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Speciation of Cu and Zn in soil solution in a long-term fertilization experiment

Abstract: The changes of the concentration of Cu and Zn in the soil solution and the percentage of particular forms of these elements in the soil solution were investigated in the long-term fertilization experiment. The soil solution was obtained following the vacuum displacement method. Speciation of copper and zinc ions was determined with MINTEQA2 for Windows software. The results of the investigation indicated that exclusive mineral fertilization (NPK) caused an increase of Cu and Zn concentration in the soil solution. Organic fertilization (FYM) resulted in a decrease of Cu and an increase of Zn concentration in the soil solution. Liming limited mobility of both analysed elements. The results of speciation analysis showed that regardless of the fertilization mode, the organo-mineral complexes are the main form of Cu occurring in soil solution. The percentage of Cu-DOC complexes ranges from 76.5 to 85.2% of the total concentration of Cu in the soil solution. The particular forms of copper can be sorted depending on the percentage in the soil solution as follows: $Cu\text{-}DOC>Cu^{2+}>Cu\text{-}CO_3$. The main form of Zn in the soil solution are active Zn^{2+} ions. The share of Zn^{2+} in total zinc concentration in the soil solution ranged from 76.9% to 86.4%. Forms of zinc in the soil solution can be arranged with regard to their percentage as follows: $Zn^{2+}>Zn\text{-}DOC>ZnCl+>ZnHCO_3^{+}$.

Keywords: soil solution, zinc, copper, speciation, MINTEQA2, fertilization

INTRODUCTION

High yields of plants of good quality can be achieved only with proper supply of nutrients. Apart from the three macronutrients (N, P, K), plants also need other elements such as Zn, Cu, B, Mo etc. The most important micronutrients for plants are copper and zinc, because of their function in the enzyme activity (Alloway 2008).

The soil solution represents the milieu for nutrient uptake, thus it can be used for diagnostics of plant needs for fertilization with microelements (Łabętowicz and Rutkowska 2001; Rutkowska et al. 2013b; Szulc and Rutkowska 2013).

Rutkowska et al. (2009) showed that long-term mineral and organic fertilization can influence on micronutrient concentration in soil solution. The concentration of Zn and Cu in soil solution increased when soil was fertilized with nitrogen. Liming had a significant effect on a decrease in the concentration of these elements in soil solution. Soil application of manure significantly increased the concentration of microelements in soil solution. Phosphorus and potassium fertilization did not affect the concentration of Zn and Cu in soil solution.

Many authors have shown that the activity of metal ions in the soil solution is a key factor in determination of element bioavailability for plants (Weng et al. 2001; Cancés et al. 2003; Degryse et al. 2009). The concentration and activity of zinc and copper in the soil solution depends on the physical and chemical properties of the soil, which can by modified by long-term fertilization (Ivezić et al. 2012). According to Cancés et al. (2003), speciation of copper in the soil solution is conditioned by soluble forms of organic substance and the reactions of complexing crucially determines copper speciation in the soil solution. The soil reaction is the main factor which determines the activity of free Zn ions and related Zn bioavailability (Stephan 2008). Nitrogen fertilization contributes to a decrease of soil pH as a result of nitrification of ions NH_4^+, and this enhances of Cu^{2+} and Zn^{2+} concentration in soil solution. Long-term farmyard manure application results in an increase of organic matter content in soil. Along with increased soil organic matter concentration, an increase in the amounts of metaloorganic complexes of Zn and Cu in soil solution was observed (Cancés et al. 2003).

The aim of the study was to determine the total concentration of Cu and Zn and the percentage of separate chemical forms of these elements in the soil solution in condition of long-term fertilization experiment.

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MATERIALS AND METHODS

The study was carried out based on the long-term fertilization experiment sited at the Experimental Station of the Faculty of Agriculture and Biology, Warsaw University of Life Sciences-SGGW, which is located in Skierniewice (central Poland). The experiment was established in 1923, following randomized block design on Luvisols (IUSS Working Group WRB 2007). The trial has been carried out in five-field crop rotation (potatoes, spring barley, red clover, winter wheat, rye) and included the following fertilizer treatments: Ca, farmyard manure (FYM), NPK, CaNPK, CaNPK+FYM. The following fertilization doses have been applied: N – 90 kg·ha^{-1} (ammonium nitrate), P – 26 kg·ha^{-1} (triple superphosphate), K – 91·kg ha^{-1} (potassium salt 50%). Liming has been applied once every 5 years at a rate 1.43 Mg Ca·ha^{-1}. FYM was applied at a rate 30 Mg·ha^{-1} once in 5 years. Selected physico-chemical properties of the soil are given in Table 1.

TABLE 1. Properties of soil in the long-term fertilizer experiment

Treatment	pH	Corg	Cu	Zn
		g kg^{-1}	mg kg^{-1}	
Ca	6.40^{b}	5.56^{a}	3.03	4.77^{a}
FYM	6.35^{b}	11.0^{c}	3.07	5.04^{b}
NPK	4.65^{a}	5.84^{a}	3.12	5.68^{b}
CaNPK	6.20^{b}	6.11^{b}	2.99	4.48^{a}
CaNPK+FYM	6.25^{b}	8.44^{c}	2.89	4.90^{a}

Explanation: Values indicated with the same letter are not significantly different.

Soil samples were collected from the soil layer 0–30 cm, after plant harvest The following soil properties were analysed:

– pH – by potentiometric method after extraction in KCl solution 1 mol·dm^{-3} (PN-ISO 10390:1997)
– total organic carbon content – by dry combustion at high temperatures in a furnace with the collection and detection of evolved CO_2 with C-MAT 5500 apparatus (Stroehlein, Germany);
– content of available forms of Cu and Zn in soil (PN-92/R-04016, PN-92/R-04017).

The soil solutions were obtained following the vacuum displacement method and using an oil vacuum pump (Dynavac OP4 Melbourne, Australia) (Wolt and Graveel 1986). The total concentration of Cu and Zn in the soil solutions was assessed with ICP-AES method (IRYS Advantage ThermoElementar, Cambridge, UK). Different Cu and Zn forms in soil solution, such as: active/free ions (Cu^{2+}, Zn^{2+}), organic complexes (Cu-DOC, Zn-DOC), complexes with chloride ($ZnCl^{+}$), complexes with carbonates ($CuCO_3$, $ZnHCO_3^{+}$) were assessed with MINTEQA2 for Windows software. MINTEQA2 represents a geochemical speciation model which can be used to calculate theoretical mass distribution of metals between free ions, dissolved complexes, metals adsorbed on the surface of hydrous iron oxide and on solid soil phases (Allison et al. 1991).

The results were statistically analysed with ANOVA and simple linear regression. The differences between means were analysed with Tukey's test at p = 0.05. The analyses were performed using Statistica software (ver. 10, Warrenton, USA).

RESULTS AND DISCUSSION

Total copper concentration in soil solution ranged from 0.40 to 0.47 μmol·dm^{-3} and total zinc concentration ranged from 2.08 to 3.27 μmol·dm^{-3}. The concentration of active copper ions (Cu^{2+}) was significantly lower (0.06–0.13 μmol·dm^{-3}), whereas concentration of Zn^{2+} was somewhat lower (1.70 to 2.51 μmol·dm^{-3}) than the total concentration of these elements in soil solution (Table 2).

TABLE 2. Total concentration of Cu and Zn and concentration of Cu^{2+} and Zn^{2+} ions in the soil solution [μmol•dm^{-3}] in different fertilization modes

Treatment	Cu	Cu^{2+}	Zn	Zn^{2+}
Ca	0.40^{a}	0.07^{a}	2.08^{a}	1.70^{a}
FYM	0.41^{a}	0.05^{a}	2.92^{bc}	2.49^{c}
NPK	0.57^{b}	0.13^{b}	3.27^{c}	2.51^{c}
CaNPK	0.47^{ab}	0.10^{b}	2.67^{b}	2.25^{b}
CaNPK+FYM	0.45^{a}	0.06^{a}	3.02^{c}	2.35^{b}

Explanation: Values indicated with the same letter are not significantly different.

The highest total concentrations and concentration of free ions of Cu and Zn were obtained in the solution of soil from the treatment with the lowest pH value (NPK). Liming (CaNPK) decreased the concentration of these elements in the soil solution. Long-term application of FYM (CaNPK+FYM) had an effect on a decrease of the total concentrations and active form concentration of copper and an increase of zinc concentration in the soil solution when compared to CaNPK treatment (Table 2). A similar effect of fertilization on the concentration of trace elements in the soil solution showed Rutkowska et al. (2009). Sosulski et al. (2013) reported that the presence of manure in the dose of fertilizers caused an increase in the mobility and leaching of zinc.

Regardless of fertilization mode, the copper exists in soil solution in three forms: free ions (Cu^{2+}), complexes with organic matter (Cu-DOC) and complexes with carbonates (Cu-CO_3). Cu-DOC complexes always predominated in the soil solution of analysed soil with differentiated fertilization. The percentage of Cu-DOC complexes ranged from 76.5 to 85.2% of the total concentration of copper in the soil solution (Table 3). The percentage of free ions Cu^{2+} in the total concentration of this element in the soil solution ranged from 12.8 to 23.5%. The increase of Cu^{2+} in soil solution was observed together with the decrease of soil pH value. The small percentage of free ions Cu^{2+} in the soil solution was observed by Rutkowska et al. (2013a). According to Yuan (2009) the small percentage of free ions Cu^{2+} in the soil solution is caused by strong copper binding by solid soil phase. As said by Cancés et al. (2003) and Zhang et al. (2013) speciation of copper in the soil solution is regulated by the dissolved organic matter.

Free ions Zn^{2+} predominated in the analysed soil solution. The share of Zn^{2+} in the total zinc concentration was from 76.9 to 86.4%. In reference to MINTEQA2 assessment, complex zinc associations with organic matter also represented substantial shares in the soil solution (from 10.8 to 19.8%) (Table 4). The highest percentage of Zn^{2+} with reference to the total concentration of zinc was observed in the soil solutions of the most acidic soil analysed (NPK). The percentage of metal – organic complexes (Zn-DOC) in soil solution increased in objects with farmyard manure application (FYM, CaNPK+FYM). The other zinc complexes such as $ZnCl^+$ and $ZnHCO_3^+$ constituted only small part of total Zn concentration in soil solution (1.6–2.8% and 0–1.9% for $ZnCl^+$ and HCO_3^+, respectively). Several studies showed that Zn^{2+} is the predominant form of Zn in soil solution in wide range of soil pH (Cancés et al. 2003; Luo et al. 2006; Stephan et al. 2008). The Zn-DOC complexes in soil solution are quite significant. The occurrence of $ZnHCO_3^+$ complexes is characteristic for neutral and alkaline solutions (Khoshgoftar et al. 2004). Percival et al. (1999) confirmed that small amounts of zinc associated with inorganic ligands (e.g., OH^-, NO_3^-, Cl^-, PO_4^{3-}) could occur in the soil solution.

TABLE 3. Percentage share of different copper forms in the soil solution in different fertilization modes

Treatment	Cu^{2+}	Cu-DOC	Cu-CO_3
Ca	17.3	79.3	3.4
FYM	12.8	85.2	2.0
NPK	23.5	76.5	0.0
CaNPK	21.6	78.4	0.0
CaNPK+FYM	15.5	79.7	4.8

TABLE 4. Percentage share of different zinc forms in the soil solution in different fertilization modes

Treatment	Zn^{2+}	Zn-DOC	$ZnCl^+$	$ZnHCO_3^+$
Ca	82.6	14.4	1.6	1.4
FYM	76.9	19.8	1.7	1.6
NPK	86.4	10.8	2.8	0.0
CaNPK	84.1	11.8	2.8	1.3
CaNPK+FYM	77.8	18.4	1.9	1.9

CONCLUSIONS

1. Long-term fertilization influenced the concentration of Cu and Zn in soil solution through the effects on physical and chemical soil properties. The highest concentration of Zn and Cu were found in the object with exclusive mineral fertilization, which has the highest soil acidification. Liming decreased the content of these elements in soil and the soil solution. Farmyard manure applications limited the concentration of Cu as well as increased Zn concentration in soil solution.
2. The results of numerical analysis showed that, regardless of fertilization mode, active Zn^{2+} ions are the major form of zinc occurring in the soil solution. Copper is present in the soil solution mainly as organo-mineral complexes.

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Specjacja Cu i Zn w roztworze glebowym w warunkach wieloletniego doświadczenia nawozowego

Streszczenie: Celem pracy była ocena zmian stężenia Cu i Zn oraz określenie procentowego udziału poszczególnych form tych pierwiastków w roztworze glebowym. Badania prowadzono w warunkach wieloletniego doświadczenia nawozowego zlokalizowanego w Stacji Doświadczalnej Wydziału Rolnictwa i Biologii SGGW w Skierniewicach. Roztwór glebowy pozyskano metodą podciśnieniową. Poszczególne, możliwe do wystąpienia formy miedzi i cynku w roztworze glebowym obliczono przy wykorzystaniu programu komputerowego MINTEQA2. Uzyskane wyniki badań wskazują, że stężenie Cu i Zn w roztworze glebowym zwiększa się pod wpływem wyłącznego nawożenia mineralnego (NPK). W warunkach stosowania obornika (CaNPK+FYM) zmniejsza się stężenie miedzi, a zwiększa stężenie cynku w roztworze glebowym w stosunku do obiektów o wyłącznym nawożeniu mineralnym (NPK, CaNPK). Wapnowanie było czynnikiem wpływającym na zmniejszenie stężenia obydwu badanych pierwiastków w roztworze glebowym. Wyniki analizy numerycznej roztworu glebowego wykazały, że niezależnie od nawożenia dominującą formą miedzi w roztworze glebowym były kompleksy metalo-organiczne. Ich udział w całkowitym stężeniu Cu w roztworze glebowym stanowił od 76,5 do 85,2%. Pod względem malejącego udziału w roztworze glebowym poszczególne formy miedzi można uszeregować następująco: kompleksy miedzi z materią organiczną >wolne jony Cu^{2+} >kompleksy miedzi z węglanami. Natomiast główną formą cynku w roztworze glebowym były wolne jony Zn^{2+}, których udział w ogólnym stężeniu cynku w roztworze glebowym wynosił od 76,9 do 86,4%. Szereg malejącego udziału poszczególnych form cynku w roztworze glebowym przedstawia się następująco: wolne jony Zn^{2+} >kompleksy Zn z materią organiczną >kompleksy cynku z chlorkami >kompleksy z węglanami.

Słowa kluczowe: roztwór glebowy, miedź, cynk, nawożenie, specjacja, MINTEQA2