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ESTIMATION OF COPPER CONTENT AND ITS FRACTIONAL COMPOSITION IN ARABLE SOILS**

Abstract. The aim of this study was estimation of total copper content and its fractional composition in arable soils in the Podlasie Province. It was found that total content of copper was typical for uncontaminated soils. In very light and light soils, more copper in available and potentially available fractions has been noted, by contrast in medium soils – in residual fraction which is unavailable for plants.

The copper is an essential element for proper growth and development of plants. It takes part in many physiological processes because it exists on a lot of oxidation states in vivo [10]. The soil is the main source of copper for plants. In Polish arable soils the average content of Cu [6] amounts to 6.5 mg kg^{-1} within the range from 1.3 to 48.2 mg kg^{-1}. According to the study from the year 1999, only 1% of investigated soils had elevated copper content (pollution of the first degree), mainly in the western part of the country (3%) [8]. The Polish podzolic sandy soils contain the least of copper, while the heavy loamy soils contain the most of it. The copper in the soil occurs as simple ions (Cu^{+}, Cu^{2+}) as well as complex ions, such as $CuOH^{+}$, $Cu(OH)_2^{2+}$, $Cu(OH)_4^{2-}$, $Cu(OH)_3^{-}$, CuO_2^{2-}, $HCuO_2^{-}$ and $Cu(CO_3)_2^{2-}$. In the soils with low pH, the high mobility of cationic copper forms is occurring, while with the pH increase the mobile anionic forms predominate. The main factors influencing the solubility, migration, and

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availability of copper in soils are as follows: pH, organic matter, clay minerals, hydroxides of Fe, Mn and Al as well as interactions with other elements [3]. It is plausible to state that copper shows little mobility in soils, thus it proves limited availability for plants. Only a small part of this element is present in soil in the easily soluble and exchangeable form. The copper has great affinity with organic matter and clay minerals, and precipitate, for example, in a form of sulphates, sulphides, and carbonates [3, 5, 7].

The plants may accumulate considerable amounts of copper despite its low mobility in soils.

The aim of the study has been to determine total copper content and its fractions (using the BCR method) in arable soils in the Podlasie Province. The influence of soil properties on the percentage share of Cu fractions as compared to the total content was also estimated.

MATERIAL AND METHODS

The research material consisted of 107 soil samples from the Podlasie Province. It included the mineral soils used as arable land and organic soils used as grassland. The samples were collected from the arable layer (0–30 cm) after the plant harvest and for the grassland – after the first mowing. Basic physicochemical properties of soil samples were determined: granulometric composition – by means of the Cassagrande's method with Proszynski's modification, organic carbon content – byapplying Tiurin's and pH in 1 mol· dm^{-3} KCl solution, by means of the potentiometric method. Available phosphorus and potassium – by means of the Egner-Riehm method as well as magnesium – by means of the Schachtschabel method in soils were also determined (Table 1). Based on the

TABLE 1. PHYSICOCHEMICAL PROPERTIES OF SOILS

Soils		pH	C_{org} [g kg^{-1}]	Content of soil fraction <0.02 mm [%]	Available phosphorus [P_2O_5 100g^{-1}]	Available potassium [K_2O 100g^{-1}]	Available magnesium [mg 100g^{-1}]
Very light and light n=35	min-max	4.0–7.6	6–37	4 –19	4.3–44.0	2.5–29.0	0.7–15.0
		–	17	12	15.7	10.5	4.7
Medium n=46	min-max	4.1–7.8	7–42	20–28	2.2– 42.0	3.2–4 8.4	1.7– 22.6
		–	24	22	13.7	13.5	9.6
Organic n=15	min-max	5.2–7.0	119– 425	–	33.3–379.9	8.0–61.0	13.2–131.2
		–	276	–	102.5	18.9	72.9
Heavy n=11	min-max	4.3–5.2	21– 40	35–	3.8–17.2	10.0–15.5	6.4–18.2
		–	28	–	10.1	12.4	10.9

percentage share of soil fraction < 0.02 mm, soils were divided into four groups: very light (0-10%) and light (11-20%), medium (21-35%), heavily (>35%) textured (further down in the text as very light, light, medium and heavy) as well as organic soils. The total copper content was determined after it had been previously digested in *aqua regia* (according to ISO 11466) by means of the GFAAS technique using Varian AA-100 apparatus.

The modified BCR method, using Sonics VCX 130 ultrasonic probe, was applied to evaluate the fractional composition of Cu in soil samples. Extraction included four stages:

1. acid soluble and exchangeable fraction (fraction I) – 1g of soil in the $100cm^3$ centrifuge tube containing 40 cm^3 of 0.11 $mol \cdot dm^{-3}$ acetic acid was sonicated for 7 minutes (output power – 20W) at the temperature of 22±5 ºC. Then the mixture was centrifuged at 3000g for 20 minutes. The extract was separated for the analysis purposes. The residue of 20 cm^3 of deionised water was sonicated for 5 minutes (output power – 20W) and centrifuged at 3000g for 20 minutes. The water was discarded.

2. reducible fraction bound to Fe/Mn oxides (fraction II) – to the residue from the first step, 40 cm^3 of 0,5 $mol \cdot dm^{-3}$ hydroxylamine hydrochloride fresh solution of pH 1.5 was added and sonicated for 7 minutes (output power – 20W) at the temperature of 22±5 ºC. Then the mixture was centrifuged at 3000g for 20 minutes. The extract was separated for the analysis purposes. The residue was rinsed with deionised water, like in the first step.

3. oxidisable fraction bound to organic matter (fraction III) – to the residue from the second step, 20 cm^3 of 30% hydrogen peroxide was added and sonicated for 2 minutes (output power – 20W) at the temperature of 22±5 ºC. Then the volume of H_2O_2 was reduced to approx. 1 cm^3 using water bath. To the moist residue, 50 cm^3 of 1 $mol \cdot dm^{-3}$ ammonium acetate was added and sonicated for 6 min. (otput power – 20W) at the temperature of 22±5 ºC. Then the mixture was centrifuged at 3000g for 20 minutes. The extract was separated for the analysis purposes. The residue was rinsed with deionised water, like in the previous steps.

4. residual fraction (fraction IV) – the residue from the third step was extracted using concentrated HNO_3 with addition of 30% H_2O_2. The extract was separated for the purpose analysis.

The content of the studied element in fractions was determined by means of the GFAAS technique using the Varian AA-100 apparatus. The percentage share of respective fractions in the total content of copper was calculated. The canonical factor analysis of obtained results for particular soil groups was conducted. The principal component analysis with varimax standardised rotation of factors was used. Variables characterised by the factor loading with modulus equal or greater than 0.65 were regarded as significantly influencing the particular factor.

RESULTS AND DISCUSSION

Among very light and light soils, loamy sands dominated, while sandy loam – among medium soils. The content of soil fraction <0.02 mm in very light and light soils ranged from 4 to 19% (12% on average) and from 20 to 28% (22% on average) in medium soils (Table 1). The reaction of soils varied (from very acidic to alkaline soils). Medium soils had a slightly higher reaction. Heavy soils were more acidic than lighter soils. The studied soils were characteristic for the Podlasie Region where light end acidic soils predominated. The content of organic carbon in both soil groups varied. In very light and light soils it amounted to 17 g kg^{-1} on average, in medium soils – 24 g kg^{-1} and in heavy soils it was higher about 4 g kg^{-1} as compared to medium soils. The content of organic carbon in organic soils amounted to 276 g kg^{-1} on average and was considerably varied. The average content of total copper in mineral soils was increasing with the increase in the content of soil fraction <0.02 mm (Table 2). In the organic soils the average content of Cu was higher approximately above 2mg than in mineral soils.

The percentage share of copper in respective fractions varied in all soil groups. The average percentage share of the fraction I was decreasing with the increase in the content of soil fraction <0.02 mm. The organic soils contained the least of Cu in the fraction under consideration. Comparing the percentage share of copper in respective fractions makes it plausible to state that in the fraction I, which is the most available for plants, it was the lowest but about 2% higher in very light and light soils than in medium soils. In the fraction II and III the percentage share of Cu was also higher in lighter soils, about 4% and 9%, respectively. The fraction II contained the most of copper as compared to the

TABLE 2. THE CONTENT OF TOTAL COPPER AND PERCENTAGE OF FRACTIONS

Soils		Total Cu	Fraction I [%]	Fraction II [%]	Fraction III [%]	Fraction IV [%]
Very light and light n=35	min.	2.62	1.10	10.56	11.68	5.17
	max	9.75	35.40	53.97	64.57	75.33
	$\bar{x}$	5.30	14.47	24.83	27.95	30.92
Medium n=46	min.	2.25	2.07	10.26	10.36	10.35
	max	13.00	26.72	58.70	49.78	73.03
	$\bar{x}$	7.08	12.49	20.79	18.80	33.13
Heavy n=11	min.	7.00	4.85	12.99	16.78	20.48
	max	10.80	16.74	18.46	26.85	58.43
	$\bar{x}$	8.31	9.73	15.74	21.04	38.61
Organic n=15	min.	3.50	3.59	12.57	7.30	21.05
	max	21.50	19.06	25.49	60.41	50.65
	$\bar{x}$	11.67	8.88	16.79	17.64	30.36

fraction I (15.74 to 24.83 on average), which was connected with the low solubility of copper oxides and hydroxides. The Cu^{2+} ion has the strongest adsorption ability on Fe/Al oxides and hydroxides among all divalent cations of heavy and transition metals [2]. Even more strongly is this cation specifically in the case of adsorption ability on manganese oxides [4]. Agbenin and Felix-Henningsen [1], investigating the mobility and solubility of copper in the Savannah soil fertilised for 50 years with mineral fertilisers, have obtained different results. The copper bound to amorphous Fe/Mn oxides, Mn oxides and crystalline Fe oxides in the top layer of soil (0-20cm) has proven to comprise 40.4% of total content. While the least of copper has been found in the water soluble fraction – 1.2%.

The percentage share of Cu in the fraction I and II in heavy soils was lower than in the case of lighter soils and in the fraction III – slightly higher as compared to medium soils. The residual fraction contained about 1/3 of total copper in the case of all the studied soils. In mineral soils the percentage share of the fraction IV was increasing with the increase in the soil fraction <0.02 mm. Shrivastava and Banerjee [9] have stated that the total pool of copper in arable soils is divided approximately in the ratio 1:1 between non-residual and residual fractions. According to these authors, the highest percentage of Cu (similarly as zinc) in non-residual fractions is related to its high mobility when introduced into the soil. Among non-residual fractions, the highest amounts of Cu they have found in the acid soluble fraction (17.2% of total content). It is a slightly higher content as compared to the soils in Podlasie.

The analysis which has been made for very light and light soils has allowed to determine the set of four factors which may account for about 72.26% of changes in soil environment (Table 3). According to the factor analysis, each

TABLE 3. FACTOR ANALYSIS OF COPPER FRACTION CONTENTS IN VERY LIGHT AND LIGHT SOILS

Variable	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.352463	0.520454	0.410215	0.000905
C_{org}	-0.404439	0.116499	0.361642	**0.695990**
P_2O_5	0.043777	**0.821114**	-0.307028	0.141235
K_2O	-0.153201	**0.757358**	0.069962	0.030208
Mg	-0.252836	0.572347	**0.657138**	0.027148
Content of soil fraction <0.02mm	0.114105	-0.198304	**0.797226**	-0.233275
Fraction I	**0.854960**	-0.049355	-0.107781	-0.100709
Fraction II	-0.066968	-0.055780	0.310991	**-0.796051**
Fraction III	0.544853	0.052653	0.568812	0.240634
Fraction IV	**0.833050**	-0.061170	0.179518	-0.079295
Initial value	2.116414	1.911232	1.929727	1.268448
Share	0.211641	0.191123	0.192973	0.126845

subsequent factor explains lesser and lesser percentage share of changes in the studied system. The factor 1 has clarified about 21.16% of changes and has been mainly influenced by the percentage share of Cu in the fractions I and IV. Both of those variables have been positively correlated with the factor 1. The factor 2 has explained about 19.11% of changes in the studied soil environment and its structure has been significantly influenced by the content of available phosphorus and potassium (variables positively correlated with the factor 2). The factor 3 has explained about 19.3% of changes in the soil environment. Its structure has been significantly influenced in the highest degree by the content of available magnesium and soil fraction <0.02 mm. Those variables have been positively correlated with the factor 3. The factor 4 has been mainly related to the changes of C_{org} content and the percentage share of Cu in the fraction II. The first variable (C_{org}) has been positively correlated with the factor 4, while the second (percentage of Cu) – negatively.

The analysis which has been carried out for medium soils has allowed to determine the set of four uncorrelated with each other factors which have explained about 70.09% of changes in the soil environment (Table 4). The factor 1 has explained about 23.55% of changes. Its structure has been influenced mainly by such variables as the content of C_{org}, available magnesium and soil fraction <0.02mm. It should be pointed out that factor loadings may be interpreted in terms of the correlation coefficients between respective variables and the factor which explains the changes in the soil environment. According to this assumption, it is plausible to state that all the variables significantly influencing

TABLE 4. FACTOR ANALYSIS OF COPPER FRACTION CONTENTS IN MEDIUM SOILS

Variable	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.546181	0.150664	0.407581	-0.484424
C_{org}	**0.853974**	-0.088551	-0.195187	-0.082666
P_2O_5	0.131820	-0.062850	**0.875345**	0.006488
K_2O	-0.087701	-0.137510	**0.720945**	0.293692
Mg	**0.756473**	0.235852	0.322788	-0.011841
Content of soil fraction <0.02mm	**0.768940**	-0.228486	0.018781	0.216731
Fraction I	-0.118918	0.633196	-0.214723	0.370100
Fraction II	-0.007669	0.048208	0.219302	**0.809970**
Fraction III	-0.013519	**0.865105**	-0.041217	-0.063423
Fraction IV	0.352402	0.396863	0.138082	0.552540
Initial value	2.354742	1.470400	1.709720	1.477259
Share	0.235474	0.147040	0.170972	0.147726

the structure of the factor 1 have been positively correlated with it. The factor 2 has clarified about 14.7% of changes and has been influenced significantly by the percentage share of Cu in the fraction III. This variable has been positively correlated with the factor 2. The factor 3 has explained about 17.1% of changes in the soil environment. Its structure has been mostly dependent on the content of available phosphorus and potassium (variables positively correlated with the factor 3). The factor 4 has been mostly connected to the changes of Cu percentage share in the fraction II (the variable positively correlated with the factor 4).

The factor analysis for organic soils has allowed to determine a set of four factors which have explained about 79.44% changes in the soil environment (Table 5). The factor 1 has explained about 25.97% of changes and mainly consisted of the following variables: the content of organic carbon, available magnesium and potassium as well as the percentage share of Cu in the fraction bound to Fe/Mn oxides. The content of C_{org}, K_2O and Mg has been positively correlated with the factor 1, while the Cu percentage share in the fraction II – negatively. The factor 2 has explained about 18.07% of changes in the studied soil environment and its structure has been influenced significantly by the percentage share of Cu in the fraction III which has been positively correlated with the factor under consideration. The factor 3 has explained about 20.51% of changes in the soil environment. Its structure has been influenced in the highest degree by pH and content of P_2O_5. These variables have been positively correlated with the factor 3. The factor 4 has been mostly connected to the percentage share of Cu in the fraction IV and has explained about 14.89% of changes in soil. This factor has been positively correlated with the Cu content in the residual fraction.

TABLE 5. FACTOR ANALYSIS OF COPPER FRACTION CONTENTS IN ORGANIC SOILS

Variable	Factor 1	Factor 2	Factor 3	Factor 4
pH	-0.025974	0.575528	**0.706762**	0.080177
C_{org}	**0.900741**	0.020681	-0.050253	-0.007087
P_2O_5	0.042973	-0.140845	**0.891099**	-0.172836
K_2O	**0.658799**	-0.426885	0.499809	0.144349
Mg	**0.701955**	-0.021553	0.115411	-0.014724
Fraction I	-0.411791	0.460450	0.369905	0.529752
Fraction II	**-0.650976**	-0.136031	0.331881	0.387704
Fraction III	0.055048	**0.928165**	-0.086876	0.025967
Fraction IV	0.021771	0.013558	-0.178252	**0.922662**
Initial value	2.337460	1.626384	1.845520	1.340335
Share	0.259718	0.180709	0.205058	0.148926

CONCLUSIONS

1. Investigated soils have been characterised by the natural content of total copper.

2. The distribution of copper among fractions has been dependent from many factors which have been correlated with each other, such as the pH, content of soil fraction <0.02mm, content of available phosphorus, potassium and magnesium, and mainly the content of organic carbon.

3. The most of copper in available and potentially available fractions has been found in very light and light soils, while in the medium, heavy and organic soils, the residual fraction has contained the highest amounts of Cu.

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OCENA ZAWARTOŚCI MIEDZI I JEJ FRAKCJI W GLEBACH UPRAWNYCH

Celem badań była ocena zawartości miedzi ogółem i jej frakcji w glebach uprawnych w woj. podlaskim. Stwierdzono, że badane gleby charakteryzowały się naturalną zawartością miedzi ogółem. Więcej miedzi w frakcji dostępnej i potencjalnie dostępnych było w glebach bardzo lekkich i lekkich, a w glebach średnich w frakcji rezydualnej niedostępnej dla roślin.