

COPPER (II), LEAD (II) AND CHROMIUM (III) DISPLACEMENT FROM SOILS OF VARIOUS REACTION

R. Gąszczyk, I. Jackowska

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

A b s t r a c t. Model studies on the behaviour of Cu^{2+} , Pb^{2+} , and Cr^{3+} cations in soils were carried out in the conditions of forced flow. Soil samples (loess, loam and sand) were saturated with the solutions of CuCl_2 , CrCl_3 and $\text{Pb}(\text{NO}_3)_2$ up to full sorptive saturation and then they were eliminated with exchangeable cations K^+ , NH^+ , Ba^{2+} , Ca^{2+} , and Mg^{2+} . The effluent from soil column was analysed as to copper, lead and chromium content with atomic absorption spectrophotometry method. The soil samples used in the study varied in their reaction.

Comparing the amount of Cu^{2+} , Pb^{2+} , and Cr^{3+} cation desorption from loess, loam and sand, it has been found that the soil liming caused the diminishing of desorption under the influence of all cations eliminating them. This diminishing was affected both by the formation of insoluble compounds in neutral reaction and their more stable binding in the soil sorption complex.

K e y w o r d s: minerals oils, copper, lead, chromium, pH

INTRODUCTION

The rapid increase of pollution in the natural environment due to development of mining, industry, motorization, and the use of mineral fertilizers and pesticides in agriculture, as well as industrial and municipal waste materials, caused the occurrence of the excess of trace elements in soil environment. These elements take part in biochemical processes in soil and because of their geo- and biochemical properties they cause a number of changes which is generally called chemical degradation of soils [6].

Sorption and desorption processes taking place in soils have various directions depend-

ing on affinity with soil sorption complex, which is characteristic for a given ion. In these changes not only heavy metal cations take part but macroelements introduced into soils with fertilizers as well.

In agricultural practice basic fertilization is often connected, among others, with the introduction of heavy metals into soil sorption complex as well as with their desorption, with its all negative effects on the natural environment [8]. This caused the attempt to determine the desorption range of the following cations: copper (II), lead (II), and chromium (III), through model studies of three soil samples of different origin. Elution method used in the experiment aimed at exact showing the chemical processes occurring during agrochemical treatment.

MATERIALS AND METHODS

Fresh soil samples were taken from arable layer (0-20 cm) of three mineral soils differing extremely in granulometric composition and their chemical properties were used in the study. The characteristics of the basic properties of soils were received from the Institute of Agrophysics of the Polish Academy of Sciences in Lublin [2]. The soil material constituted formations characterized according to pedological criteria as weakly loamy sand, loess and heavy loam.

Sandy soil was characterized by the low content of organic carbon (0.30 %) and low

specific surface area (13 m²/g). Loess material contained 36% fine fraction and 1.20 % organic carbon. Its specific surface area amounted to 24 m²/g. In the loamy soil material fine fraction amounted to 52%, organic carbon 0.98 % and the specific surface area was 59 m²/g.

Mineralogical composition of the soil materials under study differed to a great extent: quartz content reached 90 % (sand fraction), through 72 % in loess down to 48 % in loam. The content of clay minerals in soils was 4, 17, and 46 %, respectively. The composition of clay mineral fraction was less differentiated.

The soil reaction of all the materials was acid which resulted from the uniformity of soil-forming processes which these soil formations underwent. The sorption of heavy metal cations, their elution with water and exchangeable cations was carried out in a soil column placed in a cylinder made of organic glass [3].

The measurement of heavy metal content was carried out with the atomic absorption spectrophotometry method using adequate lamps with hollow cathodes (at the wavelength: Cu - 324.75, Pb - 217.0, Cr - 357.9 nm).

The study of sorption processes was led in columns with soil material through percolating, in turn, the solutions of heavy metals and exchangeable cations. The basic process of Cu²⁺, Pb²⁺, and Cr³⁺ cation desorption was done with the use of water solutions of KCl and NH₄Cl (0.1 mol/dm³), MgCl₂, CaCl₂, and BaCl₂ (0.05 mol/dm³).

Calcium carbonate dosage necessary to acidify the soil material was calculated on the basis of hydrolytic acidity H, determined by the Kappen method. Neutral soil samples were obtained by flooding the soil samples of acid reaction with 0.3% solution of CaCO₃. After four months the samples were dried and sieved, collecting the fraction below 1 mm. The measurements were carried out in the temperature of 293 °K ± 2°.

RESULTS

Soil samples used in the study were of acid and neutral reaction obtained through flooding with CaCO₃ (30 g for 10 kg of sand, 22 g for

10 kg of loess, and 40 g for 10 kg of loam). The results presented in Fig. 1 show that the obtained amounts of the desorption of Cu²⁺, Pb²⁺, and Cr³⁺ cations with the exchangeable cations differ depending on the kind of soil and its reaction. Particular exchangeable cations desorbed heavy metal cations in the following way.

In the loamy soil material of pH=6.8:

K⁺ - 29% Pb²⁺, 41% Cr³⁺ and 61% Cu²⁺,
NH₄⁺ - 26% Pb²⁺, 36% Cr³⁺ and 57% Cu²⁺,
Ba²⁺ - 29% Pb²⁺, 52% Cr³⁺ and 66% Cu²⁺,
Ca²⁺ - 26% Pb²⁺, 39% Cr³⁺ and 61% Cu²⁺,
Mg²⁺ - 27% Pb²⁺, 35% Cr³⁺ and 60% Cu²⁺.

In the loamy samples of pH=7.3:

K⁺ - 0.5% Pb²⁺, 2.7% Cr³⁺ and 12.2% Cu²⁺,
NH₄⁺ - 0.1% Pb²⁺, 2.3% Cr³⁺ and 6.8% Cu²⁺,
Ba²⁺ - 0.6% Pb²⁺, 3.8% Cr³⁺ and 14.9% Cu²⁺,
Ca²⁺ - 3.0% Pb²⁺, 3.9% Cr³⁺ and 9.2% Cu²⁺,
Mg²⁺ - 2.1% Pb²⁺, 3.0% Cr³⁺ and 7.9% Cu²⁺.

The most strongly bounded are Pb²⁺ cations for all the desorbing cations, while the most weakly bounded are Cu²⁺ cations also for all desorbing cations.

In the loessial samples of pH=4.8:

K⁺ - 18% Cr³⁺, 20% Pb²⁺ and 24% Cu²⁺,
NH₄⁺ - 46% Pb²⁺, 48% Cu²⁺ and 58% Cr³⁺,
Ba²⁺ - 43% Cr³⁺, 63% Cu²⁺ and 71% Pb²⁺,
Ca²⁺ - 47% Pb²⁺, 48% Cr³⁺ and 52% Cu²⁺,
Mg²⁺ - 40% Cr³⁺, 44% Pb²⁺ and 77% Cu²⁺.

In the loessial samples of pH=6.5:

K⁺ - 18% Cr³⁺, 20% Pb²⁺ and 24% Cu²⁺,
NH₄⁺ - 14% Cr³⁺, 17% Pb²⁺ and 25% Cu²⁺,
Ba²⁺ - 14% Cr³⁺, 30% Pb²⁺ and 34% Cu²⁺,
Ca²⁺ - 14% Cr³⁺, 17% Pb²⁺ and 31% Cu²⁺,
Mg²⁺ - 13% Cr³⁺, 18% Pb²⁺ and 34% Cu²⁺.

These results show that the cations Cr³⁺ are most strongly bounded in loess samples (except the samples of pH=4.8 for NH₄⁺ and Ca²⁺ cations), and the most weakly bounded are Cu²⁺ cations (except the soil of pH=4.8 for Ba²⁺ and NH₄⁺ cations).

In the sandy soil samples of pH=5.5:

K⁺ - 36% Cu²⁺, 44% Pb²⁺ and 99% Cr³⁺,
NH₄⁺ - 30% Pb²⁺, 40% Cu²⁺ and 63% Cr³⁺,
Ba²⁺ - 46% Pb²⁺, 49% Cr³⁺ and 66% Cu²⁺,
Ca²⁺ - 46% Cu²⁺, 67% Pb²⁺ and 85% Cr³⁺,
Mg²⁺ - 32% Pb²⁺, 35% Cu²⁺ and 55% Cr³⁺.

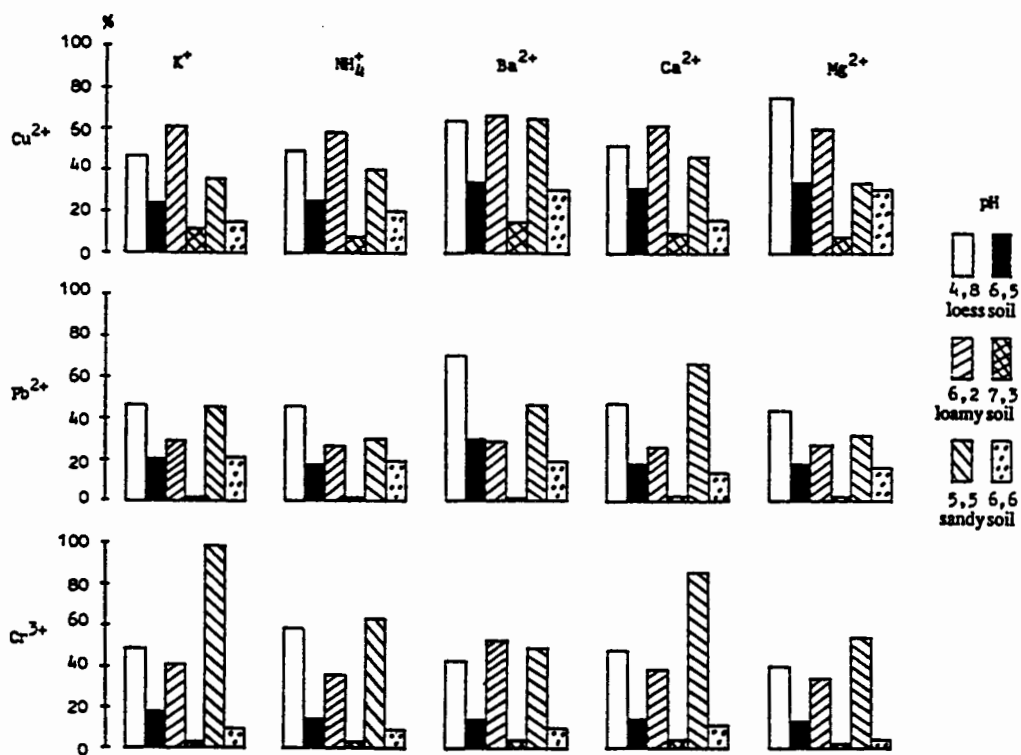


Fig. 1. Desorption degrees of heavy metal cations in soil samples.

In the sandy material of pH=6.6:
 K^+ - 9% Cr^{3+} , 16% Cu^{2+} and 20% Pb^{2+} ,
 NH_4^+ - 8% Cr^{3+} , 19% Pb^{2+} and 20% Cu^{2+} ,
 Ba^{2+} - 10% Cr^{3+} , 19% Pb^{2+} and 31% Cu^{2+} ,
 Ca^{2+} - 10% Cr^{3+} , 13% Pb^{2+} and 16% Cu^{2+} ,
 Mg^{2+} - 5% Cr^{3+} , 16% Pb^{2+} and 31% Cu^{2+} .

The most strongly bounded are Cu^{2+} and Pb^{2+} cations in soil with pH=5.5 and Cr^{3+} cations in sandy soil with pH=6.6; while the most weakly are Cr^{3+} cations in soil with pH=5.5 (except desorbing cation Ba^{2+}) and Cu^{2+} in soil of pH=6.6 (except K^+ desorbing cation).

DISCUSSION

In all kinds of soil samples the change of reaction from the acid to neutral one was accompanied by the decrease in desorption of the heavy metal cations studied under the influence of all the exchangeable cations used for their elimination.

In loess soil this decrease amounted, in case of Cu^{2+} cations from 1.7 to 2.3, for Pb^{2+} from 2.4 to 2.8, and for Cr^{3+} from 2.7 to 4.2. In loamy soil the decrease in the amount of desorption ranged from 4.5 to 8.4 for Cu^{2+} cations, from 8.8 to 187 for Pb^{2+} and from 10.0 to 15.5 for Cr^{3+} cations. In sandy soil the diminishing of desorption amount was also noted and it amounted for Cu^{2+} cations from 1.1 to 2.9, for Pb^{2+} - from 1.6 to 5.1, and for Cr^{3+} cations - from 5.1 to 11.9.

The comparison of desorption degrees for heavy metal cations allows us to state that particular desorbing cations possessed, in the conditions of the experiment, differentiated ability of exchanging the given desorbed cation in the same soil material but with different pH value [1].

In sandy soil material of pH=5.5, saturated with Pb^{2+} cations, they were eliminated, to the greatest extent, from the sorption complex by Ca^{2+} cations. However, already at pH=6.6 the

cations Ca^{2+} had the lowest eliminating ability for Pb^{2+} . A similar phenomenon was also noted in case of the remaining exchangeable cations in the same soil material as well as for Cu^{2+} cations desorbed by Mg^{2+} cations. In loamy material the change of reaction did not influence so much the input energy of exchangeable cations. The exception is an unchanged series of inputs for soil material saturated with Cu^{2+} cations.

The change of soil reaction also influenced the desorption character of cations which compose mineral fertilizers. The change of the reaction from acid to neutral immobilized the cations of Cu^{2+} , Pb^{2+} , and Cr^{3+} . In case of Pb^{2+} and Cr^{3+} cations we can talk about hardly soluble hydroxide precipitation in the condition of neutral reaction. They had a decisive influence on the desorption amount of these cations.

Such an interpretation is given, among others, by Harter [4,5] who prescribes the change of lead compounds solubility to the reaction of the environment. At $\text{pH}=5$ and lower, lead only occurs in the form of Pb^{2+} , at $\text{pH}=6$ it has already two forms: 50% as Pb^{2+} and 50% as PbOH^+ , at $\text{pH}=7$ the occurrence of 30% of Pb^{2+} and 70% PbOH^+ has been noted, and in the range of $\text{pH}=8-9$ only one form has been found, that is PbOH^+ .

CONCLUSIONS

1. The change of soil material reaction from acid to neutral caused the diminishing of sorption degree of Cu^{2+} , Pb^{2+} , and Cr^{3+} cations under the influence of cations eliminating them (K^+ , NH_4^+ , Ba^{2+} , Ca^{2+} , and Mg^{2+}). It occurred as a result of forming hardly soluble forms of the metals mentioned in the conditions of neutral reaction.

2. The introduction of macroelements (Ca^{2+} , K^+ , Mg^{2+} , and NH_4^+) to soil material containing heavy metals showed that fertilization with macroelements directly affects the desorption of heavy metals from the sorption complex.

3. The amount of desorption of Cu^{2+} , Pb^{2+} , and Cr^{3+} cations from the soil sorption complex depends on one hand on the structure of the complex itself and the soil reaction, as well as

on the chemical properties of elements both the desorbing and the desorbed on the other.

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WYPIERANIE MIEDZI (II), OŁOWIU (II) I CHROMU (III) Z GLEB O ZRÓŻNICOWANYM ODCZYNNIE

Przeprowadzono badania modelowe nad zachowaniem się kationów Cu^{2+} , Pb^{2+} i Cr^{3+} w glebach w warunkach wymuszonego przepływu. Próbkę glebową (less, glina i piasek) nasycano roztworami CuCl_2 , CrCl_3 i $\text{Pb}(\text{NO}_3)_2$ do pełnego wysycenia sorpcyjnego i następnie rugowano je przy pomocy kationów wymiennych: K^+ , NH_4^+ , Ba^{2+} , Ca^{2+} i Mg^{2+} . Wyciek z kolumny glebowej analizowano pod kątem zawartości miedzi, ołowiu i chromu metodą atomowej spektrofotometrii absorpcyjnej. Użyty materiał glebowy był zróżnicowany pod względem odczynu.

Porównując wielkość desorpcji kationów Cu^{2+} , Pb^{2+} i Cr^{3+} z lessu, gliny i piasku stwierdzono, że zwapnowanie gleb spowodowało zmniejszenie desorpcji pod wpływem wszystkich rugujących je kationów. Zmniejszenie desorpcji spowodowane zostało zarówno wytworzeniem się w warunkach odczynu obojętnego nierozpuszczalnych związków, jak też trwalszym ich związaniem w kompleksie sorpcyjnym gleb.

Słowa kluczowe: gleby mineralne, miedź, ołów, chrom, pH.