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COPPER SPECIATION IN SOILS CONTAMINATED WITH METAL-BEARING DUSTS

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Abstract. Investigations involved upper horizons of black earths – Phaeozems and deluvial soils – Phaeozems situated within the confines of the Legnica Copper Smelter sanitary protection zone. Apart from basic physico-chemical properties, different fractions of copper bound to mineral and organic soil components using McLaren's and Crawfords's speciation method were determined. With regard to total copper content, the analysed soils, especially their diagnostic horizons (epipedons mollic) belong to formations heavily contaminated with this element. The highest copper concentrations (approximately 54% total Cu) were associated with organic matter followed by copper bound with mineral colloids and Fe and Mn oxides (18% each). Distinctly lower Cu quantities (about 10%) were built into the spacial network of primary and secondary minerals. Fractions easily soluble in water and weakly bound with colloids (exchangeable forms) did not exceed 1% of total copper. Calculated correlation coefficients confirmed only a significant correlation between organic carbon and copper quantity (fraction F3) treated as the form associated with organic matter.

Keywords: heavy metals, soil contamination, speciation, copper, Phaeozems (proper black earths, humic deluvial soils).

INTRODUCTION

Heavy metals, alongside polycyclic aromatic hydrocarbons, belong to those chemical substances which are characterised by strong and persistent contamination of soil environment. They occur in pedosphere in different chemical compounds forming diversified combinations with its mineral and organic components. It is true that the determination of the total heavy metal content allows to estimate the scale of soil contamination but it does not provide information about the extent of their bioavailability and possibilities of their migration in soil environment. When trying to find an answer to the above problem, it is necessary to perform the so called speciation, i.e. identification and quantification of different forms (fractions) in which a given metal occurs in soil environment [9].

In biological sciences the most common procedure is so called operational speciation. It consists the isolation and quantification of different heavy metal fractions in soil by extraction with appropriate chemical reagents of increasing chemical strength [1,5,11,12].

The aim of this research was to determine various copper fractions occurring in the upper horizons of soils situated in the south-eastern part of the Legnica Copper Smelter sanitary protection zone.

MATERIAL AND METHODS

The object of performed investigations were samples collected in 1998 from accumulation-humus horizons of 12 soil profiles of which 5 represented black earths and the remaining samples were collected from humic deluvial soils. Proper black earths were situated approximately 1200-1600 m from smelter buildings, while humic deluvial soils were about 800-1200 m from shaft furnace chimneys.

The collected material represented the upper part of humus horizons with the thickness ranging from 0-10 cm, that is the zone theoretically most exposed to the accumulation of heavy metals released from the smelter.

Various copper fractions were determined using the procedure proposed by McLaren and Crawford [5] which employed the technique of atomic spectrophotometric absorption (ASA).

The following copper fractions were determined in the result of sequential extraction:

F1 - copper soluble in soil solution and extracted with 0.05 M $CaCl_2$ solution,

F2 - copper specifically bound by mineral colloids extracted with 2.5% CH_3COOH solution,

F3 - copper specifically bound by organic colloids extracted with 0.1 M $K_4P_2O_7$ solution, F4 - copper occluded in oxides, primarily iron and manganese, extracted with an oxalate solution of 3.25 pH,

F5 - residual copper in cristalline lattice structures of primary and secondary minerals extracted with the mixture of HF and $HClO_4$ solution.

Moreover, basic physical and chemical soil properties were determined using the following methods:

- texture composition by the Casagrande's densimetric method modified by Prószyński,
- organic carbon by Tiurin method,
- pH in water and in 1 M KCl using the potentiometric method,
- free iron and manganese oxides using the method of Mehra and Jackson [6].

RESULTS AND DISCUSSION

Upper horizons of analysed soils, similarly to those of lower levels, developed from a "clay variety of loess". Taxonomically they belong to silty loam formations (Tab. 1). Bearing in mind agronomic categories of soils currently used in Poland, soils of this area should be treated as heavy formations of category IV.

Table 1. Soil texture

Tabela 1. Skład granulometryczny

Profile no.	Depth (cm)	Sand 2-0,05	Silt 0,05-0,002	Clay < 0,002	Granulometric group PN-R-04033
			MM		
Proper black earths (Phaeozems)					
1	0-10	14	72	14	pł
2	0-10	36	56	8	płp
3	0-10	40	54	6	płp
4	0-10	20	70	10	pł
5	0-10	19	70	11	pł
Humic deluvial soils (Phaeozems)					
6	0-10	26	63	11	płp
7	0-10	22	68	10	pł
8	0-10	25	67	8	pł
9	0-10	29	62	9	płp
10	0-10	24	67	9	pł
11	0-10	21	66	13	pł
12	0-10	24	60	16	płi

The pH of the examined soils is fairly uniform and ranges from 6.60-7.40 in water and from 5.90-6.80 in 1 M KCl solution (Tab. 2). On the basis of the latter values, the examined samples can be considered as slightly acid or neutral.

The amount of organic matter found in the analysed soils varies considerably but it occurs usually in high quantities. Organic carbon concentrations range from 1.92-2.73% in the case of black earths and from 1.38-3.01% in samples derived from humic deluvial soils (Tab. 2). It is worth to emphasise that organic matter can sometimes be found even at the depth of 60-80 cm since such is the thickness of accumulative-humus horizons, especially in deluvial soils. Well developed mollic horizons are diagnostic epipedons of these soils.

Table 2. Chemical properties

Tabela 2. Właściwości chemiczne

Profile No.	Depth (cm)	pH		C org.	Fe	Mn
		H_2O	KCl		Free forms	
					%	
		Proper black earths (Phaeozems)				
1	0-10	6,90	6,10	2,73	0,36	0,02
2	0-10	6,70	5,90	1,88	0,41	0,03
3	0-10	7,40	6,80	1,92	0,24	0,02
4	0-10	6,80	6,40	2,64	0,31	0,02
5	0-10	7,00	6,60	2,32	0,43	0,03
		Humic deluvial soils (Phaeozems)				
6	0-10	6,60	6,40	2,20	0,38	0,03
7	0-10	7,00	6,30	2,44	0,36	0,02
8	0-10	6,90	6,50	3,01	0,31	0,02
9	0-10	6,70	6,20	2,38	0,40	0,03
10	0-10	6,80	6,00	2,15	0,43	0,03
11	0-10	6,90	6,30	2,86	0,25	0,02
12	0-10	6,80	6,40	1,38	0,47	0,03

Table 2 presents quantities of free iron and manganese forms. Total contents of these two elements are not excessively high and, as a rule, do not exceed 0.45%. It is evident from earlier studies that cristalline forms exceed amorphous ones in free iron [7].

Total copper contents, expressed as sums of individual fractions, range from 574.1 to 856.3 mg kg^{-1} (Tab. 3). Slightly higher quantities of this metal were found in humic deluvial soils which can be attributed to the fact that they occur closer to emission sources which, in the case of this study, were assumed to be shaft furnace chimneys. According to criteria of the degree of soil contamination developed by Kabata-Pandias *et al.* [2], the investigated soils should be classified as strongly or very strongly contaminated (IVth and Vth degrees).

The highest levels of copper determined in all examined soils were those bound to organic matter (F3). As a rule, this fraction makes up from 40 to 60% of total copper content (Fig. 1 and 2). It can be presumed that this element is associated with functional groups of humic and fulvic acids. This is confirmed indirectly by a highly significant, statistically proven correlation between organic carbon and F3 (Tab. 4).

Considerable quantities of copper were also bound to mineral colloids, primarily, of clay minerals or occluded on or inside iron and manganese oxides. This regularity was not confirmed unequivocally calculated correlation coefficients between colloidal clay concentrations and quantities of Fe+Mn free forms and appropriate copper fractions (F2 and F4).

Table 3. Content of copper fractions

Tabela 3. Zawartość frakcji miedzi

Profile No.	Depth (cm)	F1	F2	F3	F4	F5	∑F1-F5
		mg/kg					
Proper black earths (Phaeozems)							
1	0-10	1,0	115,0	408,4	131,3	99,0	754,7
2	0-10	2,3	66,2	310,7	140,2	72,5	591,9
3	0-10	1,4	60,8	340,0	120,6	44,0	566,8
4	0-10	2,5	74,3	412,2	98,0	65,3	652,3
5	0-10	2,6	85,0	330,5	104,8	51,2	574,1
Humic deluvial soils (Phaeozems)							
6	0-10	0,8	148,0	400,3	150,5	73,0	772,6
7	0-10	0,3	160,5	410,8	120,2	64,0	755,8
8	0-10	0,7	140,6	530,4	136,6	48,0	856,3
9	0-10	1,2	186,4	360,3	140,3	146,5	834,7
10	0-10	2,2	158,7	335,6	148,2	104,8	749,5
11	0-10	1,8	183,5	506,8	96,3	38,5	826,9
12	0-10	2,1	176,4	285,0	110,5	42,7	616,7

Table 4. Corelation coefficients
Tabela 4. Współczynniki korelacji

Properties of soil	Copper fractions F1	F2	F3	F4	F5	Cu-TOT ∑F1-F5
clay - %	0,105	0,446	-0,031	-0,365	-0,132	0,071
C org. - %	-0,344	0,102	0,888 *	-0,118	0,066	0,665 *
Fe+Mn free - %	0,289	0,213	-0,667 *	0,334	0,367	-0,202

* - significant at P = 0,05

Different, although distinctly lower, quantities of copper making part of the lattice system of primary and secondary minerals - referred to as F5 residual F5 (Tab. 3) – were found to occur. Copper accumulated there can either be their basic component or become part of a secondary spacial structure of aluminosilicates on the basis of the so called ionic diadochy. It cannot be ruled out altogether that, within this fraction itself, there may occur certain quantities of copper associated with difficult to break down parts of organic matter and Fe-Mn oxides.

Copper soluble in soil solution and easily exchangeable (F1) occurred in exceptionally small (almost trace) quantities as this fraction made up only less than 1% of total copper (Fig. 1 and 2). Since it is the most labile form, it does not influence chemical contamination of soil-ground waters.

The performed investigations revealed that considerable quantities of copper are bound to organic matter, clay minerals, Fe-Mn oxides or constitute part of the silicate cristalline lattice (Fig. 3). This is supported by the results of other investigations on copper fractionation both in non-contaminated soils [1, 5, 10] as well as in soils contaminated with emissions from copper smelters [3, 4, 8]. In the above quoted studies, the predominance of one of the earlier mentioned fractions depended on the method of extraction. When the method of Tessier *et al.* [11] was applied to analyse grey brown podzolic soils from Legnica region, they were found to be rich in copper associated with Fe-Mn oxides followed by that bound to organic matter. The above fractions made up approximately 76% of total copper [4]. When the method of Tessier *et al.* [11] was applied to analyse deluvial soils and black earths from the same region taken from several upper horizons it was found that copper forms associated with organic matter and Fe-Mn oxides were dominant [8]. This may point to the formation of permanent organic complexes with copper or signal some on-going processes of copper chemical sorption with hydroxyl groups of Fe-Mn hydroxides.

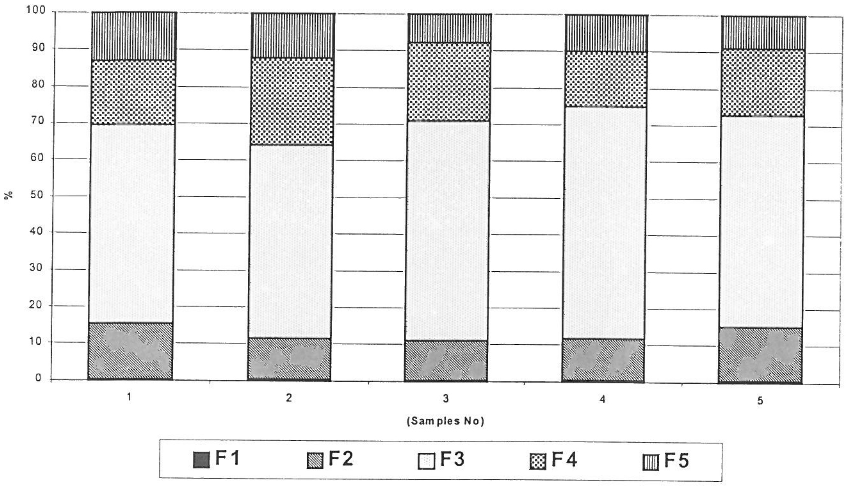

Fig. 1. Amounts of copper in individual fractions expressed as percentages of sum fractions (black earth).

Rys. 1. Procentowy udział poszczególnych frakcji miedzi w całkowitej jej ilości (czarne ziemie).

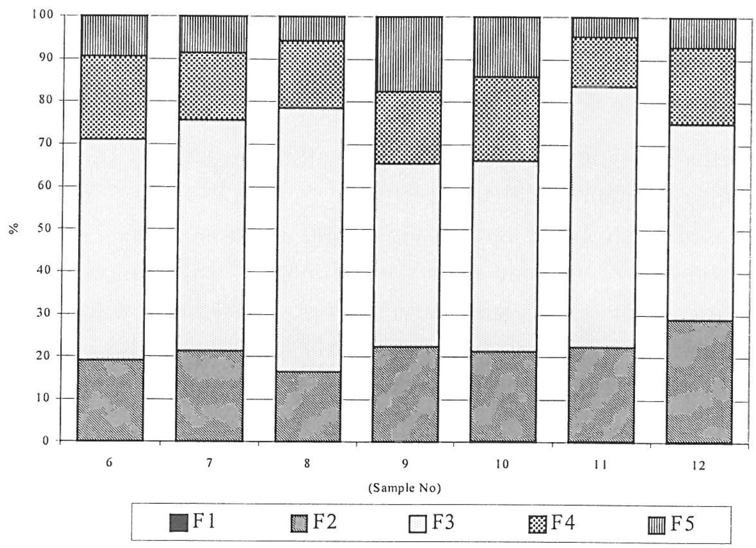

Fig. 2. Amounts of copper in industrial fractions expressed as percenntages of sum fractions (humic deluvial soils).

Rys. 2. Procentowy udział poszczególnych frakcji miedzi w całkowitej jej ilości (gleby deluwialne próchniczne).

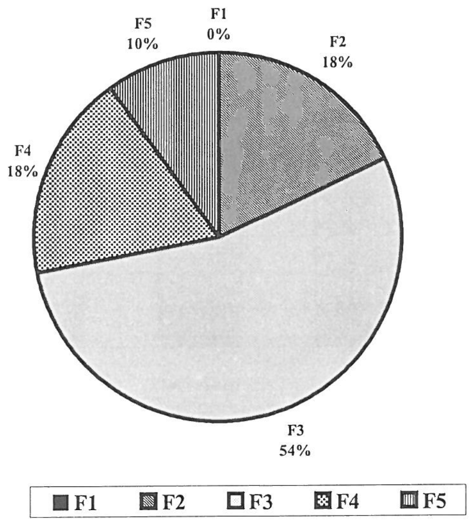

Fig. 3. Amounts of copper in industrial fractions (mean values).
Rys. 3. Zawartości frakcji miedzi (wartości średnie).

CONCLUSIONS

1. Black earths and deluvial soils occurring within the sanitary protection zone of the Legnica Copper Smelter developed from loess type formations were characterised by strong or very strong copper contamination.
2. Copper bound with organic matter was found as a dominant in the fraction composition of the examined material. Forms associated with Fe-Mn oxides and clay minerals are less frequent. Easily soluble fractions were found in trace amounts. There appears to be no danger of significant contamination of soil-ground waters with copper in the sanitary protection zone of the smelter, provided the present level of humus content and soil reaction close to neutral can be maintained.

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SPECJACJA MIEDZI W GLEBACH ZANIECZYSZCZONYCH PYŁAMI METALONOŚNYMI

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Streszczenie. Badaniami objęto poziomy wierzchnie czarnych ziem i gleb deluwialnych, usytuowanych w strefie ochrony sanitarnej Huty Miedzi Legnica. Oznaczono podstawowe właściwości fizyko-chemiczne oraz frakcje miedzi według metody McLarena-Crawforda. Największe ilości miedzi (ok. 54%) były związane z materią organiczną a następnie koloidami mineralnymi (ok. 18%), bądź okludowane na tlenkach żelaza i manganu (ok. 18%). Najmniejsze, niemal śladowe ilości tego metalu stwierdzono we frakcji łatwo rozpuszczalnej. Przy obecnej dość wysokiej zawartości materii organicznej i odczynie zbliżonym do obojętnego nie zachodzi obawa intensywnej migracji miedzi do wód glebowo-gruntowych.

Słowa kluczowe: metale ciężkie, skażenie gleby, miedź, czarne ziemie, gleby deluwialne.