
The influence of some factors on the formation of mobile copper in soil

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The aim of the research was to investigate the influence of some factors on the formation of copper mobile form in simulated aqua and soil systems.

A physico-chemical analysis of the simulated multicomponent system $\text{Cu}(\text{NO}_3)_2\text{-MeH}_2\text{PO}_4\text{-H}_2\text{O}$ (Me – K^+ , NH_4^+ , Ca^{2+}) was carried out. The results showed that K^+ and Ca^{2+} cations influenced the formation of phosphates and carbonates of copper: the presence of K^+ ions decreased, while of Ca^{2+} increased the concentration of copper ions. The endothermity of the interaction increased in the following order: $\text{K}^+ < \text{NH}_4^+ < \text{Ca}^{2+}$.

The content of mobile copper decreased with increasing the amount of humus in the simulated soil-humus system. Presence of Ca^{2+} ions in the simulated soil system decreased the mobile Cu^{2+} concentration when there was 2.28% of humus, but it had little influence on a soil system with a higher content of humus.

Also, a dependence between copper ion concentration and soil pH was established in three different soil samples. The content of mobile copper was bigger in sandy soil than in clay. The level of mobile copper in the investigated soils was much higher at pH 4 than at pH 5.5. The increase of pH value above 5.5 had a very small impact on the concentration of mobile copper.

Key words: copper, mobile form, bioavailability, simulated multicomponent systems, humus, pH, phosphates, carbonates

INTRODUCTION

Copper is a microelement of vital importance, however, it is potentially toxic when bioavailable at high concentrations [6]. Copper is found in the structure of most enzymes: superoxide dismutase, cytochrome oxidase, ascorbate oxidase, diamine oxidase, phenol oxidases, etc. It participates in chlorophyll formation, in the process of photosynthesis, as well as in nitrogen metabolism and in the formation of amino acids and proteins. There exist some forms of proteins in which copper is the metal component. Moreover, copper activates lipid formation. The critical deficiency level of copper in vegetative plant parts is generally in the range of 1–5 $\mu\text{g/g}$ dry weight, depending on plant species, plant organ, developmental stage, and nitrogen supply [12]. Copper deficiency is often observed in plants growing on soils either inherently low in total copper or rich in organic matter, where copper is complexed to organic substances [1]. Cu deficiency lowers the quality of

agricultural produce, resulting in colourless carrots, porous onion's structure, lettuce withering, decreased amount of peptides and amino acids in wheat and rye, damaged pods of peas [5]. The critical toxicity level of copper in the leaves is above 20–30 $\mu\text{g/g}$ dry weight [12]. Copper toxicity may induce iron deficiency, depending on the source of iron supply [13]. Chlorosis can also be a direct result of the effect of high copper concentrations on lipid peroxidation and thus of the destruction of membranes [9]. In nontolerant plants, inhibition of root elongation and damage of the plasma membrane of root cells, as reflected by enhanced potassium efflux, are immediate responses to a high copper supply [4]. Consuming such plants for meal and fodder increases threat for animals and man.

The copper amounts in Lithuanian soils are rather diverse and range from 0.4 to 70.8 mg/kg [7]. For various reasons there is increasing concern about copper toxicity in agriculture. These include the high copper contents in soils caused by the long-term use

of copper-containing fungicides (e.g., in orchards and vineyards), industrial and urban activities (air pollution, city waste, and sewage sludge), and the application of pig and poultry slurries rich in copper [8]. Copper amount in plants depends on its quantity in soil. However, only a third part, i.e. the mobile form, is available for plants. Copper mobility and plant availability depend on soil pH, soil texture, organic matter, cations and anions. By examining the above-mentioned factors in such multicomponent systems as soil, it is purposive to investigate copper ion interaction with various anions in simulated solutions and soil samples.

The study aims were as follows:

1. To investigate the interaction of copper ions with dihydrophosphate and hydrocarbonate anions depending on K^+ , NH_4^+ , and Ca^{2+} cations in multicomponent system Cu^{2+} -dihydrogenphosphate or hydrogencarbonate-water in a full range of concentrations.

2. To determine changes in the enthalpy of copper ions' interaction with potassium dihydrophosphate, ammonium dihydrophosphate or calcium dihydrophosphate.

3. To investigate the copper mobile form formation depending on organic matter and Ca^{2+} ions in simulated soil samples.

4. To investigate the copper mobile form formation depending on pH and soil texture in natural soil samples.

MATERIALS AND METHODS

The interaction of copper ions with some dihydrophosphates and hydrocarbonates was investigated in simulated aqueous solutions of different molar proportions and total molal concentration $\Sigma_m = 1$ mol/kg aqua. After an equilibrium between the solution and the formed insoluble phase was settled, the pH of the system was determined using a potentiometric method. The insoluble phase was filtered, weighed and dissolved in 0.25 M solution of sulphate acid. The concentration of copper ions in equilibrium solution and in solution of deposit was determined by the trilonometric method. The concentration of phosphate ions was determined photometrically with molybdenum vanadate.

Termochemical investigations were carried out with an adiabatic calorimeter, sensing of temperature – platinum wire, sensitiveness of temperature – $9 \cdot 10^{-5}$ K, calorimetric – $3 \cdot 10^{-2}$ J. Molar relation between the study salts was 1:1.

Solution of ammonium or potassium dihydrophosphate or salt of calcium dihydrophosphate was settled in an ampoule. Solution of copper salt was in a calorimetric vessel.

Model soil samples were prepared from air-dry sandy loam with a low content of humus and peat with a high content of humus. The content of humus, total potassium, total and mobile phosphorus, mobile calcium and pH were determined in soil and peat. By mixing soil and peat in different ratios four model examples of soil with different contents of humus (2.3–8.0%) were obtained. The chemical composition of these simulated soil samples is shown in Table 1. Each sample has been enriched with calcium ions (3 or 6%) by addition of calcium nitrate solution. Soil samples were exposed to copper nitrate solutions of different concentrations (20, 50, 100, 200 and 300 mg Cu^{2+} /kg soil). After an equilibrium was reached, the concentration of mobile copper was determined with an atomic absorption spectrophotometer in the ammonium acetate solution (pH 4.8) extracts of air-dry soil samples.

The influence of pH on the concentration of extractable copper was determined using three different soil types: two samples of alluvial sand with a different content of humus and clay.

Soil samples were air-dried, ground and sieved through a 2 mm sieve. The characteristics of these soil samples are shown in Table 2.

Soil samples were exposed to solutions of different pH (4, 5.5, 7 and 8.5). These solutions were prepared from 0.03 M $NaNO_3$ solution. The pH value was modified by adding 0.01 M HCl or 0.01 M NaOH solutions. After equilibrium had been reached,

Table 1. Chemical composition of simulated soil samples

| | I | II | III | IV |
|------------------------|-------|-------|-------|-------|
| Content of humus, % | 2.28 | 4.06 | 6.0 | 8.0 |
| Total K amount, g/kg | 1.025 | 1.014 | 0.998 | 0.989 |
| Mobile Ca amount, g/kg | 0.2 | 0.2 | 0.2 | 0.2 |
| Total P amount, mg % | 190 | 194.3 | 199.1 | 203.1 |
| Mobile P amount, mg% | 7.4 | 7.3 | 7.2 | 7.1 |
| pH_{KCl} | 6.6 | 6.0 | 5.6 | 5.3 |

Table 2. Some properties of soil samples, 'total' copper content and mobile copper content (% from 'total' amount) depending on pH in three various soil samples

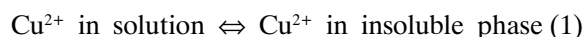
| Soil properties | Sand (I) | Sand (II) | Clay |
|-----------------|------------------------|-----------|------|
| PH | 5.71 | 6.18 | 6.0 |
| C, % | 1.7 | 2.01 | 2.14 |
| 'Total' Cu | 3.4 | 5.1 | 9.5 |
| | Mobile copper contents | | |
| pH 4 | 11.23 | 7.42 | 2.16 |
| pH 5.5 | 8.98 | 4.95 | 1.08 |
| pH 7 | 8.24 | 4.45 | 1.08 |
| pH 8.5 | 8.24 | 2.97 | 1.89 |

ched (and soil samples air-dried) the soil samples were extracted with ammonium acetate solution (pH 4.8) for 24 h, then filtered. The amount of mobile copper was determined in each filtrate with an atomic absorption spectrophotometer.

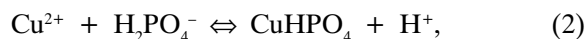
RESULTS AND DISCUSSION

Data on pH and equilibrium concentration of copper ions in solutions in simulated three-component $\text{Cu}(\text{NO}_3)_2\text{-MeH}_2\text{PO}_4\text{-H}_2\text{O}$ ($\text{Me}=\text{K}^+, \text{NH}_4^+, \text{Ca}^{2+}$) systems in all the range of molar relations of salts are given in Figs. 1 and 2.

In all cases at the equilibrium



in the systems with dihydrophosphates the pH value decreases. This can be explained by shifts of the equilibrium given below to the right:



These shifts corroborate the data of X-ray analysis. In the system $\text{Cu}(\text{NO}_3)_2\text{-KH}_2\text{PO}_4\text{-H}_2\text{O}$ the insoluble phase was formed from the following com-

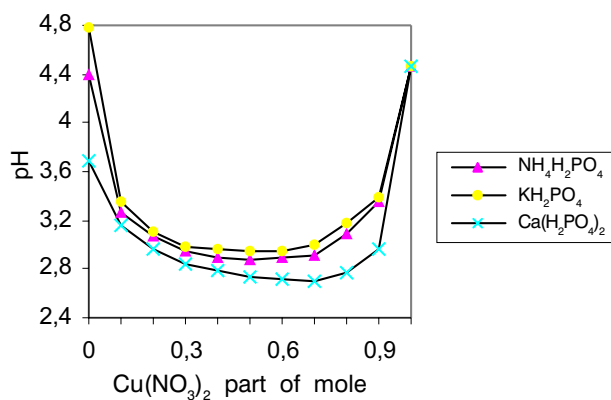


Fig. 1. Change of pH in isomolal series of systems $\text{Cu}(\text{NO}_3)_2\text{-MeH}_2\text{PO}_4\text{-H}_2\text{O}$

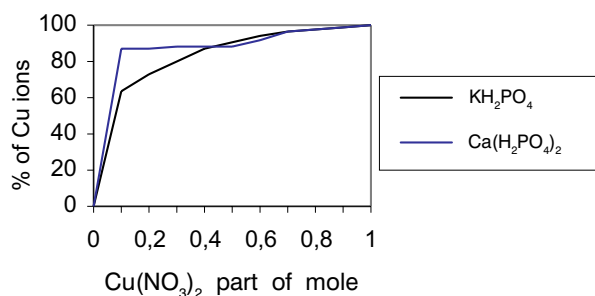


Fig. 2. Percentage of mass of copper in equilibrium solution

pounds: $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (ratio $\text{Cu}^{2+}:\text{H}_2\text{PO}_4^- = 2:3$) and $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ (ratio 4:1).

Changes of pH and equilibrium (1) depend on the nature of other cations present in the system ($\text{K}^+, \text{NH}_4^+$ or Ca^{2+}). Data in Table 3 and Figs. 1 and 2 show that the mentioned cations decrease the pH of the system and increase the concentration of Cu^{2+} ions in the equilibrium solution in the following order: $\text{K}^+ < \text{NH}_4^+ < \text{Ca}^{2+}$. Calcium ions had the greatest effect on the shift of equilibrium (1) to the left.

Table 3. Interaction enthalpies between copper salts and ammonium, potassium or calcium dihydrogenphosphates at a temperature of 25 °C

| Copper salt | Phosphate | Enthalpy of interaction ΔH , kJ/mol |
|----------------------------|--------------------------------------|---------------------------------------------|
| $\text{Cu}(\text{NO}_3)_2$ | $\text{NH}_4\text{H}_2\text{PO}_4$ | 4.30 |
| | KH_2PO_4 | 4.11 |
| | $\text{Ca}(\text{H}_2\text{PO}_4)_2$ | 5.27 |
| CuSO_4 | KH_2PO_4 | 3.35 |

In the systems with hydrocarbonates at a low concentration of copper ions a slight increase of pH was determined. The greatest part of copper ions passed to insoluble phase, and the concentration of copper ions in equilibrium solution was very low (Fig. 3).

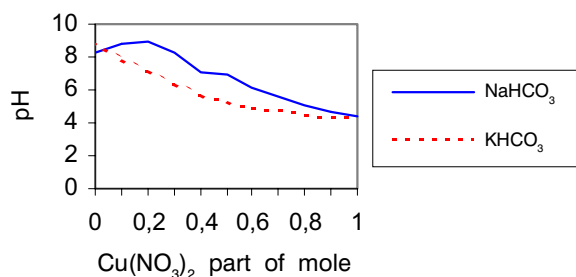
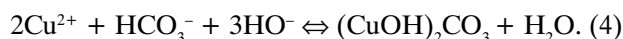


Fig. 3. Change of pH in the system $\text{Cu}(\text{NO}_3)_2\text{-MeHCO}_3\text{-H}_2\text{O}$

The obtained data allow to presume the formation of the following equilibrium with a clear shift to the right:



The influence of sodium and potassium ions on these systems differed negligibly.

The influence of the cations on the interaction between copper ions and dihydrogenphosphates was determined by thermochemical investigations (Table 4).

| Soil sample | Added Ca ²⁺ % | Added Cu ²⁺ , mg/kg | | | | |
|-------------|--------------------------|--------------------------------|------|------|------|------|
| | | 20 | 50 | 100 | 200 | 300 |
| I | 0 | 12.5 | 30.0 | 36.5 | 34.5 | 36.6 |
| | 3 | 7.5 | 16.0 | 17.0 | 19.8 | 27.3 |
| | 6 | 7.5 | 20.0 | 24.0 | 16.3 | 26.0 |
| II | 0 | 10.5 | 8.0 | 15.0 | 23.5 | 31.7 |
| | 3 | 5.0 | 6.0 | 10.0 | 21.2 | 20.0 |
| | 6 | 5.0 | 3.0 | 20.0 | 18.8 | 20.5 |
| III | 0 | 5.0 | 8.0 | 7.5 | 14.2 | 20.0 |
| | 3 | 2.5 | 4.0 | 8.5 | 11.8 | 13.0 |
| | 6 | 5.0 | 2.0 | 13.5 | 13.3 | 23.0 |
| IV | 0 | 3.8 | 4.0 | 5.5 | 11.8 | 11.8 |
| | 3 | 0 | 4.0 | 4.0 | 3.8 | 11.3 |
| | 6 | 7.5 | 3.5 | 3.5 | 16.0 | 18.3 |

The obtained data show that the enthalpies of interaction are endothermic values. The endothermicity of interaction increased in the following order: $K^+ < NH_4^+ < Ca^{2+}$. The determination of enthalpy of interaction in the system $CuSO_4 - KH_2PO_4 - H_2O$ shows that the nature of the anion has an influence on the interaction, too. The enthalpy of interaction in the system with copper nitrate was more endothermic than in the system with copper sulphate. The enthalpies of interaction reflect different components of this effect: the endothermic effect of ion dehydration and the exothermic effect of ions interaction. Perhaps processes of dehydration predominated in the system with calcium dihydrophosphate. A correlation with the hydration energy of these ions, which is equal: $Ca^{2+} -1516.02$ kJ/mol, $K^+ -338.9$ kJ/mol and $NH_4^+ -326.4$ kJ/mol can be found.

This part of investigation shows some peculiarities of the interaction among the study ions in the three-component systems. The obtained data allow to continue investigation of a natural and such a complex system as soil.

The content of mobile copper in mass percent depending on the concentration of copper and calcium ions in soil samples is presented in Table 4.

The content of mobile copper decreased with increasing the amount of humus in the soil. This tendency was stronger at low concentrations of copper ions. The increase of humus content has a weaker influence on the formation of insoluble copper compounds at higher concentrations of copper ions in soil. The influence of calcium ions on the concentration of mobile copper differs in soil samples with a low (sample I) and with a high content of humus (sample IV) (Fig. 4).

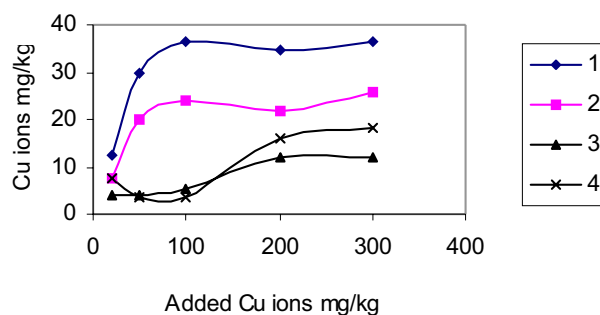


Fig. 4. Influence of humus and Ca ion content on the concentration of mobile copper in soil:

- 1 – humus 2.28%, Ca ions not added;
- 2 – humus 2.28%, Ca ions added 6%;
- 3 – humus 8%, Ca ions not added;
- 4 – humus 8%, Ca ions added 6%

As has been determined in simulated solutions, only in soil samples with a high humus the concentration of mobile copper increases with increasing the concentration of calcium ions. In soil samples with a low content of humus, the concentration of mobile copper was higher in the sample without calcium ions.

The concentration of mobile phosphorus was low in all investigated soil samples (Table 1). As the concentration of humus in soil samples had been increased by addition of peat (pH 3.9), the acidity of model soil samples decreased from pH 6.7 to 5.5. However, this increase of acidity had no effect on the experimental data.

The influence of pH on the concentration of extractable copper was determined using three different soil types (with a different granulometric structure and humus content). The properties of investigated soil samples are presented in Table 2.

The highest concentration of total copper was determined in clay-rich soil. The highest mass part of mobile copper from 'total' concentration in soil was determined in sandy (I) soil and the lowest in clay-rich soil, as copper ions are specifically adsorbed by clay minerals [10]. Adsorption of copper ions depends strongly on the value of soil pH. At $pH < 5.5$ adsorption of copper ions decreases and the concentration of mobile copper increases [5]. Our data listed in Table 2 confirm this hypothesis. The content of mobile copper in the soils studied was much higher at pH 4. An increase of pH value above 5.5 had a very weak impact on the concentration of mobile copper in all soil samples. The content of organic matter in soil is another very important factor. Analysis of 24 different soil fractions in Great Britain showed that about 30% of copper ions were linked with organic matter [11]. The results of our investigation showed that the amount of mobile cop-

per was lower in sandy soil with a higher content of humus (II), too.

CONCLUSIONS

To study the factors determining the formation of mobile copper as well as other heavy metals in such a complex multicomponent system as soil, consequent investigation of multicomponent aqueous systems and model soil samples is purposeful.

The potentiometric, analytic and thermochemical investigations of three-component systems copper salt–dihydrogenphosphate–water showed that an increase of copper and hydrogen ion concentration in equilibrium solution depended on the nature of cations in the following order: $K^+ < NH_4^+ < Ca^{2+}$. These cations formed the same line according to the increase of interaction enthalpies between copper and dihydrogenphosphate ions in a three-component system. A very low copper ion concentration was determined in ternary systems with hydrocarbonates.

In model soil samples with a high content of humus, the dependence of mobile copper content upon the concentration of calcium ions was the same as in model three-component solutions: the content of mobile copper increased with an increase of calcium ion concentration in soil. The opposite dependence was determined in soil samples with a low humus content.

The concentration of mobile copper increased with an decrease in the pH value in soil. The total content of copper was the highest in clay-rich soil, but the bulk of mobile copper from the total amount of copper with changing the pH value was the lowest in clay-rich soil.

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KAI KURIŲ VEIKSNIŲ ĮTAKA VARIO JUDRUMUI DIRVOŽEMYJE

S a n t r a u k a

Sunkiųjų metalų tyrimai dirvožemyje turi aprėpti jų bendrojo kiekio ir judriosios formos, kuri sąlygoja metalų jonų patekimą į augalus bei gruntinius vandenius, nustatymą. Darbo tikslas buvo iširti modelinėse sistemose – tirpaluose ir dirvožemiuose kai kuriuos veiksnius, kurie turi įtakos vario judriosios formos susidarymui.

Buvo atlikti fizikiniai ir cheminiai tyrimai daugiakomponentuose tirpaluose su vario druskomis bei kalio, amonio ar kalcio divandenilio fosfatais, taip pat kalio ar natrio vandenilio karbonatais. Gauti duomenys parodė, kad vario jonų sąveikai su fosfatais ir karbonatų anijonais turi įtakos sistemoje esantys katijonai: (K^+ jonai mažina Cu^{2+} jonų koncentraciją tirpale, o Ca^{2+} – didina). Minėtų katijonų įtaka pasireiškė nustačius vario ir divandenilio fosfatų jonų sąveikos entalpijas tiriamose sistemose. Sąveikos endotermiškumas mažėja eilėje $Ca^{2+} < NH_4^+ < K^+$. Vario jonų sąveikai su vandenilio karbonatais kalio ir natrio jonų įtakos skirtumai mažesni.

Dirvožemio mėginiai, praturtinti humusu nuo 2,3 iki 8%, buvo paveikti vario druskomis (20, 50, 100, 200 ir 300 mg/kg dirvožemio) ir, nusistojus pusiausvyrai, nustatytas judriojo vario kiekis. Didėjant humuso kiekiui dirvožemyje judriojo vario koncentracija mažėjo. Kalcio jonai, kaip ir modeliniuose tirpaluose, judriojo vario koncentraciją didino, esant dirvožemyje 8% humuso. Esant mažiau humuso, tai nepasireiškė.

Nustatyta judriojo vario koncentracijos priklausomybė nuo pH trijuose skirtingose granulometrinės sudėties ir skirtingo humusingumo dirvožemiuose. Dirvožemio mėginių pH buvo keičiamas nuo 4 iki 8,5. Molio dirvožemyje bendrojo vario buvo 9,5 mg/kg, o judriojo, esant pH 4, rasta tik 2,2% jo bendrojo kiekio ir, didinant pH, judriojo vario koncentracija kito nedaug. Smėlio dirvožemiuose bendrojo vario – 5,1 ir 3,4 mg/kg, o esant pH 4, judriojo vario susidarė atitinkamai 7,4 ir 11,2%. Padidinus pH labiau sumažėjo judriojo vario.