

THE INFLUENCE OF OXYGEN CONDITIONS ON SORPTION OF CATIONS Ni^{2+} , Cu^{2+} , Zn^{2+} AND Cr^{3+} IN MINERAL SOILS

R. Gąsczyk, I. Jackowska

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

Abstract. This study examined the courses of sorption and of leaching with water of the heavy metal cations Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cr^{3+} in three mineral soils (two lessive soils derived from weakly loamy sand and from loess and brown soil derived from heavy loam) under different oxygen conditions. ODR and Eh were measured as indices of soil oxygenation. It was found that soil redox equilibrium conditioned the changes of sorption magnitude of all the heavy metal cations studied.

INTRODUCTION

Basic fertilization often brings the enrichment of soil sorption complex with heavy metals with all the negative consequences accompanying this process for the environment. The sorption-desorption processes occurring there show various directions depending on the chemical affinity of a given ion with the sorption complex. Basing on the above, model studies were undertaken to determine the range of heavy metal cations sorption on soil material originating from three soil kinds. The aim of the elution method applied here was to create a possibly true chemism of the processes occurring during mineral fertilization [2].

MATERIALS AND METHODS

Three mineral soils with differentiated texture and chemical properties were chosen for investigation. Soil samples were taken from the arable layer (0-20 cm). Characteristics of the basic soil properties

were obtained from the Institute of Agro-physic and are given in Tables 1-3.

Typologically the soils represented lessive and brown soil types, whereas according to texture they represented weak loamy sand (locality-Sobieszyn), loess (Gródki), and heavy loam (Sobieszyn).

All the soils showed acid reaction. The mineralogical composition was differentiated. The content of quartz ranged from 90 % in sandy soil to 72 % in loess and 48 % in loam. The clay content was 4 %, 17 %, and 46 %, respectively.

The sorption was carried out in columns in which were placed 100 g of soil material formerly sieved through a 1 mm sieve. The samples were wet with distilled water by the method of capillary rise. Then 140 cm³ of a given heavy metal solution (with a concentration of 0.05 M Me^{2+} or 0.033 M Cr^{3+}) were introduced on the top of the column to obtain a constant sorptive saturation. Afterwards, the columns were washed out with 120 cm³ of distilled water. The effluent was collected as individual 10 cm³ portions and analysed with the atomic absorption spectrophotometric method (at the following wave lengths: Ni - 232.0 nm; Cu - 324.75 nm; Zn - 213.9 nm; and Cr - 357.9 nm) [3].

The dose of lime was calculated on the basis of hydrolytic acidity (H), determined

Table 1. Some properties of the soils studied

Soil	Grain size distribution (%)				C _{tot} (%)	N _{tot} (%)	Humus (%)	pH	Specific surface area m ² /g
	1.0-0.1	0.1-0.02	0.02-0.002	<0.002					
Lessive from weakly loamy sand (Podzoluvisols)	80	14	2	4	0.30	0.04	0.50	6.6	13
Lessive from loess (Orthic Luvisols)	1	63	27	9	1.20	0.10	2.13	6.5	24
Brown soil from heavy loam (Eutric Cambisols)	29	19	34	18	0.99	0.12	1.70	7.3	59

Table 2. Mineralogical composition of the soils studied

Soil	Quartz	Feldspars	Clay minerals
Lessive from weakly loamy sand	90	6	4
Lessive from loess	72	11	17
Brown soil from heavy loam	48	6	46

Table 3. Composition of the clay fraction of the soils studied

Soil	Content of minerals (%)						
	Quartz	Plagio- class	Potassium feldspar	Vermicu- lite, smectite	Kaolinite	Illite	Chlorite
Lessive from loess	12	3	14	23	-	34	14
Brown soil from heavy loam	7	1	-	23	12	57	-

by Kappen's method. The soil samples with neutral reaction were obtained by modifying acid soils with the help of CaCO₃ (30 g/10 kg of sandy soil, 22 g/10 kg of loessial soil, and 40 g/10 kg of loamy soil) and were then dried and sieved. The fraction below 1 mm was gathered.

In the experiment the course of the sorption of Ni²⁺, Cu²⁺, Zn²⁺, and Cr³⁺ cations were determined in limed soils at a pH of 6.6 (sandy soil), 6.5 (loessial soil) and 7.3 (loamy soil) in two variants: in conditions of good oxygenation, obtained by loose

packing of the soil, and in conditions of deoxygenation (oxygen deficiency in the soil), by means of a nitrogen stream [5]. ODR and Eh values were chosen as the soil aeration indices. They were measured according to standard methods [1,6]. The ODR values in both the oxygenation variants were differentiated; the difference was approximately 18 g 10⁻⁸cm⁻²min⁻¹. The Eh values varied approximately 125 mV. These data show that in the first variant good conditions of soil aeration were maintained, whereas in the second, conditions of a distinct oxygen

deficiency, close to critical state for many plants, were recorded [4].

RESULTS

The saturation of soil material with Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cr^{3+} cations and their subsequent leaching out with water resulted in a differentiated sorption magnitude depending on the kind of cation being sorbed and on the degree of sorbent aeration. This effect was most distinctly observed in both the sandy and loamy soil: in deoxygenated conditions the sorption of all four cations decreased (Table 4). In the loessial material, in conditions of oxygen deficiency the sorption of Ni^{2+} , Cu^{2+} , and Zn^{2+} cations increased while that of Cr^{3+} decreased.

Analysing the effect of insufficient soil oxygenation on sorption of a particular heavy metal cation, one can easily observe that the decrease of sorption magnitude was only recorded for Cr^{3+} cations, but such a decrease occurred in all the sorbents. An analysis of the course of saturation of soil material with Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cr^{3+} cations shows that they appear in different volumes of the effluent (Figs 1-4). The presence of Ni and Zn cations in the effluent from the sandy soil (in both aeration states) was already recorded in the first 20 cm^3 effluent. The presence of these cations in the effluents

from the loessial and loamy soils, in both aeration conditions, was observed in the 4-6th portions (40-60 cm^3). The remaining cations, i.e., Cu and Cr, appeared in the 2-6th portions (20-60 cm^3) in the case of sandy soil and in the 2-10th portions (20-100 cm^3) in the case of loessial and loamy material.

Faster 'cut-through' of the column with heavy metals in the case of sandy soil is also reflected by the shape of the sorption curves, where a state close to saturation was reached from the 8th portion of the effluent (80 cm^3), while in the two other soils such a state appeared in the 10-14th portion of the effluent.

Leaching the previously sorbed cations out of the soil column with water showed that the desorption process in the loessial material was different from that in sandy and loamy soil. On the leaching curves, marked 'peaks' are visible where rising part can be distinguished (desorption increase). Such a phenomenon might point to the occurrence of forces connected with exchangeable sorption, forces higher than those responsible for physical sorption. Such a phenomenon was not observed in the sandy soil. The desorption of Ni^{2+} and Zn^{2+} cations from the loamy material was similar to their desorption from the loessial soil. A similar course of desorption was observed for Cr^{3+} and Cu^{2+} cations when leached from the loamy soil in the first condition of the experiment.

Table 4. The degree of sorption of heavy metal cations (%) in soils with good (I) or insufficient (II) oxygenation state

Soil	Oxygen variant	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cr^{3+}
Lessive from weakly loamy sand (Podzoluvisols)	I	24.90	34.61	31.30	35.24
	II	22.26	27.32	12.12	25.49
Lessive from loess (Orthic Luvisols)	I	41.74	51.88	47.84	50.10
	II	45.52	61.30	50.45	41.33
Brown soil from heavy loam (Eutric Cambisols)	I	66.80	78.66	73.44	77.99
	II	62.87	48.55	66.97	69.16

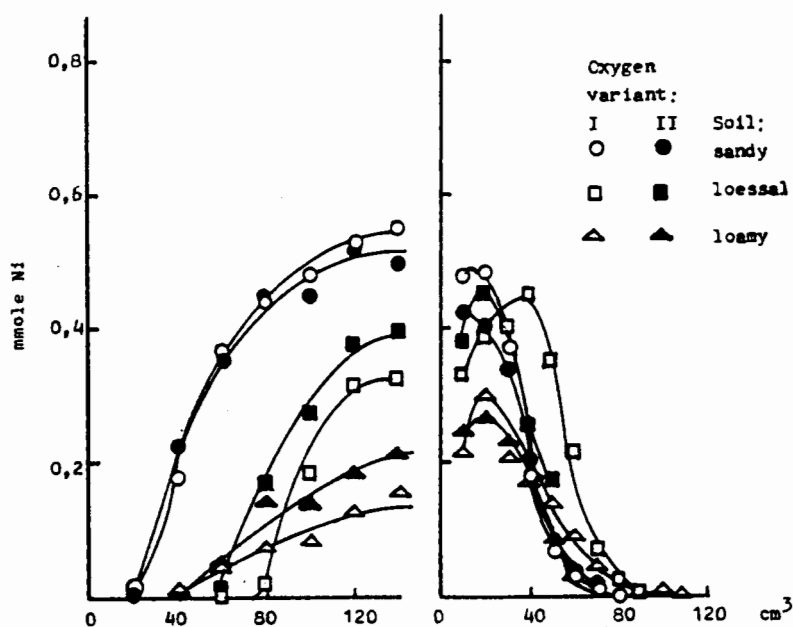


Fig. 1. Course of sorption and leaching out with water of heavy metal cation - Ni^{2+} in soil materials under different oxygen conditions.

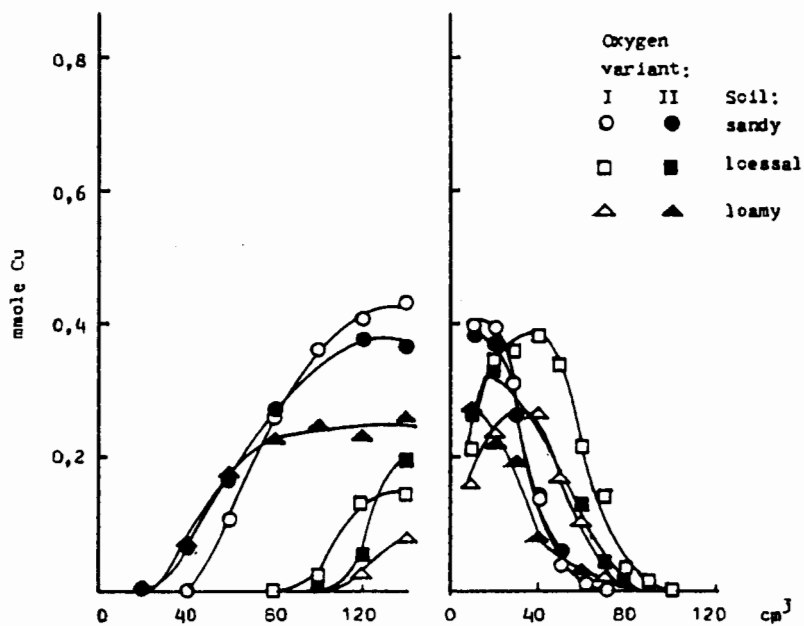


Fig. 2. Course of sorption and leaching out with water of heavy metal cation - Cu^{2+} in soil materials under different oxygen conditions.

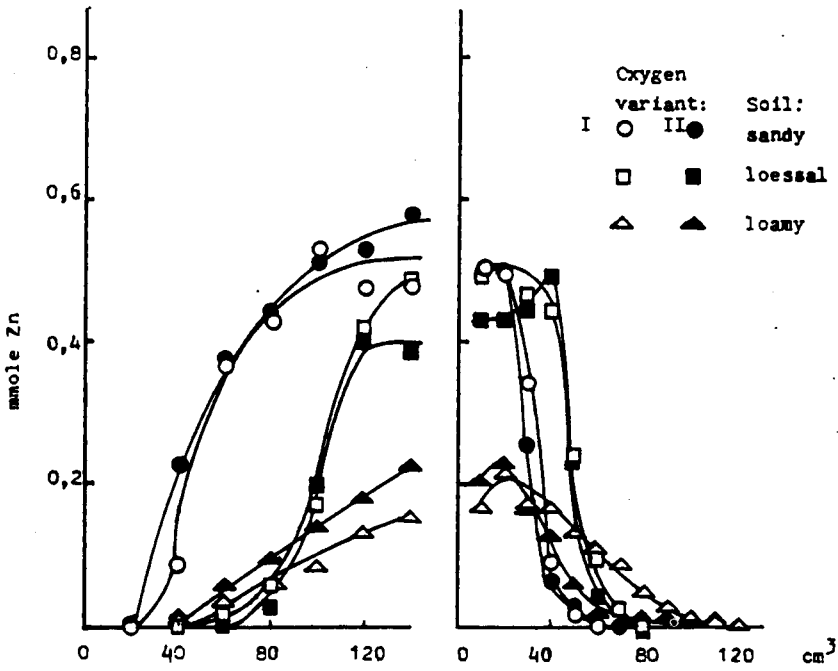


Fig. 3. Course of sorption and leaching out with water of heavy metal cation - Zn^{2+} in soil materials under different oxygen conditions.

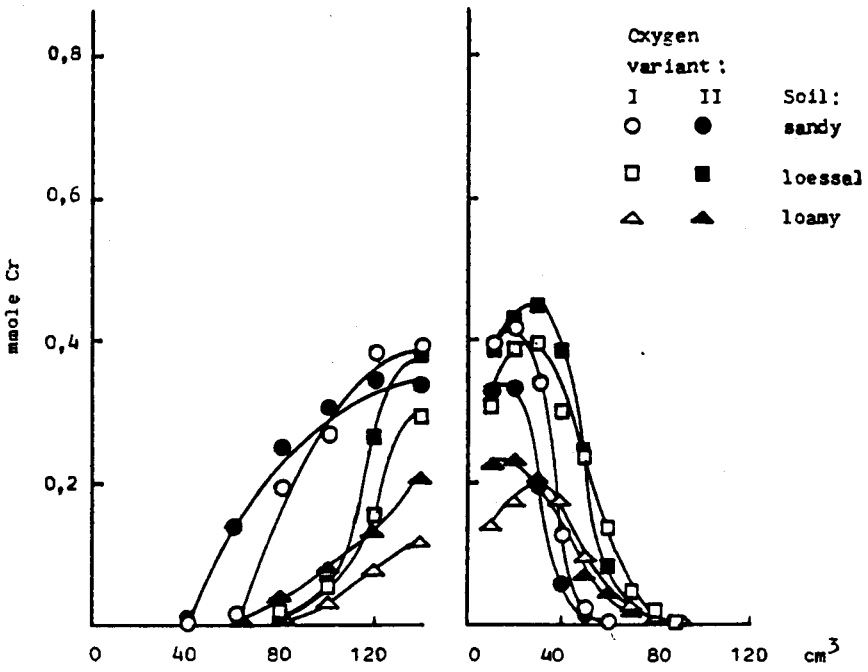


Fig. 4. Course of sorption and leaching out with water of heavy metal cation - Cr^{3+} in soil materials under different oxygen conditions.

CONCLUSIONS

The performance of the course of desorption processes of Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cr^{3+} cations from three kinds of mineral soils allow us to draw the following conclusions:

1. Changes in the soil aeration status from good to insufficient oxygen supply cause decreases in the sorption capacity of the sandy and loamy soil.

2. Insufficient oxygenation of soil material causes a decrease in sorption properties of all three soils investigated only in respect to Cr^{3+} cation.

3. In the loessial soil, the heavy metal cations studied were bound due to exchangeable sorption. This phenomenon can be explained by the high humus content and the formation of insoluble complexes.

REFERENCES

1. Gawlik J.: An attempt to determine the upper critical moisture limit of some hydrogenic soils on the basis of the ODR index under laboratory conditions. Polish J. Soil Sci., 13, 99-101, 1980.
2. Gańczczyk R.: Desorption of heavy metals in soils under the influence of exchangeable cations. Part I.

Podzolic soils formed from loess. Polish J. Soil Sci., 21, 29-34, 1988.

3. Gańczczyk R.: Desorption of heavy metals in soils under the influence of exchangeable cations. Part II. Podzolic soil formed from a weakly loamy sand. Polish J. Soil Sci., 22, 15-20, 1989.
4. Gliński J., et al.: Graniczne wartości ODR i Eh w glebie dla wschodów wybranych roślin uprawnych. Roczn. Glebozn., 35, 1, 2-8, 1984.
5. Jackowska I., Gańczczyk R., Bubińczak M.: Desorption of the Fe^{2+} , Fe^{3+} , and Mn^{2+} in different oxygen and pH conditions in podzolic soil formed from weakly loamy sand. Polish J. Soil Sci., 22, 9-14, 1989.
6. Malicki M., Walczak R.: A gauge of the redox potential and the oxygen diffusion rate in the soil with an automatic regulation of cathode potential. Zesz. Probl. Post. Nauk Roln., 220, 2, 447-452, 1978.

WPLYW WARUNKÓW TLENOWYCH NA SORPCJĘ KATIONÓW Ni^{2+} , Cu^{2+} , Zn^{2+} ORAZ Cr^{3+} W GLEBACH MINERALNYCH

Zbadano przebieg sorpcji i wymywania wodą kationów Ni^{2+} , Cu^{2+} , Zn^{2+} i Cr^{3+} w glebach mineralnych: płowej wytworzonej z piasku słabogliniastego, płowej wytworzonej z lessu i brunatnej wytworzonej z gliny ciężkiej w warunkach zróżnicowanego natlenienia. Jako wskaźniki natlenienia gleby mierzono ODR i Eh. Stwierdzono, że równowaga redox gleb jest czynnikiem warunkującym zmianę wielkości sorpcji badanych kationów metali ciężkich.