METHODOLOGICAL DEVELOPMENT IN DETERMINATION OF COPPER CONTENT IN THE ROOT ZONE OF HUNGARIAN SOIL TYPES: PRELIMINARY RESULTS

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History reveals that heavy metals have been used since ancient times. The human body contains about 80 mg copper, which can be present mostly in eyes, brain, liver, heart, kidneys and musculature. In our study we determine the adsorption capacity of copper in five different concentrations and in four different soil types: brown forest soil, chernozem, meadow and sand with humus. In our method we prepared soil columns, in which we put 50 g experimental soil samples and poured on copper solutions of known concentrations. The concentrations of runoff filtrates were determined by titration methods. The adsorption capacity of soil samples were calculated from the two different concentration values.

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Introduction

Heavy metals have been used in the history since ancient times.[1] Copper was the first heavy metal in the history, which was used in large quantities. There was the Copper Age in Europe between 3500 2500 B.C.[2] Shortly copper turned out to be easily mixable. It was used for various castings and in bronze also. An important feature of copper is the resistance to corrosion that makes it a functional and decorative material in construction since the Middle to present ages of the history. [3]

The chemical, physical and biological reactions between the soil components and the pollution affect the form of pollutions conditions of heavy metal. Considering the adsorption, it is important that the humus is generally negatively charged in 4.5 – 9.0 pH range. In aqueous phase the interaction can be physical, phisico-chemical or chemical bond between the solutes and solid surface. In the physical adsorption (physisorption) the molecules bind to surface with long-range, low bonds or electrostatic attraction. The chemisoprion (chemical adsorption) results stronger interactions than physisorption, in which small-range chemical bonds are formed.[4,5,6]

Earth crust contains 10-50 mg kg^{-1} copper, especially in the form of copper sulphides. The copper content of uncontaminated soil is 1-140 mg kg^{-1} in global average - it strongly depends upon the soil's clay fraction content. [7,8]. Most of the copper is in divalent form bonded to organic or inorganic adsorption surface in soil. Because of strong tendency of complex formation it develops complex formation with varied biological molecules. The copper binds strongly to these complexes, where as other cations can only displace them with difficulty, except the hydrogen ion. Consequently, the soluble copper content increases in acidic medium. Mobility of copper is very low in soils. In humus soil its deficiency has been observed. It was found, that the humus complex forms have high stability, which is typical in low pH [9,10].

Materials and methods

In this study our aim was to determine the adsorption capacity of copper as laboratory method in root zone of Hungarian soil types.

Four different soil types were examined: brown forest soil, meadow soil, chernozem and sand with humus. Each soil type came from two sampling sites, so eight soil samples were processed. The sampling sites and the soil types are given in Table 1.

Table 1. Sampling sites and soil types

Sampling site	Soil type
	sand with humus
Tiszavasvári	meadow soil
	chernozem
Gödöllő	brown forest soil
	sand with humus
Budapest - Soroksár	meadow soil
	brown forest soil
Dunaújváros	chernozem

The soil samples were collected from 0-30 cm depth, in the month of March 2012. After sampling, exhaustive soil analysis were done, e.g. pH (distilled water (DW) and KCl), conductivity, total salt content, N-P-K-content, humus content and quality, CaCO$_3$% content were determined.

One can observe the chemical properties of soil types from different sampling sites in Table 2.

Table 2. Soil chemical analysis results of brown forest soil samples

Sampling site	pH		Content		
	DW	KCl	Total salt, mg L^{-1}	CaCO$_3$, %	Humus, H %
Gödöllő	6,72	5,92	29,9	0,21	2,98
Budapest - Soroksár	6,36	5,63	45,4	0,47	1,77

The brown forest soil came from Gödöllő and the Experimental and Research Farm of Corvinus University of Budapest, Soroksár. The chemical properties (pH, total salt and carbonate content) of both soil showed similarity. In humus content a small difference was noticeable, but copper is expected to behave similarly in case of both soil samples.

Table 3. Soil chemical analysis results of chernozem soil samples

Sampling site	pH		Content		
	DW	KCl	Total salt, mg L^{-1}	CaCO$_3$, %	Humus, %
Dunaújváros	7,94	7,35	100,8	11,65	5,37
Tiszavasvári	5,83	4,49	38,5	0,84	3,29

The chernozem samples came from an oil trap from Dunaújváros and from a cultivated area from Tiszavasvári. The effect of cultivation shows clearly in soil test results. The acidifying effect of fertilizer resulted lower pH. Plants detracted Ca ions and various ion forms, so the salt and carbonate content were less in soil sample from Tiszavasvári. There is a difference in humus content, because the effect of cultivation and ventilation starts mineralization in humus. A Difference is expected in copper adsorption capacity in case of the two soil samples.

Table 4. Soil chemical analysis results of sand with humus samples

Sampling site	pH		Content		
	DW	KCl	Total salt, mg L^{-1}	CaCO$_3$, %	Humus, H%
Budapest – Soroksár	7,78	7,31	69,3	4,2	1,42
Tiszavasvári	8,15	7,37	57,0	3,19	0,53

The humus with sand samples came from Soroksár and Tiszavasvári. The sample from Tiszavasvári is also cultivated (as the previous chernozem) which is reflected in the analysis values: a CaCO$_3$ % smaller, because the plants are utilized the Ca ions, besides the humus content is lower because of the cultivation. A difference is expected in case of these two soil samples after copper pollution.

Table 5. Soil chemical analysis results of meadow soil samples

Sampling site	pH		Content		
	DW	KCl	Total salt mg L^{-1}	CaCO$_3$, %	Humus, H%
Budapest - Soroksár	7,63	7,34	115,7	13,28	4,15
Tiszavasvári	5,56	4,59	39,2	0,26	6,12

The meadow soil samples came from Soroksár and Tiszavasvári. The effect of agricultural cultivation is noticeable in pH, total salt content and carbonate content. A difference was found in humus content. The meadow soil sample from Tiszavasvári was after ploughing – the crop residues have begun to humificate, therefore higher humus content was measured. Differences are expected in copper adsorption capacity from these meadow soil samples.

The copper pollution in laboratory was carried out with soil column experiments. The soil columns are shown in Figure 1 a and b.

Figure 1. Soil column.　　**Figure 2**. Copepr pollution in laboratory

The soil column was prepared as follows: a cork was placed on top of a glass tube; a funnel was put in the middle of the cork. The bottom of the glass tube was tied up with mesh. 50 g pre-treated, air-dried soil samples were poured into the top of the funnel. There was also a funnel at the bottom of the soil column to guide the filtrate to the glass cup directly.

The copper pollution was carried out with CuSO$_4$ aqueous solution. 50 g L^{-1} concentrated copper solution was made, which was extenuated to 25, 10, 5 and 1 g L^{-1} concentrated solutions. 200-200 cm^3 copper solution were poured from each concentration to each prepared soil columns, and then the copper content of filtrate were determined by complexometric titration method.

Before titration, 10 cm^3 filtrates were pipette out into titration flask, pH 9.0 – 10.0 was adjusted by concentrated ammonia. Samples were titrated with murexid indicator, 0.05 mol L^{-1} EDTA from red to violet.

The adsorption capacity of the soil samples were calculated from the two different concentration values.

$$c_{adsorbed} = c_{pollution} - c_{filtrate}$$

Statistical analysis was carried out by two-factor ANOVA (soil type and contamination concentration) for copper adsorption of soil using SPSS 20 software (http://www.spss.com). In order to normalize the data, after a shift of +0.3, Box-Cox transformation was executed with $\lambda = 0.2$.[11] We also considered the effect size measure (denoted by partial η^2) which gives the variance explained

by a given independent factor of the variance remaining after excluding variance explained by the other independent factors as well as the observed power of the test. Normality of residuals was proved using the Kolmogorov-Smirnov's test ($p = 0.2$). Homogeneity of variances was tested by Levene's test ($p = 0.19$) and it was followed by Tukey's post hoc test for the contamination concentration.

Results and Discussion
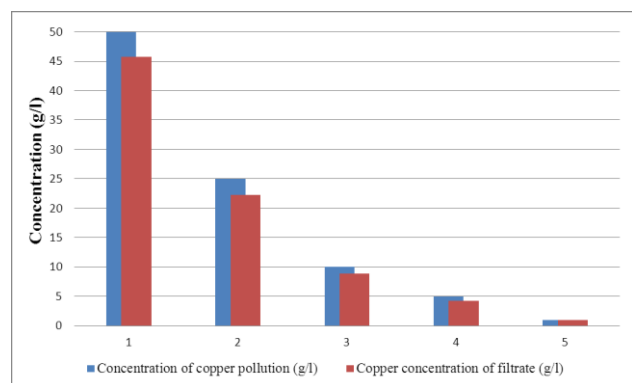
The adsorption results of the brown forest soil are shown on Figure 3 and Figure 4.

Figure 3. The copper adsorption results of brown forest soil from Gödöllő
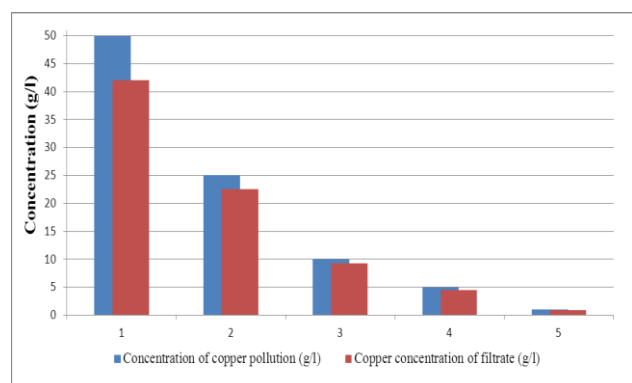
Figure 4. The copper adsorption results of brown forest soil from Soroksár

Analysis results of these two soil samples showed similarity. The same was expected by contamination. Adsorption was observed in case of both soil samples by each concentrations, so these two samples behave similarly after copper pollution.

Figure 5 and 6 show the results of copper pollution in chernozem samples.

The results of soil analysis showed difference in humus content, which may result difference in copper adsorption. It was confirmed by the laboratory analysis, because copper adsorption capacity was higher in sample from Dunaújváros (expect 1 g L^{-1} concentrated pollution), as more humus were in the soil. According to the literature, the soluble copper content increases in acidic medium, which is demonstrated well in case of the sample from Tiszavasvári.
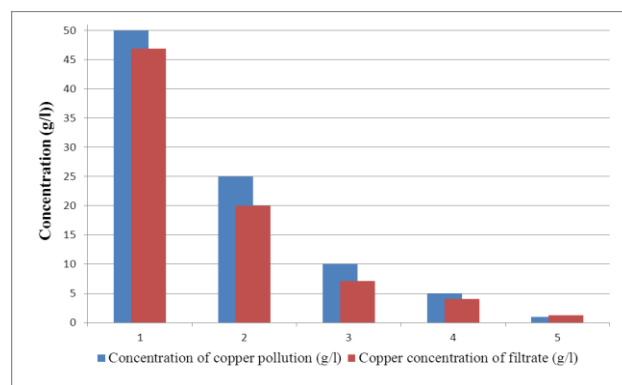

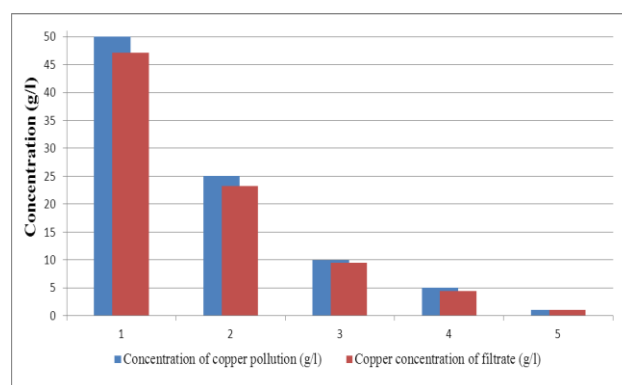**Figure 5.** The copper adsorption results of chernozem from Dunaújváros

Figure 6. The copper adsorption results of chernozem from Tiszavasvári
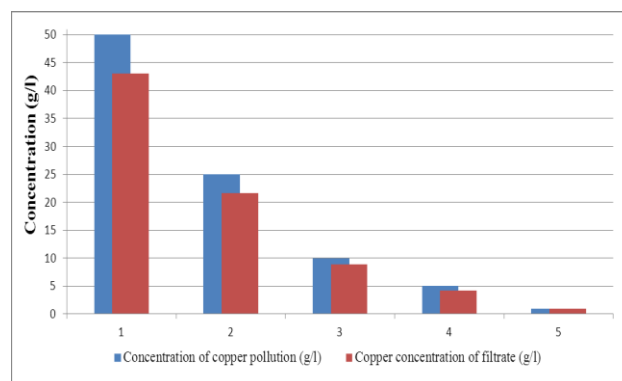

Figure 7. The copper adsorption results of sand with humus from Soroksár

Figure 7 and 8 show the results of sand with humus samples., A difference was measured in humus content as in the previous sample, which also resulted different copper adsorption. The humus-rich sample from Soroksár adsorbed more copper, than sample from Tiszavasvári in case of every concentration.

Figure 9 and 10 show the results of copper adsorption capacity in meadow soil samples from Soroksár and Tiszavasvári. Although the sample from Soroksár has less humus content, than sample from Tiszavasvári, the pH was having more important role in this soil type. During pollution demonstration very fast flow was observed, it was a very short time to complex formation, but the small pH resulted increasing soluble copper content, so the larger concentrations were measured by sample from Tiszavasvári.
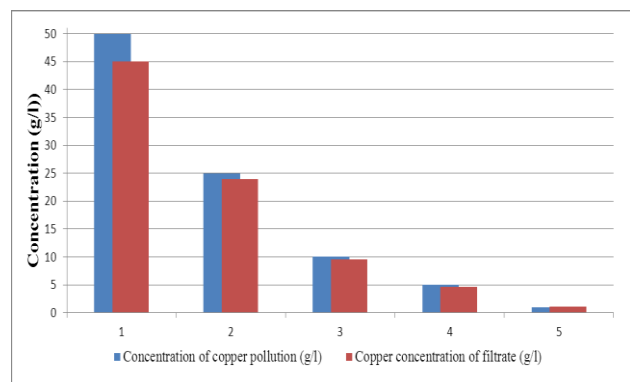
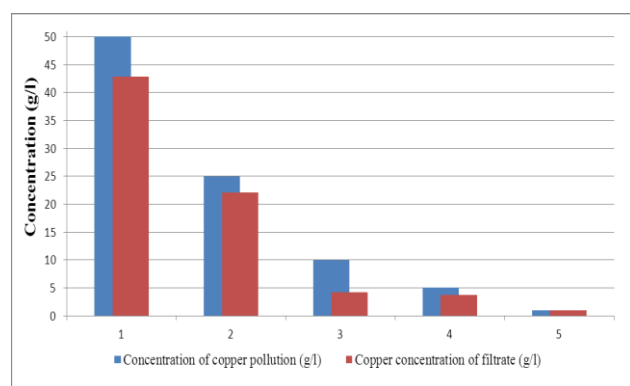**Figure 8.** The copper adsorption results of sand with humus from Tiszavasvári

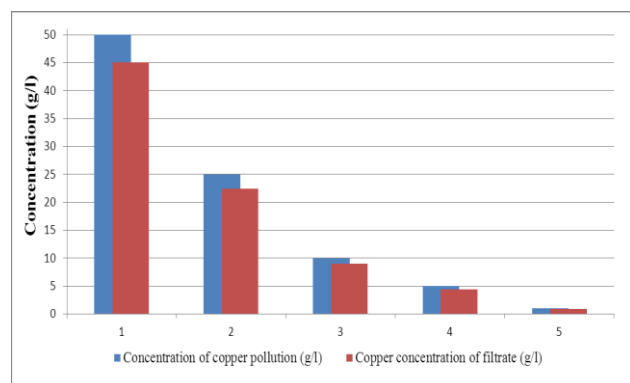**Figure 9.** The copper adsorption results of meadow soil from Soroksár

Figure 10. The copper adsorption results of meadow soil from Tiszavasvári

Table 6. The results of the Tukey's post hoc test for the contamination concentration for each soil type

Concentration	Soil type			
	brown forest	Cherno-zem	sand with humus	meadow soil
1 g L^{-1}	0,036 a	-0,138 a	-0,058 a	0,061 a
5 g L^{-1}	0,630 ab	0,765 ab	0,596 ab	0,945 ab
10 g L^{-1}	0,937 bc	1,691 ab	0,742 ab	3,418 ab
25 g L^{-1}	2,625 cd	3,399 b	2,171 bc	2,710 ab
50 g L^{-1}	6,084 d	3,034 b	5,950 c	6,049 b

Conclusion

Overall, it was observed that the copper adsorption capacity of soils depends on pH and humus content. At higher humus content, the copper adsorbs better in form of chelate complex, so the copper adsorption increasing. At lower pH level, more copper could be stationary, because the soluble copper content of soil increases in acidic medium.

Our results showed that the copper adsorption of soil is significantly varied at different contamination concentration ($F(4 ; 20) = 11.81$; $p < 0,001$) with high effect size (partial $\eta^2 = 0.88$) and observed power (> 0.99). However, the difference is insignificant in case of the four soil types ($F(3 ; 20) = 1.45$; $p = 0.26$). The results of the Tukey's post hoc test for the contamination concentration for each soil type can be found in Table 6.

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