

# Studies of the Effectiveness of $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ and $\text{Cr}^{3+}$ Desorption with $\text{K}^+$ in Grey-Brown Podzolic Soils

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## Abstract

Model studies were carried out using the three-component  $\text{CuCl}_2$ ,  $\text{CoCl}_2$  and  $\text{CrCl}_3$  solution in two grey-brown podzolic soils. After saturation of soil with the three-component solution and elution with water, desorption was carried out with the  $0.1 \text{ mol dm}^{-3}$   $\text{KCl}$  solution. For comparison, desorption with the  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions was also conducted. Desorption of  $\text{Cu}^{2+}$  with  $\text{K}^+$  was in both soils similar to that of  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  but smaller in comparison with  $\text{Ca}^{2+}$ . In the case of  $\text{Co}^{2+}$  desorption with the studied exchangeable cations was not differentiated. Desorption of  $\text{Cr}^{3+}$  with  $\text{K}^+$  and  $\text{NH}_4^+$  was greater than with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The differences in desorption efficiency can be explained based on the theory of hard and soft acids and bases (HSAB).

**Keywords:** heavy metals, soils, competitive sorption

## Introduction

Mobility of heavy metals in soil depends on many factors like properties of metals, number and type of sorption sites of soil and pH [3]. Also important is type and concentration of organic and inorganic anions in the soil solution that can form insoluble compounds with metal ions or soluble complexes causing mobility growth [11].

Heavy metal ions are bonded in soil with specific and non-specific sorption forces (ion exchange reactions) [3, 21] and therefore they are susceptible to desorption with exchangeable cations. There are many reports about the decrease of heavy metal ion sorption in the presence of exchangeable cations [8, 13, 21]. Desorption with these cations has attracted little attention so far, though there is need for determination of applicability of these cations for in-situ remediation of metal-contaminated subsurface soils [21]. The problem of mineral fertilizers' effect on heavy metal availability for plants has also been scarcely discussed and usually as of marginal importance [4, 7]. These facts were the reasons for undertaking this study.

The presented results are part of a broader investigation [5, 6, 14, 15, 16] concerning heavy metal ions sorption and desorption in multi-component systems. Acquiring knowledge about sorption and desorption of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  is essential because they are characterized by average or large toxicity for plants and mammals [9] and human activity has led to an increase of their contents in soils to hazardous levels in some areas.

The aim of this study was to determine the course of desorption of the three-component  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  system with  $\text{K}^+$  and to compare efficiency of desorption with  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

## Materials and Methods

### Soils

Studies were carried out on the grey-brown podzolic soil, one of the most common arable soils in Poland. The samples were taken up from the  $A_p$  level of soil derived from slightly loamy silty sand and that derived from clay silt (due to the character of bed-rocks they are called sandy and loess soils). The soil samples were dried, sieved using a 1 mm diameter sieve and averaged. The basic

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physicochemical properties of the sandy and loess soils were as follows: contents of floating fraction – 10 and 39%, contents of colloidal clay – 2 and 3%, pH in 1 mol dm<sup>-3</sup> KCl – 3.9 and 4.3, specific surface area (total) – 8.67 and 20.05 m<sup>2</sup> g<sup>-1</sup>, contents of humus – 1.24 and 1.52 %, sum of basic cations – 8.0 and 37.0 mmol<sub>c</sub> kg<sup>-1</sup>, total sorption capacity – 41.4 and 77.5 mmol<sub>c</sub> kg<sup>-1</sup>. The total contents of heavy metals in soils determined after hot etching in concentrated HNO<sub>3</sub> and HClO<sub>4</sub> were the following: Fe – 156.3 and 201.9 mmol kg<sup>-1</sup>, Mn – 2.2 and 8.9 mmol kg<sup>-1</sup>, Cu – 0.047 and 0.094 mmol kg<sup>-1</sup>, Co – 0.027 and 0.14 mmol kg<sup>-1</sup>, Cr – 0.19 and 0.61 mmol kg<sup>-1</sup>.

### Column Experiments

Samples of 100 g soil were placed into columns made of the methyl polymetacrylate of the inner diameter 44 mm and the length 75 mm. The intergranular space was filled with deionized water introduced from the bottom of the column at the rate of 1.5 cm<sup>3</sup> min<sup>-1</sup>. Then 140 cm<sup>3</sup> of the three-component CuCl<sub>2</sub>, CoCl<sub>2</sub> and CrCl<sub>3</sub> solution were dropped onto the column top with the constant rate 4 cm<sup>3</sup> min<sup>-1</sup> (maintained in all stages of the experiment). The introduced solution contained 2.33 mmol Cu<sup>2+</sup> and Co<sup>2+</sup> as well as 1.55 mmol Cr<sup>3+</sup>. Then the soil column was washed with 140 cm<sup>3</sup> deionized water and desorption of heavy metal cations was carried out passing 320 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> KCl. The effluent from the column was collected by means of a fraction collector in the portions of 10 cm<sup>3</sup> volume and pH was measured.

For possibly accurate determination of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> desorption efficiency with K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, the effluent from the column was collected into measuring flasks of suitable volumes (140 cm<sup>3</sup> – saturation with the three-component solution, 140 cm<sup>3</sup> – washing out with deionized water, 320 cm<sup>3</sup> – desorption with the exchangeable cation solution). The cation concentration in each of the solutions was 0.1 mol<sub>c</sub> dm<sup>-3</sup>. To determine heavy metal ions unsusceptible to desorption with the exchangeable cation solution, 200 cm<sup>3</sup> of the HCl and HNO<sub>3</sub> solution of the concentration 1 mol dm<sup>-3</sup> for each acid were passed through the column. Each experiment was repeated twice.

As the HCl and HNO<sub>3</sub> solution caused a partial desorption of natural contents of Cu, Co and Cr in the soils, in a separate experiment 200 cm<sup>3</sup> of the nitric(V) acid and hydrochloric acid solution were passed through the soil column and metals were determined in the effluent. The solution of acids desorbed in 1 kg of the sandy and loess soils: Cu<sup>2+</sup> – 0.018 and 0.018 mmol, Co<sup>2+</sup> – 0.007 and 0.013 mmol, Cr<sup>3+</sup> – 0.010 and 0.022 mmol. The contents of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> in the soil after passing the exchangeable cation solution were diminished by the above quantities.

The metals were determined using flame atomic absorption spectrometry (FAAS). The measurements of pH were carried out with the pH-meter CP-315. The obtained results were analyzed using the Statgraphics Plus V.3.1 program. The method of one-way analysis of the variance using Tukey's test was applied assuming the confidence level 95%.

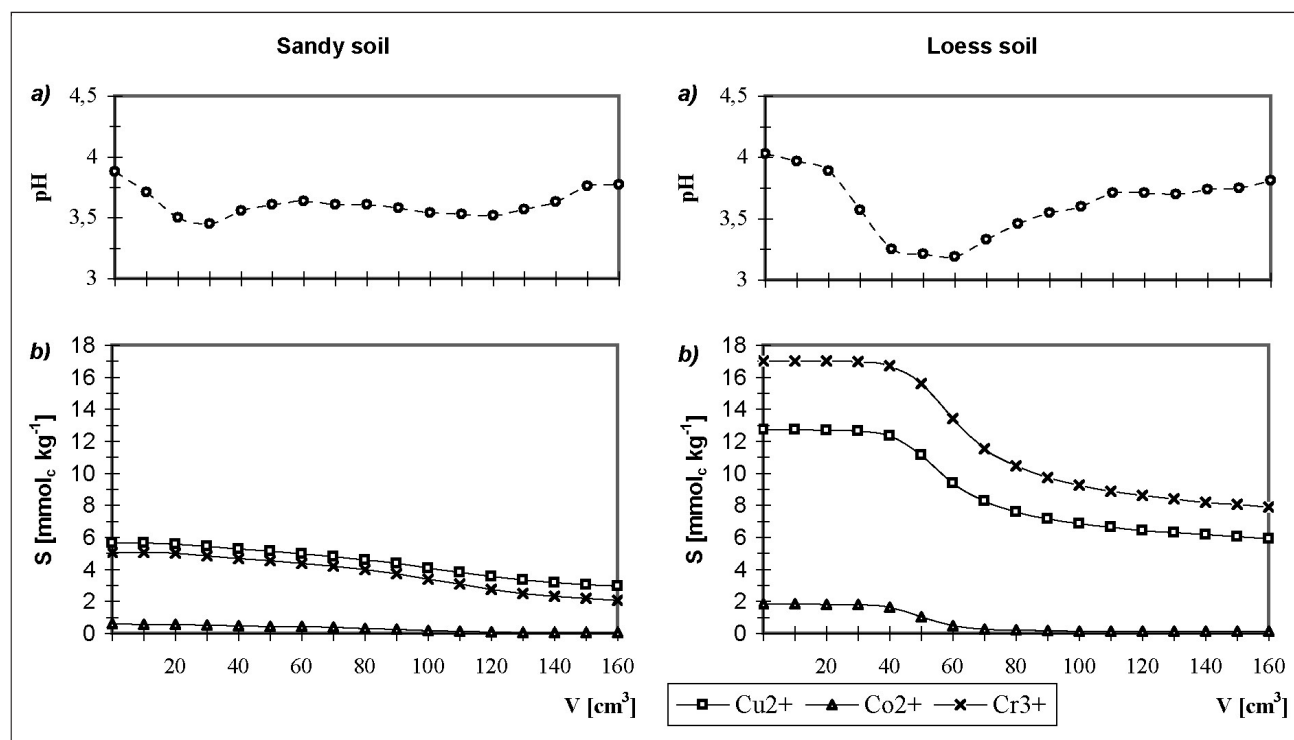


Fig. 1. The course of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> desorption in sandy and loess soils: a) changes of reaction of the effluent from desorption with KCl solution, b) the course of desorption process.

### Results

The three-component solution introduced into the column contained totally 14 mmol<sub>c</sub>  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  cations, much more than the total sorption capacities of soils used for this study. After sorption and elution with water (described in detail in [16]), the largest amount of Cu, slightly less of Cr and the least of Co remained in the soil columns (Figs 1 and 2). In the columns with loess soil the amount of Cr (expressed in mmol<sub>c</sub>) was larger than that of Cu and that of Co was also the smallest.

The course of desorption of heavy metal ions with the KCl solution is presented in Fig. 1. At first the water in the soil pores was displaced by the KCl solution and the changes in metal contents in the effluent from the column were small. Further passing of the solution (more than 20 cm<sup>3</sup> in the sandy soil and 40 cm<sup>3</sup> in the loess soil) was connected with fast desorption of heavy metal ions. The pH values of the effluent decreased rapidly, which resulted from the increase of heavy metal chloride concentration. Next, the amounts of desorbed heavy metal cations decreased and pH increased gradually.

The efficiency of desorption with exchangeable cations was compared based on the experiment using the

soils containing the same amounts of sorbed heavy metal ions. As follows from the variance analysis, the contents of Cu, Co and Cr in individual soil samples were similar and the differences statistically insignificant (Fig. 2).

In both soils desorption of  $\text{Cu}^{2+}$  with  $\text{Ca}^{2+}$  was the largest; desorption with  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  was smaller and not differentiated practically. No significant differences of  $\text{Co}^{2+}$  desorption with the studied exchangeable cations were observed. Desorption of  $\text{Cr}^{3+}$  with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was larger than with  $\text{NH}_4^+$  and  $\text{K}^+$  in both soils. In the loess soil desorption of  $\text{Cr}^{3+}$  with  $\text{NH}_4^+$  was larger than with  $\text{K}^+$  (Fig. 2). At the significance level  $p = 0.1$  (not marked in Fig. 2), desorption with  $\text{Ca}^{2+}$  was significantly smaller than with  $\text{Mg}^{2+}$ .

### Discussion

From the course of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  desorption with  $\text{K}^+$  cations (Fig. 1) it results that the ion-exchange process proceeded quickly. As the last portions of the effluent did not contain heavy metal ions (Fig. 1 shows only the first 16 portions), significant contribution of slow kinetics reaction mechanisms is rather unlikely. Decrease of effluent pH resulted from hydrolysis of desorbed heavy metal ions and possibly to a small extent from  $\text{H}^+$  desorption with

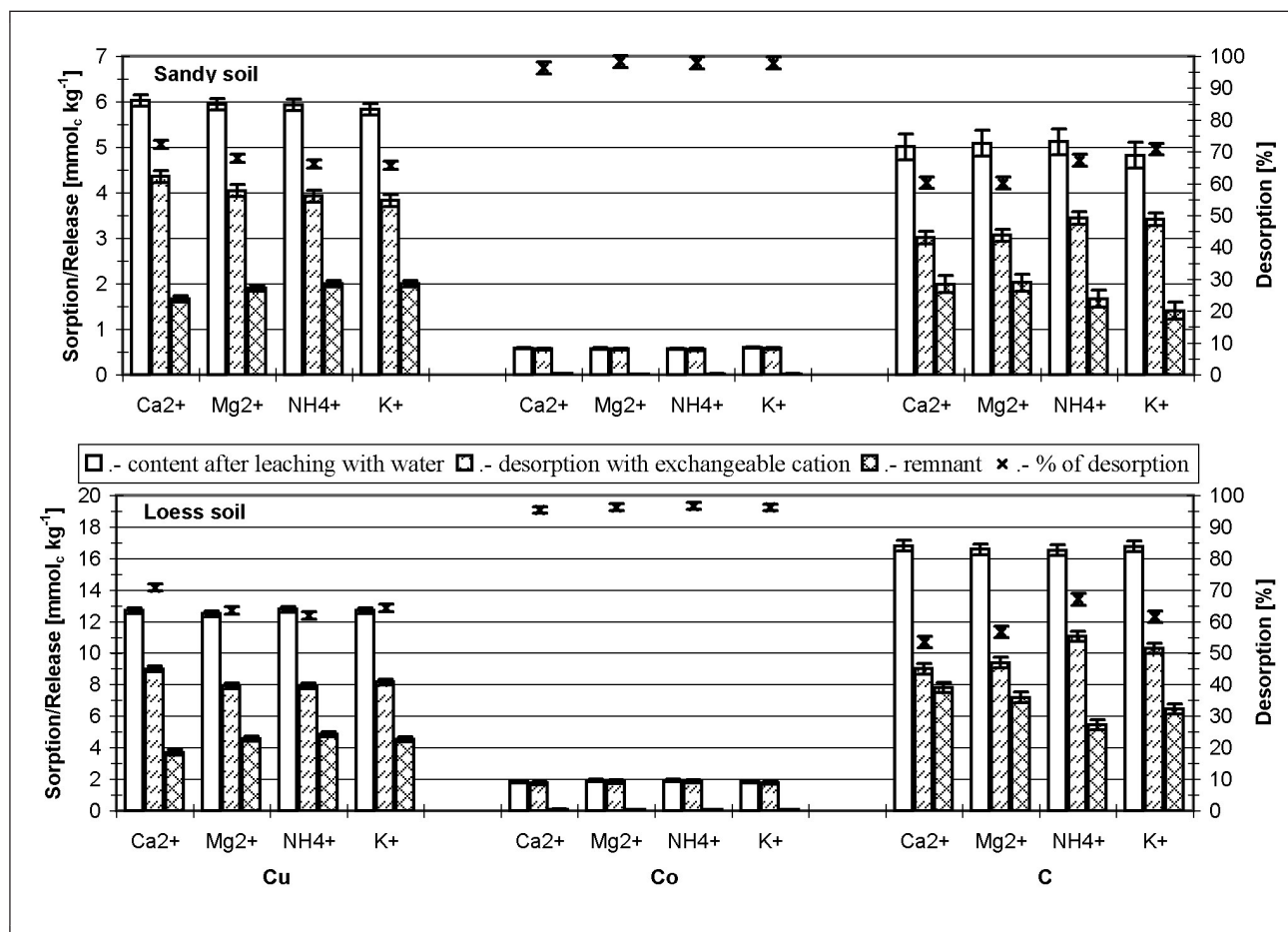


Fig. 2. Contents of Cu, Co and Cr in soil/effluent from the soil columns and percentage of desorption. The presented confidence levels are calculated for  $p = 0.05$ .

K<sup>+</sup> cations (H<sup>+</sup> cations susceptible to desorption were replaced in sorption sites in the first stage of the experiment – sorption of heavy metal ions).

The earlier studies of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> desorption with Ca<sup>2+</sup>, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> cations [6, 14, 15] show that the amounts capable of desorption are almost the same. The results of the experiments presented in this paper allow determination of essential differences. This is of cognitive importance because it allows us to define which properties of metal ions are responsible for their affinity for soils and thereby for the course and the range of sorption-desorption processes.

As follows from the paper by Plus and Bohn [17], it is possible to explain the course of ion exchange processes only for the cations of metals from groups 1 and 2 of the periodic table. In the case of heavy metal cations ionic potential and values of the first hydrolysis constant were also taken into account [2]. The agreement between the obtained results and the theory of hard and soft acids and bases (HSAB) was also observed [2, 17]. In this theory soils are considered to be relatively soft bases forming the most stable complexes with the least hard and borderline acids [19]. The values of *Y* parameters calculated by Misono et al. [10] softness equation for the heavy metal ions and exchangeable cations that are acids of differentiated hardness are as follows:

Mg<sup>2+</sup> (0.87), K<sup>+</sup> (0.92), Ca<sup>2+</sup> (1.62), Cr<sup>3+</sup> (2.70) – hard acids; Cu<sup>2+</sup> (2.89), Co<sup>2+</sup> (2.96) – borderline acids\*.

The obtained results are largely in agreement with theory. Desorption of Cu<sup>2+</sup> with Ca<sup>2+</sup> was more effective than desorption with other cations because it is the least hard exchangeable cation of all. Moreover, Cr<sup>3+</sup> cations included into hard acids were desorbed to a larger extent by K<sup>+</sup> that are of greater hardness than Ca<sup>2+</sup>. In the loess soil at confidence level 90% Cr<sup>3+</sup> desorption with Mg<sup>2+</sup> was, in agreement with theory, larger than that with Ca<sup>2+</sup>. No differences in Co<sup>2+</sup> desorption with exchangeable cations can be explained by small sorption of ions of this heavy metal caused by competition with Cu<sup>2+</sup> and Cr<sup>3+</sup> of greater affinity for soils, which resulted in large discrepancies of the results.

Small differences in efficiency of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> and other heavy metal ions [5] desorption with exchangeable cations are not of significant importance in agricultural practice; it can be assumed that desorption efficiency is the same. From this study and reports in literature it can be assumed that heavy metal ion desorption is more affected by exchangeable cation concentration [12], concentration and kind of anions present in soil solution [20] and even soil structure [4] than by kind of cations.

As follows from the study of Rimmer and Luo [18], the fraction of heavy metal ions susceptible to desorption with the 0.05 mol dm<sup>-3</sup> CaCl<sub>2</sub> solution is easily accessible for plants. Its removal from soils can diminish sig-

nificantly the accessibility of heavy metals for plants. As differences in efficiency of heavy metals desorption with the studied exchangeable cations are small, it is likely that their application in appropriate concentrations for in situ remediation of metal-contaminated subsurface soils can bring good results. It can be presumed because the results of desorption efficiency with these cations do not differ much from desorption efficiency with other eluents [1].

## Conclusions

1. The observed differences in efficiency of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> desorption with Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> or K<sup>+</sup> were small, but partly significant.
2. The theory of hard and soft acids and bases is useful to explain the course of ion exchange process between heavy metal cations and exchangeable cations.
3. Effectiveness of desorption of the studied heavy metal cations with Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> or K<sup>+</sup> seems to be large enough for application of any of them for in situ remediation of metal-contaminated subsurface soils.

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\*Lack of data for NH<sub>4</sub><sup>+</sup>

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