day at rest, after which they were filtered. The metal content was determined by the atomic absorption spectrometry (AAS). The amount of absorbed Zn$^{2+}$ cations was calculated based on the difference between the metal concentrations in the initial and equilibrium solutions.

To study the effect of the ratio of solid and liquid phases on Zn adsorption in meadow soils, a series of experiments was conducted: the solution ratios were 1:10 and 1:5. The range of metal concentrations ranged from 0.05 to 1.0 mM/L.

The study of the patterns of ion-exchange adsorption of Zn with the participation of cations of other metals (Cu and Pb) was carried out using Ca-saturated samples. For this, the initial soil was converted into a monoionic Ca-form by 10-fold treatment with 0.25 M Ca(NO3)$_2$ solution. Then the soil was washed with distilled water, brought to an air-dry state and homogenized. The first experiment was carried out according to the following procedure: contamination of soil samples was simulated by introducing various amounts of Cu nitrates with calcium nitrate to maintain a constant ionic strength of 0.01 M/L. The transfer of soil samples to the Ca-saturated form was carried out in order to exclude the influence of other cations on the absorption of the metals and study the competitive nature of the absorption for adsorption sites. It was taken into account that Ca content is 80-90%; therefore, the conversion of soil into a monoionic Ca form does not affect its structure and function. The second experiment was conducted similarly,
except that the initial solutions simultaneously contained Zn, Cu, and Pb in equal amounts. The ratio was 1:10. The concentration of the initial solutions ranged from 0.05 to 1 mmol/L. Further study of Zn sorption by meadow soil with separate and joint application with Cu and Pb was carried out according to the above method.

The repetition of all experiments was three times. Statistical processing of the results and calculation of determination coefficients were performed in SigmaPlot 12.5 and MS Excel 2007 with a confidence level of 0.95.

3. Results
3.1. The dependence of parameters of adsorption processes on the range of introduced metal concentrations

Figure 1 shows the adsorption isotherms of Zn nitrates in meadow soil from solutions of nitrate metal salts in the range from 0.05 to 100 mM/L and 0.05 to 1 mM/L. With an increase in the concentration of metal in the initial solutions, its absorption also increases. The shape of the isotherms is described by the Langmuir equation:

$$C_{\text{ad}} = C_\infty \frac{K_L C_s}{1 + K_L C_s},$$

where $C_{\text{ad}}$ – amount of cations absorbed, $C_\infty$ – value of maximum metal adsorption, mM·kg$^{-1}$; $C_s$ – metal concentration in equilibrium solution, mM·L$^{-1}$; $K_L$ – Langmuir constant, L·mM$^{-1}$.

![Figure 1](image1)

Figure 1. Isotherms of Zn adsorption by meadow soil from solutions of nitrate metal salts in the concentration ranges of 0.05-1.0 mM/L (A) and 0.05-100 mM/L (B).

With an increase in the metal concentration from 0.05 to 100 mM/L, the amount of Zn adsorbed by the soil gradually increases, but the share of its absorption gradually decreases. At the same time, the calculated values of the Zn adsorption parameters differ significantly for the low and high ranges of its concentrations (Table 1).

| Range of metal concentrations, mM / L | $C_\infty$, mM·kg$^{-1}$ | $K_L$, l·mM$^{-1}$ | $R^2$ |
|---------------------------------------|--------------------------|-------------------|-------|
| 0.05–1.0                              | 13.24±0.37              | 3.96±0.41         | 0.99  |
| 0.05–100                              | 446.06±21.83            | 0.05±0.006        | 0.99  |

With an increase in the range of initial metal concentrations from 0.05 to 100 mM/L, the $K_L$ constant, which characterizes the bond strength of the metal with the organo-mineral matrix of soils, decreases 79 times. In this case, the value of $C_\infty$ increases 34 times.

This nature of changes in the adsorption parameters can be due to two reasons: the presence of several types of adsorption centers, which differ in the degree of affinity for the studied metal cations. Moreover, the centers with the highest affinity are filled according to the type of specific sorption (initial sections of isotherms characterized by a large angle of inclination (equilibrium concentration of 0–10 mM/L)). As they are filled, metal cations are adsorbed on sorption centers with a lower affinity and binding energy (nonspecific adsorption), which corresponds to the final sections of the curves.
Similar data were obtained by M.S. Panin and T.I. Siroml [10] for Cu in leached chernozems. One more reason is an increase in the probability of the formation of precipitates of sparingly soluble Zn salts on the surface of soil particles at high metal concentrations in the initial solutions.

### 3.2. The effect of the ratio of solid and liquid phases on the metal absorption

Zn adsorption isotherms at different soil / solution ratios have the form of curves with saturation and are described by the Langmuir equation (Fig. 2). The absorption of Zn from the same solutions at a ratio of 1:10 is higher than at a ratio of 1:5.

![Figure 2. Isotherms of Zn adsorption from solutions of metal nitrate salts at a soil / solution ratio of 1:10 (1) and 1:5 (2).](image)

| Soil / solution ratio | \( C_{\infty} \), mM kg\(^{-1} \) | \( K_l \), l mM\(^{-1} \) | \( R^2 \) |
|-----------------------|--------------------------|-----------------|--------|
| 1:10                  | 13.24±0.37               | 3.96±0.41       | 0.99   |
| 1:5                   | 7.29±0.13                | 2.93±0.16       | 0.99   |

The maximum adsorption capacity \( (C_{\infty}) \) of meadow soil at a soil / solution ratio of 1:10 is 1.8 times higher than at a ratio of 1:5. In this case, the bond strength constant of metals (C) significantly decreases with a narrowing of the soil / solution ratio by 1.4 times.

An increase in the sorption ability at a soil / solution ratio of 1:10 can be due to the concentration-valence effect, since with a decrease in the volume of the liquid phase, the concentration of readily soluble salts increases. When diluting an equilibrium solution in accordance with the law of masses, the ion-exchange equilibrium shifts toward an increase in the adsorption of ions with a large charge. Thus, the system counteracts a change in the external factor. The consequence is a higher selectivity of the soil to metal ions in solutions with a wider soil / solution ratio.

In [1], it is noted that with an increase in the soil / solution ratio, the ionic strength of the solution decreases and the number of active sites capable of absorbing the metal increases. In this case, the state of the metal changes which leads to changes in ion pairs, concentrations of free, hydrated and complexed metal [5].

### 3.3. The effect of the joint presence of ions of other metals on the absorption of Zn by meadow soil

Figure 3 shows the adsorption isotherms of Zn\(^{2+} \) in a Ca-saturated form when it is introduced separately and combined with Cu\(^{2+} \) and Pb\(^{2+} \) from solutions of nitrate salts. The adsorption isotherms are convex curves that can be described by the Langmuir equation (1). The isotherm section in the region of low equilibrium concentrations characterizes the high affinity of the soil for the cations of the metal and passes into a smoother curve in the region of high concentrations. The amount of
absorbed metal increases with an increasing degree of soil contamination, but its soil retention strength decreases as a result of a decrease in the affinity of the remaining adsorption sites for Zn\(^{2+}\) cations. A decrease in absorption capacity can be due to the presence of several types of sorption centers on the surface of soil particles, which differ in the affinity and selectivity to various cations, including heavy metals [2]. In the process of adsorption of PPC of metal cations, the centers with the highest affinity are filled first (initial sections of the isotherm), and centers with lower affinity for metal cations are involved in the process which corresponds to the final sections of the curves (Fig. 3).

The values of the parameters of the Langmuir equation calculated from the experimental isotherms are presented in Table 3. High values of the determination coefficients (R\(^2\) = 0.99) indicate an agreement between the experimental isotherms and the adsorption equation (1).

When comparing the isotherms of the poly-element sorption of metals and the thermodynamic parameters obtained during their approximation, we can conclude that one metal in the system can affect the maximum adsorption and bond strengths of ions of other metals with the soil.

![Figure 3. Zn adsorption isotherms in a Ca-saturated form under mono-element (1) and poly-element (2) contamination from solutions of nitrate salts](image)

Table 3. Parameters of Zn\(^{2+}\) cations absorption by meadow soil in a Ca-saturated form under mono-element and polyelement contamination from solutions of nitrate salts

| Adsorption          | C\(_\infty\), mM·kg\(^{-1}\) | K\(_L\), lmM\(^{-1}\) | R\(^2\) |
|---------------------|------------------------------|-----------------------|--------|
| Mono-element        | 9.09±1.46                    | 3.96±0.41             | 0.99   |
| Poly-element        | 4.05±0.80                    | 4.75±1.22             | 0.99   |

Under the conditions of the simultaneous presence of Zn\(^{2+}\) ions with Cu\(^{2+}\) and Pb\(^{2+}\), the adsorption parameters change. With the joint introduction of metals, a decrease in C\(_\infty\) is characteristic. According to M.S. Panin and T.I. Siroml [10], under the poly-element contamination, the adsorption capacity of meadow soil decreases: Pb is absorbed 5 times less, Cu – 2 times less, and Zn – 4 times less.

The K\(_L\) constant increases. However, it is in the error determination range.

The tendency to increase the bond strength of metal ions while decreasing C\(_\infty\) values can be explained as follows. In a system with cations of only one metal, they are interacting with all types of reaction centers. In this case, the fact that different reaction centers have different affinities for metal cations does not matter much, since there are no other metal cations in solution. As a result of this interaction, we have a curve of metal absorption by the soil and calculate the parameters of the Langmuir equation. Both the curve and the parameters of the equation do not take into account different affinities of heavy metal cations for different types of reaction centers.

If there are cations of three metals in the system, they are redistributed between different reaction centers. Ions of each metal interact with those reaction centers for which they have the highest affinity.
Those reaction centers for which ions have a lower affinity turn out to be occupied by ions of other metals. Zn is the least competitive element in comparison with Cu, and Pb. An element absorbed by the exchange mechanism is most susceptible to the competition impact of elements in which the soil is dominated by a specific exchange or the non-exchange mechanism. That is why the differences in the values of $K_L$ for Zn are not significant (Table 3).

Under the poly-element contamination, ions of different metals tend to interact with the same soil reaction centers. In this case, a decrease in soil absorption of ions of the element that has a lower affinity for these reaction centers is inevitable [3].

It can be assumed that under the poly-element contamination of soils with heavy metals, there are two types of competitive relationships: 1) between different chemical elements from the TM group, seeking to interact with the same reaction centers of soil components; 2) between different types of reaction centers seeking to interact with the same metal ions. Superimposed on each other, these types of relations create a complex picture of the behavior of heavy metal ions.

4. Conclusion
The adsorption parameters of Zn$^{2+}$ cations are affected by metal solutions, the ratio of solid and liquid phases of the soil, and ions of other metals.

A change in the soil / solution ratio and concentration intervals of the initial metal solutions changes adsorption parameters due to the concentration-valence effect. When reducing the ratio of solid and liquid phases two times, the maximum adsorption capacity is $C_\infty$ decreases 1.8 times. The value of $K_L$ with a narrowing of the soil / solution ratio decreases slightly. As the initial concentration of Zn increases, a significant decrease in adsorption intensity and an increase in the number of absorbed metal cations can be observed. This may be due to several reasons:

- energy heterogeneity of the exchange places of the soil PPC;
- gradual filling of exchange sites with an ever lower relative affinity for the absorbed metal cation;
- formation of surface sediments of sparingly soluble metal salts.

The simultaneous presence of Zn$^{2+}$ cations and Cu$^{2+}$ and Pb$^{2+}$ cations decreases the maximum adsorption of the metal. In this case, the bond strength of Zn$^{2+}$ with the soil does not change, since it is the least competitive element.

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