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Original Research

Fate of Copper in Soils from Different Fertilizer Doses in Relation to Environmental Risk Assessment

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Abstract

Total copper distribution in the soil profile was determined, depending on the type of soil and Cu dose, 5 years after the application of this element. Soil samples were taken from 5 layers to 50 cm depth from microplots filled with 3 types of soil that 5 years earlier had been treated with 5 doses of Cu: 4, 8, 12, and 16 kg ha^{-1}. There was an uneven distribution of Cu in the soil profile. In general the Cu decreased in the subsurface layers (10-30 cm) and increased in deeper layers (30-50 cm) in relation to the surface layer (0-10 cm). Using PCA analysis, both soils and doses of similar Cu distribution in the soil profile were pointed out. The distribution pattern in the sandy soil differed from the other two sandy loam soils. Additionally, for 4 and 8 kg ha^{-1} doses, we recorded a similar Cu distribution as for the soil with natural Cu concentration. On the other hand, in the case of the doses of 12 and 16 kg ha^{-1}, there was a distinctly different pattern of distribution. The maximum dose of Cu, which can be applied every 5 years, is 8 kg ha^{-1} for the sandy soil with a low content of organic matter and 12 kg ha^{-1} for sandy loam.

Keywords: copper, soil, doses, vertical distribution, environmental hazard

Introduction

In small quantities, Cu is absolutely necessary for plants to grow and develop. The deficiency of this element in soil leads to a decrease in crop yield and should be supplemented by fertilization [1-2]. In the case of a significant Cu deficit, soil fertilization is recommended, which compensates for this deficit for a few following years. As many as 40% of soils in Poland are deficient in Cu and should be fertilized when growing plants that are sensitive to the absence of this element [3].

The recommended dose is 6-12 kg ha^{-1} once every few years, depending on plant species [4]. However, there are reports in the literature that an intensive use of Cu in agricultural practices can lead to soil contamination. For example, the use of Cu-based fungicides has led to an excessive accumulation of Cu in soils in Australian [5] and French vineyards [6], coffee fields in Tanzania [7], and apple orchards in Taiwan [8]. Similarly, using soil fertilization of wheat with Cu for 17 years in Shaanxi Province, China significantly increased its concentration in the top layer of the soil [9]. Excessive accumulation and leaching of Cu from agricultural soils can contaminate groundwater and pose a risk to humans and animals through the food chain. Cu toxicity and transport deep into the soil profile is closely related to its solubility [10].

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Cu of natural origin shows a rather low mobility in the soil. In general, it forms insoluble complexes with organic matter and mineral soil fractions, and its content is highest in the several centimeters of topsoil [11]. The solubility of Cu involves the formation of its mobile species and depends on many soil factors such as pH, oxidation, and reduction potential, the amount and type of organic matter, the texture of the soil, temperature, and humidity. High mobility in the soil is characteristic for Cu complexes with dissolved organic carbon (DOC). More intensive movement of Cu by the soil profile can be expected in soils with higher DOC compared to the soils with its lower content [12].

Cu of anthropogenic origin acts differently than the natural one. Cu fertilizers contain soluble, highly mobile Cu that can migrate deep into the soil profile. Over time, Cu transforms into less mobile compounds [13]. The effectiveness of this process depends on the sorption capacity of the soil. Soils that are more compact and rich in organic matter are able to fix more Cu [14].

Although determining the fertilization requirements involves assessing the so-called available Cu in the soil [15-17], in order to estimate the contamination, determining total Cu in aqua regia is still used in many countries. The limits for total Cu apply generally to the topsoil and vary depending on the country. For example, in the Netherlands "remediation intervention value" is 190 mg kg^{-1} for 10% of organic matter and 25% of clay [18]. In Poland, "admissible concentration" oscillates between 100 and 300 mg kg^{-1} Cu depending on the pH and soil texture [19].

Many authors describe the mobility and vertical distribution of heavy metals, including Cu, in soils fertilized with sediment sewage sludge [20-22] contaminated by industry [23-25] or as a result of the use of Cu-based fungicides [5, 7-8]. There is no information about the transport of Cu into the soil profile when applied in the form of fertilizers – especially in relation to the dose.

The aim of our study was to examine the vertical distribution of Cu in the soil a few years after the application of Cu sulphate in the aspect of a potential threat to groundwater.

Experimental Procedures

In autumn 2016 we collected soil samples from microplots located in Jelcz-Laskowice in Lower Silesia, Poland (51°01′N, 17°18′E). In earlier years, these microplots were used for an experiment with the fertilization of winter wheat with Cu. Five years before sampling, a concrete-framed microplot with a surface area of 1 m^2 and a depth of 1 m (without bottoms) were filled with 3 soils and treated with different Cu doses. All 3 soils belonged to the Luvisols type, the most common type of soil in both Lower Silesia and across Poland [26].

Five doses of Cu were applied in the form of $CuSO_4 \times 5H_2O$: Cu_0 – control (without Cu), Cu_1 – 0.4, Cu_2 – 0.8, Cu_3 – 1.2, and Cu_4 – 1.6 g m^2 Cu. Cu sulphate dissolved in water was applied to the microplots with a hand-held watering can and then thoroughly mixed with the soil.

The microplots were located under the open sky, where the soil was exposed to the weather. Annual rainfall totals and annual average temperatures for the period from fertilization to soil sampling are shown in Table 1. In 2012-2015, winter wheat was cultivated on the microplots, while in 2016 no plant cover was used.

Soil samples were collected at the beginning of November 2016 from the layers of 0-10, 10-20, 20-30, 30-40, and 40-50 cm with a 21 mm steel core tube. Five random cores were collected from each plot. Each sample was created by mixing five soil cores. In total, we collected 300 samples (3 soils x 5 Cu doses x 5 layers x 4 replicates). All samples were air-dried, sieved through a 2 mm diameter, and stored in plastic boxes at room temperature.

Soil samples were analyzed for Cu concentration in aqua regia. After the digestion, Cu was determined using the FAAS method. In addition, soil pH was determined potentiometrically in 1 mol KCl dm^{-3} (ISO10390: 2005), total organic carbon (TOC) by Tiurin method using potassium dichromate (PN-ISO14235:2003), and texture by the aerometric method (PN-R-04033:1998). The accuracy of the method was verified by reference material CRM028-50G trace metals-sandy loam 11 (Sigma-Aldrich RTC) with a total Cu content of 8.51±0.602 mg kg^{-1}. All chemical analyses were done by the Central Laboratory of the Institute of Soil Science and Plant Cultivation – State Research Institute, certified by the Polish Centre of Accreditation according to PN-EN ISO/IEC 175 17025 (certificate No. AB 339).

The results of Cu concentration in the soil were given as the means from 4 replications. Calculations of ANOVA were performed with Statgraphics Centurion XV software (StatPoint, Inc.). Statistical significance was determined using Tukey's test ($P<0.05$). Principal component analysis (PCA) was perform using Statistica 10.0 software (StatSoft, Inc.).

Results and Discussion

Physicochemical Properties of Soils

Of the three soils used for our study, soil A was the least compact, with its texture changing with depth (Table 2). In the upper layers of soil A, there was a sand

Table 1. Total annual precipitation and average temperature in the region of the Experimental Station in Jelcz-Laskowice.

Year	2012	2013	2014	2015	2016	1961-2010
Precipitation (mm)	579	670	598	346	526	565
Temperature (C°)	8.9	8.7	10.1	10.5	9.8	8.7

Table 2. Characteristics of the experimental soils.

Soil	Depth cm	pH	TOC %	Soil fraction (mm) 2.0-0.05	0.05-0.02	0.02-0.002	<0.002	Texture
				%				
A	0-10	5.8	0.60	87	6	5	1	S
	0-20	5.3	0.60	86	7	6	1	S
	20-30	5.5	0.51	80	8	10	2	LS
	30-40	5.7	0.32	65	11	20	4	SL
	40-50	6.0	0.30	68	11	17	3	SL
	Average	5.7	0.46	77	9	12	2	
B	0-10	5.5	0.86	68	11	18	3	SL
	0-20	5.5	0.65	70	10	16	3	SL
	20-30	5.5	0.74	71	10	16	3	SL
	30-40	5.5	0.40	70	8	18	4	SL
	40-50	5.9	0.39	70	10	16	3	SL
	Average	5.6	0.61	70	10	17	4	
C	0-10	5.5	1.12	69	11	16	3	SL
	0-20	5.4	1.00	68	12	17	3	SL
	20-30	5.6	0.75	68	10	18	4	SL
	30-40	6.0	0.63	67	9	19	5	SL
	40-50	6.1	0.48	67	10	19	4	SL
	Average	5.7	0.79	68	11	18	4	

S-sand, LS-loamy sand, SL-sandy loam

that then changed into loamy sand, and deeper into the sandy loam. At the same time, the TOC decreased from 0.60% to 0.30%, respectively. Soil pH varied in the range of 5.3-6.0, depending on the soil layer. The lowest value of this parameter was recorded in the layer of 10-20 cm, while in the deeper layers pH increased.

Soils B and C were very similar in terms of texture. The entire tested profile of these soils (0-50 cm) was sandy loam. However, these soils differed in TOC distribution and soil pH. Soil B contained 0.86-0.39% of TOC, which decreased with depth, but there was a clear difference between 0-30 cm and 30-50 cm. The average TOC for these two layers was 0.75% and 0.40%, respectively. On the other hand, soil pH in the layers down to the depth of 40 cm was equal to 5.5 while deeper it rose to 5.9.

In soil C, the pattern of TOC distribution in the soil profile was different from that in soil B. It systematically decreased in the following layers ranging 1.12-0.48%. Soil pH increased together with depth, from 5.5 to 6.1.

Considering the values of soil parameters throughout the entire soil profile (0-50 cm), it should be noted that the soils did not differ in pH, but there were some differences in TOC and silt content.

Concentration and Vertical Distribution of Cu

The distribution and migration of metals in the soil is affected by soil texture, soil layer, the origin of the metal (anthropogenic or natural), and the total concentration of the metal [24, 28]. In our studies, the Cu concentration found in soil 5 years after its application depended on the Cu dose and soil type (Table 3). The average Cu concentration in the soil profile to 50 cm depth on the treatments with natural Cu (Cu_0) and ones fertilized with the lowest dose of this element (Cu_1) ranged from 6.2 to 8.6 kg^{-1}. In the treatments fertilized with higher doses (Cu_2-Cu_4), we recorded from 7.8 to 15.7 mg kg^{-1} Cu. element. These concentrations, even after the application of the highest Cu dose, were many times lower than the admissible limits for soil contamination with Cu (Table 3).

In soils B and C that were not fertilized with Cu (Cu_0), the concentration of this element was distributed relatively evenly in the soil profile layers, whereas in soil A it increased together with depth (Fig. 1, Table 4). Other authors reported that in the soils with natural Cu, its concentration in sandy soils decreased down the depth of the profile, while in more compact soils it increased together with an increasing clay content [5].

Table 3. Cu concentrations in soil profile depending on the Cu dose after 5 years from its application (average over 5 layers).

Dose	Soil		
	A	B	C
	mg kg^{-1}		
Cu0	6.2 a	8.6 a	7.6 a
Cu1	6.6 a	8.4 a	8.5 ab
Cu2	7.8 b	10.1 b	8.9 b
Cu3	10.7 c	11.5 c	13.2 c
Cu4	15.7 d	14.8 d	14.4 d
Average	9.4	10.7	10.5
*	100	100	100
**	30	30	30

*Admissible Cu concentration according Regulation of the Minister of the Environment [19]; **first level of Cu contamination (increased content) according Kabata-Pendias et al. [27]; the same letters for each soil indicate the lack of significant differences according to Tukey's test (P<0.05)

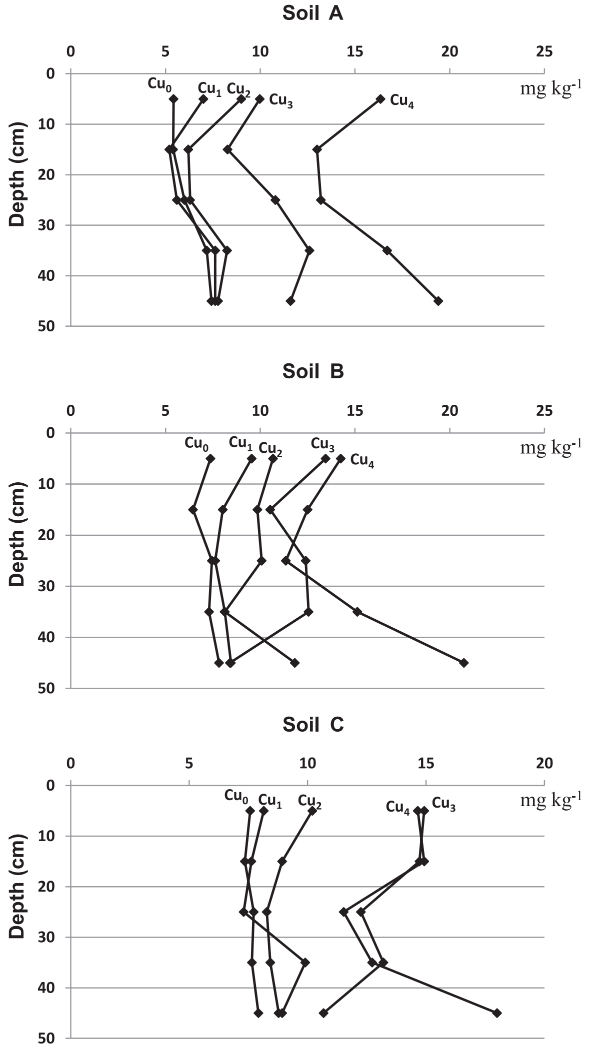

Fig. 1. Vertical distribution of Cu in soil profiles after 5 years from Cu application; Cu_0 – control without Cu fertilization, Cu_1 – 0.4 g m^{-2}, Cu_2 – 0.8 g m^{-2}, Cu_3 – 1.2 g m^{-2}, and Cu_4 -1.6 g m^{-2}.

In our study, in the soil treated with Cu (Cu_1-Cu_4), vertical distribution of this element after 5 years from application was different than in the soil with its natural content. The relations among individual soil layers in terms of Cu concentration were different in each soil and for each level of Cu fertilization.

We found generally less Cu in the subsurface soils (10-20 and 20-30 cm) than in the surface soil (0-10 cm). This is confirmed by the results of Pietrzak and McPhail (2004), who recorded the depletion of Cu in the 10-20 cm layer (or even deeper than 25 cm) compared to the surface layer. In our studies, the decrease of Cu in the subsurface layers was greatest in soil A, amounting to 40%, while in soils B and C it did not exceed 21%, whereas the impact of dose on the level of the decrease was uneven. In contrast, in deeper layers (30-40 and 40-50 cm), we observed both the decrease and increase in Cu concentrations in relation to the layer of 0-10 cm. This increase was found in soil A for Cu_3 and Cu_4 (16-26%), and in soil C for Cu_1 and Cu_4 (10-23%). In soil B, however, the increase of Cu concentration in relation to the layer of 0-10 cm was found only at a depth of 40-50 cm for Cu_3 and Cu_4 (11% and 46%, respectively). Li et al. (2005), in the soil contaminated anthropogenically, found an uneven distribution of Cu in the soil profile, decreasing from the surface to the deeper layers, whereas the differences between the layers and the correlation between them in the content of Cu were significant.

An uneven distribution of total Cu among the soil layers is probably connected with a different Cu mobility and its movement to the deeper layers, or with Cu immobilization. According to Pietrzak and McPhail (2004), in soils not contaminated with Cu, this element occurs mainly in less mobile forms (residual fraction + oxides of Fe and Al), while potentially available Cu constitutes only about 10% of total Cu in the soil profile. Antonkiewicz and Pelka [29] showed that in the uncontaminated silt loam, residual fraction constituted 38% of total Cu. In the soils uncontaminated with Cu, however, Kabala and Singh [24], in the case of sandy soil, found a low percentage of residual fraction in the surface and subsurface layers, which was a result of poor soil sorption capacity of this soil. In the silty and clay-loamy soils, the residual fraction in the subsurface layer was, respectively, 88 and 97% of total Cu.

Fertilizing the soil with Cu as well as using Cu-containing fungicides can pose a threat to the environment. Xiaorong et al. [9] showed that Cu soil fertilization for many years caused the accumulation of this element in the surface layer of the soil and its transportation deep down the soil profile. Mobile Cu forms moved even deeper than to a depth of 400 cm.

The most mobile fractions are exchangeable Cu, Cu weakly bound with organic matter, and Cu in carbonate

Table 4. Cu concentrations in soil layers expressed as a percentage of Cu concentrations in the surface layer (0-10 cm).

Soil	Depth cm	Cu_0	Cu_1	Cu_2	Cu_3	Cu_4
		%				
A	0-10	100	100	100	100	100
	10-20	100	74	60	83	79
	20-30	111	80	61	108	80
	30-40	133	109	80	126	102
	40-50	138	109	75	116	118
B	0-10	100	100	100	100	100
	10-20	87	84	92	78	88
	20-30	101	80	94	92	80
	30-40	99	85	76	93	106
	40-50	106	88	111	62	146
C	0-10	100	100	100	100	100
	10-20	97	94	88	99	102
	20-30	102	94	81	82	79
	30-40	101	121	83	88	87
	40-50	105	110	86	72	123

bonds. The authors found more of the abovementioned fractions in the layer of 15-60 cm than in 0-15 cm. In addition, they documented that approximately 40% of the applied Cu was leached down the soil profile, below 60 cm. According to Pietrzak and McPhail [5], who studied soil in vineyards after fungicide applications, the transformation between the Cu fractions is very slow, so Cu can be active in soil for a long time, which can cause its leaching and relocation to the deeper soil layers and into water.

In our study, Cu_1-Cu_3 doses did not cause Cu to translocate below 40 cm in soils B and C. Only the Cu_4 dose resulted in a significant Cu transport below this level. In soil A, however, already Cu_3 dose caused the translocation of this element down into the soil profile, below 30 cm. This was due to a different texture and content of C org in soil A than in soils B and C.

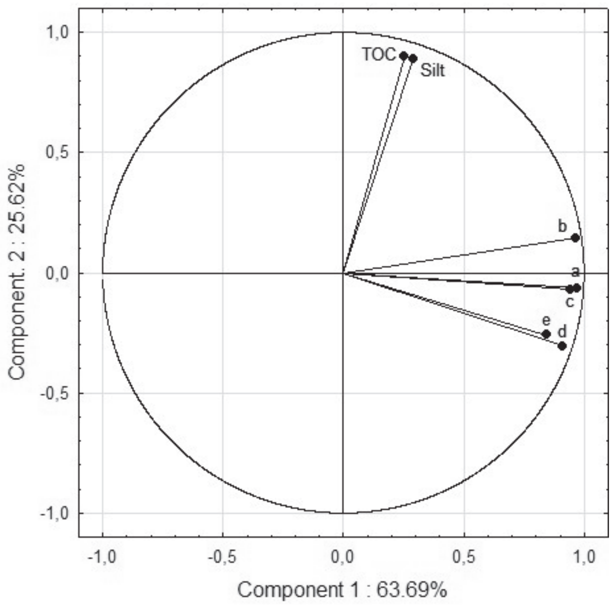

Fig. 2. Results of PCA for Cu in soil layers and soil factors; a-e soil layers: a 0-10 cm, b 10-20 cm, c 20-30 cm, d 30-40 cm, and e 40-50 cm.

PCA Analysis of Data

We used PCA to point out both soils and Cu doses of similar vertical Cu distribution in the soil profile. As the original variables, we used Cu concentration in each soil layer, TOC, and silt. The pH of soils was not taken into account because it was not diversified, and therefore it was assumed that this parameter had no effect on Cu variability in the soil. Cu_0-Cu_4 treatments on each soil were assumed as individual cases. Two principal components that explained data variability in 89.3% were established (Fig. 2). The first principal component (63.69% of variability) represented the Cu concentration in soil layers, whereas the highest impact on this component was exerted by layers a (0-10 cm) and c (20-30 cm), which were additionally highly correlated with each other.

Layers d (30-40 cm) and e (40-50 cm) were also highly correlated with each other, but had a lower effect on the principal component than layers a and c. The second principal component (25.62% of variability) represented TOC and silt, which were highly correlated with each other.

The cases projection of the plane of the two principal components allowed us to assess similarities and differences between them in terms of Cu distribution in the soil profile (Fig. 3).

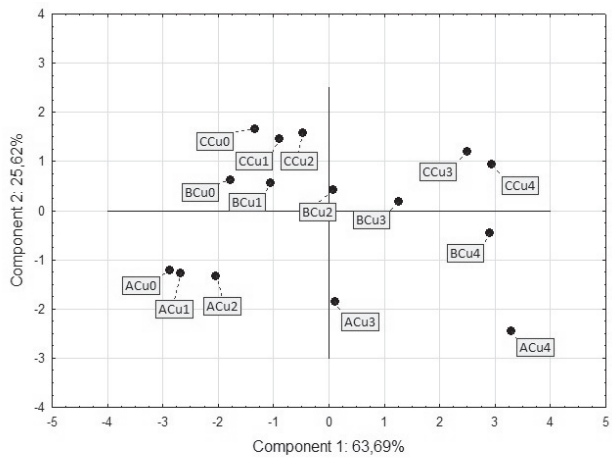

Fig 3. Results of PCA-projection of cases (Cu in soil related to type of soil and Cu dose) on the principal components plane.

We found that soil A in general was different in terms of the vertical transport of Cu in the soil profile from soils B and C, which were similar to each other. At the same time, a very similar distribution of Cu in 5 years after its application was found for Cu_0, Cu_1, and Cu_2. On the other hand, Cu_3 and Cu_4 had a significantly different distribution pattern than Cu_0-Cu_2. These doses were characterized by a similar distribution of Cu in soil C while being different in other soils, especially in soil A.

Conclusions

1) A soil fertilization with Cu at doses of 4-16 kg ha^{-1} in 5 years after the application increased the amount of Cu in the soil profile to a depth of 50 cm from the natural amount (6.2-8.6 mg kg^{-1}) to 14.4-15.7 mg kg^{-1} after applying the highest dose of this element.
2) Fertilization with the doses of 4-16 kg ha^{-1} did not exceed the admissible limit of Cu concentration for the arable layer in any of the tested soil layers down to a depth of 50 cm.
3) After 5 years from Cu application, uneven Cu distribution was observed in the soil profile down to 50 cm. In general, the Cu concentration decreased in the subsurface layers (10-30 cm) and increased in deeper layers (30-50 cm) in relation to the surface layer (0-10 cm).
4) Based on the Cu distribution in the soil profile, it can be assumed that Cu doses up to 8 kg ha^{-1}, irrespective of soil type, do not pose a risk to the environment in relation to Cu translocation to deeper soil layers and groundwater.
5) The maximum dose of Cu that can be applied once every five years is 8 kg ha^{-1} for sandy soil with a low content of organic matter and 12 kg ha^{-1} for sandy loam.

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