

DYNAMICS OF COMPETITIVE SORPTION OF HEAVY METAL CATIONS IN MINERAL SOILS

R. Gąszczyk, P. Muszyński

Department of Chemistry, Agricultural University, Akademicka 15, 20-033 Lublin, Poland

A b s t r a c t. Model research on competitive sorption of heavy metal cations (Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} and Cr^{3+}) with Pb^{2+} cations was carried out in the following mineral soils: grey-brown podzolic derived from weakly loamy sand (Podzoluvisols) and grey-brown podzolic derived from loess (*Orthic Luvisols*) using a dynamic method.

Investigation on the course and the range of the sorption from the two-component solutions allowed to determine mobility of individual heavy metal cations in relation to lead (II) cations. At the same time, it allowed to evaluate their phyto-availability. Elements, which most easily entered sorptive complexes of both of the investigated soils were copper (II) and chromium (III) cations. The rest of the cations showed different energy levels of entrance with simultaneous sorption with lead (II) cations.

During competitive sorption of heavy metal cations, i.e. at saturation the columns with two-component solutions, the presence of the second, opposite process namely desorption of the following cations from the soil: Co^{2+} , Zn^{2+} , Ni^{2+} , and Cd^{2+} , was observed. Desorption levels were characteristic for particular cations and depended on the type of soil.

K e y w o r d s: heavy metals, competitive sorption, mineral soils.

INTRODUCTION

Mobility of heavy metals, their activity and bio-availability are influenced by many factors, such as: pH, temperature, oxidation-reduction potential, sorptive soil capacity, complexing by anions, composition and concentration of soil solution components, and competition with ions of other metals [1].

Reactions of ion exchange are reversible, influenced by diffusion, stoichiometric, and selective. They occur between the cations situated in the Guy-Chapman's double diffusion layer and cations in the solution. The processes of adsorption are then explained as generation of outer-sphere complexes with surface functional groups on the basis of electrostatic bindings [13]. In such complexes, at least one

particle of the solvent (water) is situated between the functional group and the ion [15].

A dynamic research method for the competitive sorption of lead (II) cations with cobalt (II), copper (II), zinc, nickel (II), cadmium, and chromium (III) cations in mineral soils is presented in this paper. The aim of this research with model character, was to evaluate chemical affinity of the six heavy metal cations introduced, together with lead (II) cations, into the soil material with different physical-chemical properties. The aim was also to evaluate durability of their bindings in the sorptive complex.

MATERIAL AND METHODS

The following two soils were examined: grey-brown podzolic derived from weakly loamy sand (Podzoluvisols) and grey-brown podzolic derived from loess (Orthic Luvisols). Characteristics of the fundamental properties of the investigated soils is given in Table 1.

Sorption of heavy metal cations was carried out in columns, in which 100 g of loose poured soil material was placed. The material was then moistened with re-distilled water with the capillary rise method. Then, a two-component solution containing $\text{Pb}(\text{NO}_3)_2$ and respectively NiCl_2 , CoCl_2 , CdCl_2 , CuCl_2 , or ZnCl_2 (with the Me^{2+} concentration 0.0166 M) and CrCl_3 (with the Cr^{3+} concentration 0.0111 M) was dropped in on the top of the column with a constant rate of 2 cm^3/min . The rate was achieved with the help of a peristaltic pump. This operation was being performed until sorptive saturation was reached after putting through 180 cm^3 of the solution. The effluent was collected into 10 cm^3 portions using a fraction collector. The content of metals in those portions was evaluated with the AAS method [6].

Table 1. Some properties of the soils used in the experiments

Soil	Percent of soil fractions (mm)				N_{tot} (%)	C_{org} (%)	pH		Specific surface area (m^2/g)	Available forms (mg/kg soil)		
	1.0- 0.1	0.1- 0.02	0.02- 0.002	<0.002			H ₂ O	KCl		P ₂ O ₅	K ₂ O	Mg
	Podzo- luvisols	80	14	2			4	0.04		0.50	5.5	4.7
Orthic Luvisols	1	63	27	9	0.10	2.13	4.8	4.3	24	40.0	22.7	4.1

RESULTS

Pouring two-component solutions, that contained lead (II) cations, also cations of cobalt (II), copper (II) zinc, nickel (II), cadmium, and chromium (II), through soil columns beside a permanent component resulted in varied sorption in the soils with different physical-chemical properties.

Among all the two-component combinations used in the $\text{MeCl}_x - \text{Pb}(\text{NO}_3)_2$ solution type the cations that were most frequently subject to sorption were: lead (II) in both investigated soils. The sorption level depended on the soil type, as well as co-sorbed cations (Figs 1 and 2).

In the loess soil, the sorption of Pb^{2+} cations occurred in a much wider range than in the sandy soil, which seems comprehensible considering high differentiation in the contents of clay fractions and specific surface areas of both soils.

Differentiation of the level of Pb^{2+} cations sorption and co-sorbed cations of heavy metals occurred also within the same soil. The highest differentiation in the sorption of Pb^{2+} cations in the sandy soil was observed in the solutions with Ni^{2+} and Co^{2+} cations, and in the case of loess soil - in the solutions with Ni^{2+} and Zn^{2+} cations. Presence of Cu^{2+} and Cr^{3+} cations in the saturating solutions caused a decrease in the magnitude of sorption of Pb^{2+} cations in both investigated soils (Table 2 - columns A).

Presence of Pb^{2+} cations in all the solutions introduced to the soil columns directly affected the level of sorption of the second component, as well. Antagonisms between the co-sorbed cations, as well as competition while filling sorptive positions in the sorptive complex, occurred in the process of sorption from the two-component solution.

The greatest affinity to both investigated soils was observed for (beside the Pb^{2+} cations described previously) Cu^{2+} cations which had been subjected to sorption in certain conditions in the widest range (Table 2 - columns B). Other heavy metal cations were sorbed in respectively smaller ranges: about 0.2-0.3 mmol less in the sandy soil and about 0.2-0.4 mmol less in the loess soil.

Considering the sorption level of individual cations from two-component solutions with Pb^{2+} cations as permanent components we can create sequence of entrance into the investigated soils: into the sandy soil: $\text{Cu} > \text{Zn} > \text{Ni} > \text{Co} > \text{Cr} > \text{Cd}$; into the loess soil: $\text{Cu} > \text{Ni} = \text{Zn} \geq \text{Cr} > \text{Cd} > \text{Co}$.

The research described above had also proved that there is competition, which could be observed as for example, desorption of heavy metal cations during the process of sorption from two-component solutions (Table 2 - columns C).

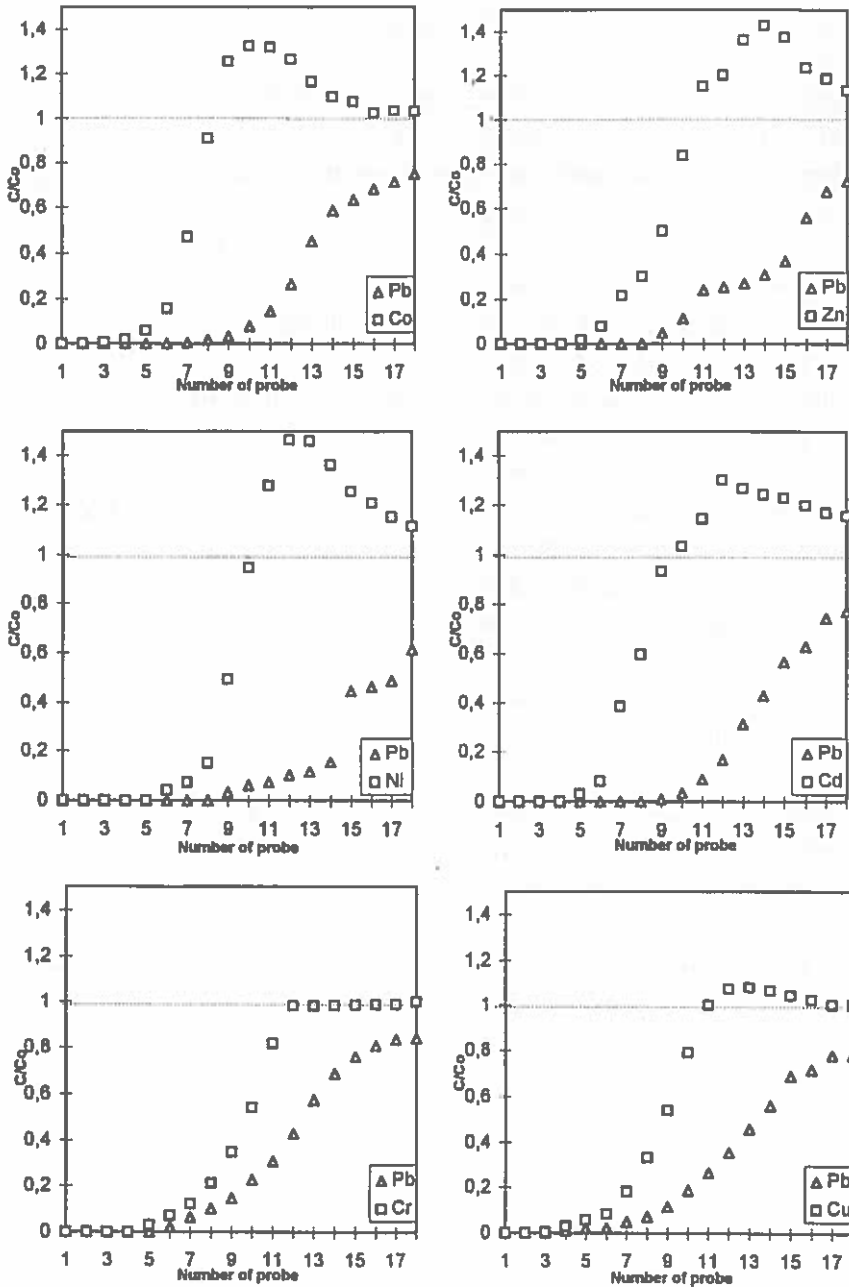


Fig. 1. Course of competitive sorption of heavy metal cations with lead (II) cations in sandy soil. c - concentration of Me^{n+} in a given effluent portion; c_0 - concentration of Me^{n+} in the solution introduced to the column.

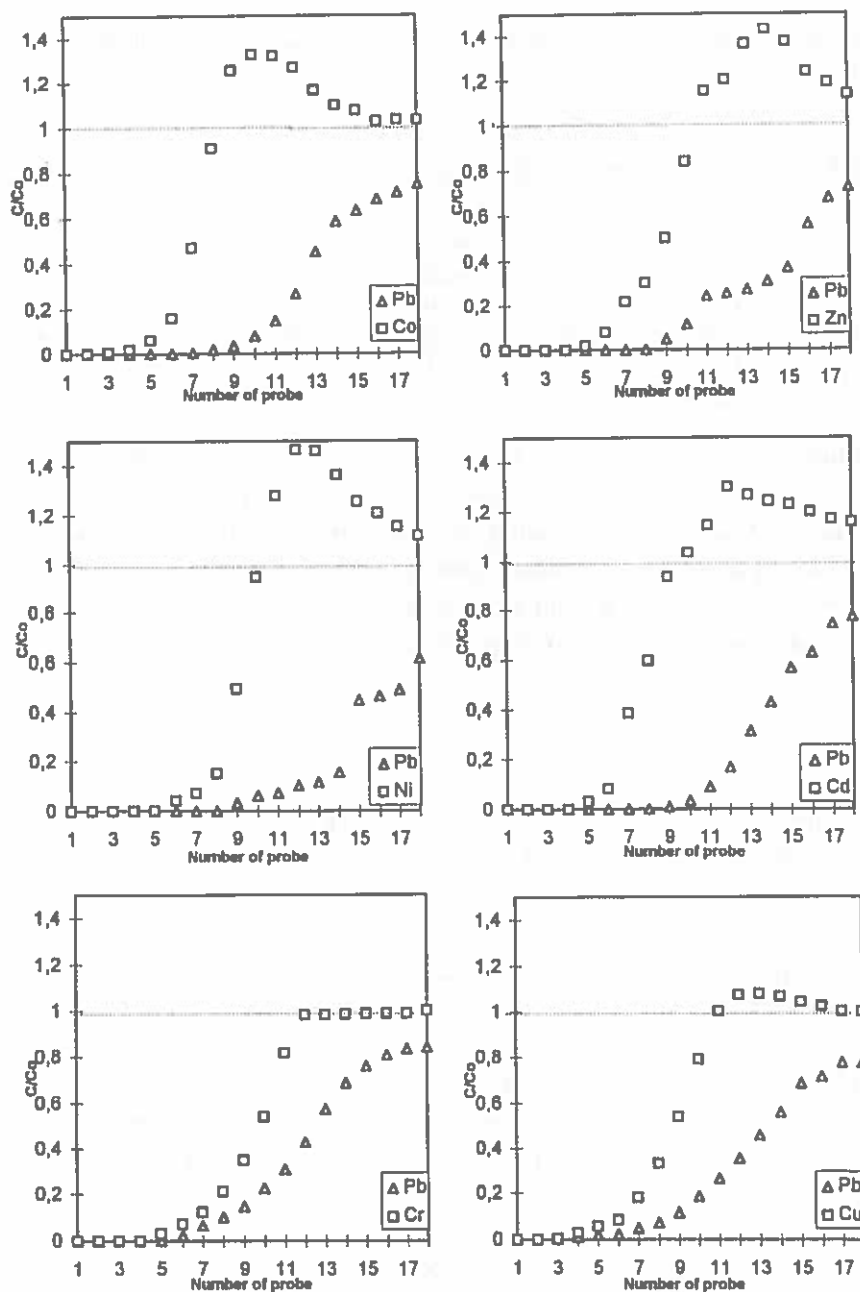


Fig. 2. Course of competitive sorption of heavy metal cations with lead (II) cations in loess soil. c - concentration of Me^{n+} in a given effluent portion; c_0 - concentration of Me^{n+} in the solution introduced to the column.

Table 2. Quantity of the sorbed and desorbed heavy metal cations in the soils after competitive sorption (in mmol)

Cation	Soil					
	Podzoluvisols			Orthic Luvisols		
	A	B	C	A	B	C
Cu ²⁺	1.272	0.769	0.012	2.156	1.240	0.047
Zn ²⁺	1.303	0.596	0.096	2.408	1.004	0.343
Cr ³⁺	1.282	0.469	0.009	2.177	0.999	0.000
Ni ²⁺	1.366	0.569	0.106	2.579	1.009	0.379
Cd ²⁺	1.299	0.447	0.177	2.378	0.880	0.289
Co ²⁺	1.362	0.494	0.133	2.277	0.805	0.266

In those conditions Cd²⁺ and Co²⁺ cations in the sandy soil and of Ni²⁺ and Zn²⁺ cations in the loess soil, were most exposed to desorption. We should emphasize here that Cu²⁺ and Cr³⁺ cations were desorbed in very small amounts (Cr³⁺ cations did not appear in the effluent from the loess soil at all).

Therefore, on the basis of this criterion, we can create a sequence of exit of heavy metal cations from the investigated soils: from the sandy soil: Cd > Co > Ni > Zn >> Cu ≥ Cr; from the loess soil: Ni > Zn > Cd > Co >> Cu > Cr.

DISCUSSION

This research on the competitive sorption in dynamic conditions proved that the presence of Pb²⁺ cations in two-component solutions saturating soil columns caused a decrease in the sorption of the following cations: Cd²⁺, Co²⁺, Ni²⁺ and Zn²⁺.

Similar conclusions were drawn by Rimmer and Yongming [12] and Bibak [3], who investigated competitive sorption and found that Cu²⁺ cations were the factors that caused a decrease in the sorption of Ni²⁺ and Zn²⁺ cations. Chen *et al.* [4] and Gosponder and Schmidt [7] proved that the presence of Pb²⁺ and Cu²⁺ cations in soils caused an increase in the bio-availability of cadmium and its greater uptake by plants. Zhu and Alva [17] explained a decrease in Cu²⁺ adsorption in the presence of Ca²⁺ and Mg²⁺ cations by the phenomenon of ion competition towards places of exchange in soil colloids.

Competitive sorption of cations and their influence on one another was also investigated by Harter [8], who stated that Ni²⁺ sorption did not affect on the Cu²⁺ sorption while the presence of Cu²⁺ cations influenced the level of Ni²⁺ sorption. The above author proved also that Ni²⁺ cations competed with Co²⁺ cations in the soil sorptive complex.

However, no one has managed to determine the rules governing selectivity of organic matter in relation to cations of heavy metals, yet. That sorption depends, among others, on the chemical nature of organic ligands, on the reaction, and on the ion force of the saturating solution [10]. According to Eliot *et al.* [5], Cu^{2+} and Cd^{2+} cations are mostly bound to organic matter, while Pb^{2+} and Zn^{2+} cations get bound on the surface of minerals. Schmidt and Sticher [14] explained binding of organic matter with metals by creation of complexes with great selectivity and by the presence of two active centers in the soils: specific in relation to metal cations and non-specific, causing desorption and a decrease in the sorption intensity [16].

According to Murali and Aylmore [11], the course of competitive sorption in dynamic conditions is characterized by the appearance of desorptive processes in some of the components, and further sorption in the rest of them. That phenomenon explains the occurrence of the surplus of some heavy metal cations in various parts of natural environment, which was also proved by the results presented in this paper.

CONCLUSIONS

When two-component solutions with Pb^{2+} cations and other heavy metal cations, such as: Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , and Cr^{3+} were run through columns of two mineral soils, the following effects were observed in the conditions of competitive sorption:

1. Pb^{2+} cations had the greatest entrance energy into both investigated soils and they significantly limited the sorption of Zn^{2+} , Ni^{2+} , Co^{2+} and Cd^{2+} cations.

2. Transient levels in the desorption of Cr^{3+} cations indicate that these ions fill sorptive place with great binding energy, i.e. places with great affinity towards the investigated soils.

3. Cu^{2+} and Cr^{3+} cations caused the greatest decrease in the level of Pb^{2+} sorption in both investigated soils.

4. Shapes of the desorption isotherms indicate that the forces binding cations of the investigated heavy metals to the sandy soil were greater than in the loess soil.

5. The succession of heavy metals in the created sequences of entrance did not conform to the levels of ion potential, the first constants of pK hydrolysis, or to the succession based on the Pearson's theory of hard and soft acids and bases (HSAB).

The analysis of course of sorption isotherms suggested the existence of two kinds of sorptive places: those with high and those with low binding energy in relation to individual ions of metals. This research showed that Pb^{2+} and Cr^{3+} cations showed the greatest specificity towards sorptive places with high binding energy compared to other, co-sorbed cations: Cd^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Cu^{2+} .

REFERENCES

1. Alloway B.J.: Heavy Metals in Soils. (Ed.: Blackie and Son Ltd), Glasgow, London, Scotland, England, 1990.
2. Basta N.T., Tabatabai M.A.: Effect of cropping system on adsorption of metals by soils. III. Competitive adsorption. *Soil Sci.*, 153, 331-337, 1992.
3. Bibak A.: Competitive sorption of copper, nickel, and zinc by an Oxisol. *Commun. Soil Sci. Plant Anal.*, 28, 927-937, 1997.
4. Chen C.T., Lee D.V., Houg K.H.: Competitive adsorption of Cd, Cu, and Pb by acid soils. *J. Chinese Agr. Chem. Soc.*, 30, 83-99, 1992.
5. Elliot H.A., Liberati M.R., Huang C.P.: Competitive adsorption of heavy metals by soils. *J. Environ. Qual.*, 15, 215-219, 1986.
6. Gaśczyk R., Paszko T.: Adsorption and desorption of cadmium, copper, and lead in Polish mineral soils. *Environ. Sci Res.*, 51, 329-335, 1996.
7. Gsponder R., Schmidt H.W.: Einfluss der Schwermetall-Kompetition im Boden auf die Aufnahme durch die Pflanzen. *Bull. BGS*, 10, 45-50, 1986.
8. Harter R.D.: Competitive sorption of cobalt, copper, and nickel ions by a calcium saturated soil. *Soil Sci. Soc. Am. J.*, 56, 444-449, 1992.
9. Kurdi F., Doner H.E.: Zinc and copper sorption and interaction in soils. *Soil Sci. Soc. Am. J.*, 47, 873-876, 1983.
10. McBride M.B.: Environmental Chemistry of Soils. Oxford University Press, New York, Oxford, United States, 1994.
11. Murali V., Aylmore L.A.G.: Competitive adsorption during solute transport in soils. 3. A review of experimental evidence of competitive adsorption and an evaluation of simple competition models. *Soil Sci.*, 136, 279-290, 1983.
12. Rimmer D.L., Yongming L.: Zn-Cu interaction affecting Zn adsorption and plant availability in a metal - contaminated soil. *Pedosphere*, 6, 335-339, 1996.
13. Schindler P.W., Sposito G.: Surface Complexation at (Hydr)oxide Surfaces. In: Interactions at the Soil Colloid - Soil Solution Interface (Eds G.H. Bolt, M.D. DeBoodt, M.H.B. Hayes, M.B. McBride). Series E, Applied Sciences. Kluwer, Dordrecht, Netherlands, 115-145, 1991.
14. Schmitt H.W., Sticher H.: Heavy metals compounds in the soil. In: Metals and Their Compounds in the Environment (Ed. E. Merian). VCH Verlagsgesellschaft mbH, Weinheim, Federal Republic of Germany, 311-331, 1991.
15. Stumm W., Morgan J.J.: Aquatic Chemistry. John Wiley and Sons, New York, United States, 1996.
16. Yu S.F.: Competitive adsorption of heavy metals by soils. *Acta Pedol. Sin.*, 28, 50-57, 1991.
17. Zhu B., Alva A.K.: Differential adsorption of trace metals by soils as influenced by exchangeable cations and ionic strength. *Soil Sci.*, 155, 61-66, 1993.