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Original Research

Comparison of Three Methods of Copper Speciation in Chemically Contaminated Soils

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Abstract

In the presented study, three methods of copper fractionation – Tessier et al., BCR, and Zeien-Brümmer – were compared. The object of experiments comprised soil samples collected from the drilling level (0-25 cm) of soils situated at two transects (eastern and western) and at different distances from the source of emission (i.e. shaft furnace chimneys) near the Legnica Copper Smelter. Copper content was determined by the AAS method using appropriate reference materials.

A significant dependence was found in the copper concentration at a distance from the emitter that declined markedly at points more distant from it. Mean values of copper in individual fractions as well as confidence intervals exhibited a higher similarity between Tessier et al. and Zeien-Brümmer methods. In the case of all methods, copper quantities in fraction B (associated with Fe and Mn oxides) and C fractions (associated with organic matter) were similar. In the remaining fractions, i.e. A (easily exchangeable and carbonate) and D (residual), considerably greater differences were determined. The performed solubility indices analysis (fraction A/Σ fraction A+B+C+D) revealed that the results obtained using the Tessier et al. method differed considerably from those obtained by employing BCR and Zeien-Brümmer procedures.

Keywords: copper, contaminated soils, sequential extraction, Tessier et al., BCR, and Zeien-Brümmer fractionation procedures

Introduction

Generally speaking, soils situated in the neighborhood of non-ferrous metal smelters exhibit considerable amounts of heavy metals [1-4]. In the case of copper mills, the environment is contaminated, primarily by high quantities of copper and lead [5-7]. Legnica Copper Smelter, operating since the 1960s, emitted huge quantities of metalliferous dusts (about 8000 Mg/year) in the 1980s that contained the above-mentioned heavy metals. At the present time, following introduced technological changes, quantities of these mineral xenobiotics released into the atmosphere and then finding their way into soil are much lower. This is confirmed by the fact that quantities of emitted copper declined almost 15 times in the course of the last 30 years (from about 1000 Mg/year in 1980 to about 70 Mg/year at the present time) and those of lead – even 30 times (from about 1700 Mg/year in 1980 to about 50 Mg/year at the present time) [8]. The amount of accumulated metals, mainly in top layers of the soil, depends on the distance from shaft furnace chimneys, wind direction and physico-chemical properties of soil pedons. The presence of higher copper and lead concentrations in soils poses increased hazards of their dangerous migrations into

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ground and underground waters and transfer into the biomass of plants growing in these soils. Apart from the total heavy metal content used, as a rule, as a basis for the determination of the degree of soil contamination, quantities of so-called potentially mobile forms that may easily pass into soil solution and then percolate into deep soil horizons play an exceptionally important role. The presence of different forms of heavy metals in soils can be determined with the assistance of so-called speciation methods [9-11], which consist of sequential extraction of a soil sample using chemical solutions characterized by various degrees of aggressiveness.

The objective of this article was to compare the results of copper forms (fractions) obtained by treating the same samples with reagents in accordance with the three most commonly applied procedures of sequencing extraction methods, namely of Tessier et al. [12], BCR [13], and Zeien-Brümmer [14]. This referred, in particular, to the comparison of methods regarding fractions associated with individual soil components as well as the so-called solubility indices calculated on the basis of the ratio of the most easily soluble fractions to total copper content.

Object and Methods

Our investigations included humic diluvial soils as well as black and brown earths situated on two transects in the neighborhood of the Legnica Copper Smelter. They derived from accumulative-humic horizons (0-25 cm) and constituted pooled samples collected in a given spot from the surface of approximately 25 m^2 as individual samples with the assistance of a soil stick. Samples designated with numbers 1 to 4 derived from the first transect, east of the smelter, whereas samples numbered 5-9 were collected west of the copper smelter. Distances of individual test sites from the source of emissions are shown in Table 1.

Table 1. Soil taxonomy, distance and direction from the source of emission.

Soil sample designation	Type of soil	Distance to emitter (m)	Direct
1	Diluvial soils Phaeozems acc. to WRB [16]	500	E
2		1000	E
3		1500	E
4	Black earths, Phaeozems acc. to WRB [16]	2000	E
5	Brown soils Cambisols acc. to WRB [16]	200	W
6		400	W
7		600	W
8		800	W
9		1100	W

E – eastern, W – western

Table 2. Metal fractions and fractionation procedures in the Tessier et al., BCR, and Zeien and Brümmer methods.

Fraction No.	Tessier's et al. method		BCR method		Zeien and Brümmer method	
	Cu form – name of fraction	Extracting agent	Cu form – name of fraction	Extracting agent	Cu form – name of fraction	Extracting agent
I	Water soluble and exchangeable	1M $MgCl_2$	Exchangeable and bound to carbonate	0.1M CH_3COOH	Mobile (weak soluble)	1M NH_4NO_3
II	Bound to carbonates (acidic)	1M CH_3COONa + CH_3COOH	Bound to Fe and Mn oxides (reducible)	0.1M $NH_2OH{\cdot}HCl$ in HNO_3 (pH 2)	Exchangeable and occluded carbonates	1M CH_3COONH_4 (pH 6)
III	Bound to Fe and Mn oxides (reducible)	0.04M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH	Bound to organic matter and sulphides	30% H_2O_2 1M CH_3COONH_4 (pH 2)	Bound to Mn oxides	0.1M $NH_2OH{\cdot}HCl$ + 1M CH_3COONH_4 (pH 6)
IV	Specifically bound to organic matter (oxidisable)	0.02M HNO_3+H_2O_2 and 3.2M CH_3COONH_4	Residual	HCl and HNO_3 (3:1)	Bound to organic matter	0.025M NH_4-EDTA (pH 4.6)
V	Residual	concentrated HCl and HNO_3 (3:1)			Bound to amorphic Fe oxides	0.2M NH_4-oxalate (pH 3.25)
VI					Bound to crystalline Fe oxides	0.1M ascorbine acid in 0.2M NH_4-oxalate (pH 3.25)
VII					Residual	concentrated HF+$HClO_4$

Table 3. Texture of soil (%).

Soil sample designation	Sand	Silt	Clay	Textural group	
	2.0-0.05 mm	0.05-0.002	<0.002	PTG*	USDA**
1	19	73	8	pyg	SiL
2	31	57	12	pyg	SiL
3	31	56	13	pyi	SiL
4	21	64	15	pyi	SiL
5	29	62	9	pyg	SiL
6	26	63	11	pyg	SiL
7	36	53	11	pyg	SiL
8	58	30	12	gl	SL
9	60	29	11	gl	SL

* PTG – Polish Society of Soil Science
** USDA – United State Department of Agriculture

The following properties were determined in the collected material:

- Texture composition by hydrometer method [15]
- Soil reaction in 1M KCl by potentiometric method [15]
- Organic carbon concentration by Tiurin method [15]
- Copper speciation by the Tessier et al. [12], BCR [13], and Zeien-Brümmer [14] methods

A diagram of copper fractionation procedures is presented in Table 2. Copper content was determined by the AAS method using appropriate reference materials. The obtained results were subjected to statistical analysis using Statistica 7 software.

Results and Discussion

From the point of view of texture (Table 3), the analyzed soil samples belonged – according to classification by the Polish Society of Soil Science – [17] to dust formations (loamy or silty) or light clays, whereas according to international criteria [18], to silt loam (SiL) and sandy loam (SL), respectively. Despite distinct differences in sand (ϕ 2-0.05 mm) and silt (ϕ 0.05-0.002 mm) fraction content, the quantities of the clay (ϕ <0.002 mm) fraction in the examined fractions were more homogenous, which can exert an important influence on heavy metal sorption through the mineral part of their solid phase.

The content of organic carbon and, consequently, organic matter exhibited slightly lower differentiation (Table 4). All in all, it should be said that the examined soils were fairly rich in organic matter and, therefore, should accumulate significant quantities of copper. Soil reaction is among important parameters determining copper soil mobility (solubility); together with the increase of its acidity, more easily soluble forms of the metal, i.e. those that are more mobile and accessible to plants, are released in the soil. The majority of the analyzed soil samples revealed slightly acid reaction, although samples with neutral and alkaline reaction also occurred (Table 4). Hence, varying quantities of copper fractions of different degree of solubility should be expected in the analyzed material.

Table 4. Content of organic matter and reaction.

Soil sample designation	$C_{org.}$	Organic matter	Reaction pH_{KCL}
	$g \cdot kg^{-1}$		
1	11.1	19.1	6.92
2	23.6	40.7	5.76
3	20.6	35.5	5.33
4	14.9	25.7	4.37
5	41.1	70.9	5.28
6	16.0	27.6	7.40
7	17.1	29.5	7.16
8	10.1	17.4	6.67
9	9.0	15.5	6.16

Copper concentrations in individual fraction determined using the adopted methods are presented in Table 5. It should be emphasized that for purposes of certain unification facilitating the interpretation of the obtained results, some fractions were combined according to the diagram shown in Table 6. The adoption of such a form made it possible to calculate and compare copper content in individual fractions determined by the adopted methods. On the other hand, percentage proportions of individual copper fractions with respect to the total content of this metal in accordance with the Tessier et al., BCR, and Zeien-Brümmer methods are illustrated in Figs. 1-3.

In the Tessier et al. method (Fig. 1), the percentage proportion of individual Cu fractions most frequently assumes the following sequence: Fr. II > Fr. IV > Fr. III > Fr. I > Fr. V.,

Table 5. Content of different fractions (Cu) (mg·kg^{-1} ±SD).

Symbol of fraction	Method								
	1	2	3	4	5	6	7	8	9
Tessier et al. method									
A	1369.9±76.2	373.0±31.2	229.0±19.8	404.3±23.1	1508.5±130	260.3±25.3	75.9±6.3	45.3±4.3	47.8±4.6
B	514.3±36.1	151.3±13.6	74.2±6.5	87.9±7.6	344.2±26.2	96.2±8.7	33.3±2.9	22.1±2.3	25.1±2.6
C	252.9±23.2	281.0±21.4	197.6±15.6	129.8±11.3	514.1±39.3	154.2±13.6	103.4±7.4	53.9±4.9	44.8±4.3
D	28.1±2.65	38.8±3.7	41.0±3.7	27.5±2.6	89.1±7.8	26.5±2.5	23.2±2.2	15.5±1.4	15.1±1.6
Total	2165.2±155	844.1±75.1	541.8±46.2	649.5±61.3	2455.9±160	537.2±51.2	235.7±18.9	136.8±12.6	132.8±9.8
BCR method									
A	1311.9±91.2	138.4±9.8	59.1±4.9	177.3±14.6	806.7±70.3	73.2±6.2	19.3±1.8	17.7±1.8	23.9±2.1
B	552.4±50.9	243.1±19.6	158.5±14.2	212.8±18.4	728.3±69.8	148.7±12.1	51.7±4.9	35.2±2.9	30.3±2.9
C	173.2±16.3	216.9±20.2	152.9±13.8	90.8±8.7	33.5±2.9	131.9±10.7	66.1±5.8	27.6±2.4	24.3±2.5
D	33.8±2.8	52.9±4.8	41.8±3.7	25.2±2.4	110.6±9.8	29.3±2.8	24.1±2.5	11.9±1.3	10.3±1.2
Total	2071.3±150	651.3±54.3	412.3±36.1	506.1±47.3	1679.1±147	383.1±25.1	161.2±15.3	92.4±8.6	88.8±6.8
Zeien-Brümmer method									
A	1040.7±95.2	161.5±14.6	87.0±7.3	319.0±27.3	830.9±71.2	110.8±8.9	26.1±2.6	19.4±2.1	25.3±2.4
B	667.1±51.3	221.6±15.3	144.7±10.6	178.1±14.2	366.6±27.1	148.3±12.1	59.5±5.3	45.5±3.7	52.6±4.8
C	417.1±38.6	440.0±36.2	334.8±22.8	187.4±16.1	696.9±57.3	254.6±14.8	139.0±11.2	69.3±6.2	59.2±5.2
D	100.2±9.11	56.4±4.6	45.0±3.9	49.5±4.4	99.2±7.8	66.7±5.1	26.3±2.4	20.6±1.9	14.4±1.6
Total	2225.1±161	879.5±75.2	616.5±53.1	734.0±61.2	1993.6±153	580.4±43.1	250.9±21.3	155.0±11.3	151.5±12.3

although in some samples the above regularity is somewhat different. The percentage proportions of the fractions determined according to the BCR method differ slightly. In the majority of samples, the exchangeable fraction and the fraction associated with carbonates (Fr. I), and with Fe and Mn oxides (Fr. II) are dominant (in total, from 43% to 91%). The amount of copper associated with organic matter occupies an intermediate position, whereas copper built into the mineral crystalline network (Fr. IV) is characterized by the smallest percentage proportion. The results obtained using the Zeien-Brümmer procedure indicate unequivocal domination of copper fractions associated with organic matter (Fig. 3). Proportions of other fractions vary considerably and fail to indicate a clear trend.

It is evident from the data in Table 5 that total quantities of copper constituting the determined fractions vary greatly for the examined samples and range from 88.8 to 2225.1 mg·kg^{-1} soil. Points situated closest to the source of emissions are characterized by distinctly highest values. In general, the degree of soil contamination in the neighborhood of the Legnica Copper Smelter allows their inclusion into formations classified according to criteria elaborated by IUNG-PIB in Puławy as moderately contaminated (III°) to strongly contaminated (V°) soils [19]. According to the criteria currently in force in Poland [20], the majority of analyzed soil samples also exceeded acceptable copper soil concentrations (600 mg·kg^{-1}), classifying them as contaminated. Similar regularities with respect to the extent of copper contamination were reported by other researchers [21-24]. Fractionation of copper in soils of the copper smelter protection zone using the McLaren-Crawford method [25] proved the domination of the Cu form associated with organic matter as it constituted about 40-60% of the total content of this metal [6].

Table 6. Scheme of specification.

Name and symbol of fraction	Method		
	Tessier et al.	BCR	Zeien-Brümmer
Weak soluble and carbonates – A	I + II	I	I + II
Bound to Fe and Mn oxides – B	III	II	III + V + VI
Bound to organic matter – C	IV	III	IV
Residual – D	V	IV	VII

By the use of two-way analysis of variance the hypotheses about the influence of the place of sample collection (distance), the employed analytical method and appropriate fractions, as well as the interaction between fraction and method, were tested. It is clear from the data that copper content depended to a considerable extent on distance from emitters ($p<0.01$) and on the determined fraction ($p<0.01$). On the other hand, these data fail to show any significant difference between the Tessier et al., BCR, and Zeien-Brümmer methods ($p=0.53$).

The dependence of the copper content on the distance from emitters is obvious. It is worth emphasizing the fact that up to a distance of 1000 m in eastern direction (E) and 400 m in the western direction (W), no significant differences were found between mean copper concentrations (Fig. 4).

No indicator was found for interactions between the analyzed fractions and methods used during laboratory analyses ($p=0.15$).

The analysis of variance for solubility indices, which expresses the share of fraction A to total copper content,

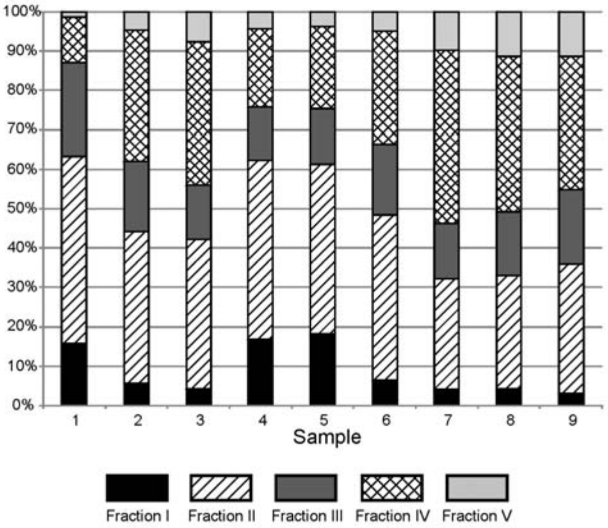

Fig. 1. Amounts of copper in individual fractions expressed as percentages of total copper according to the Tessier et al. method.

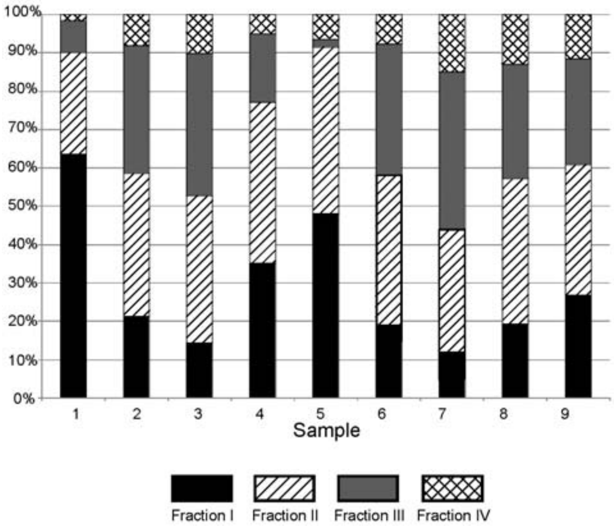

Fig. 2. Amounts of copper in individual fractions expressed as percentages of total copper according to the BCR method.

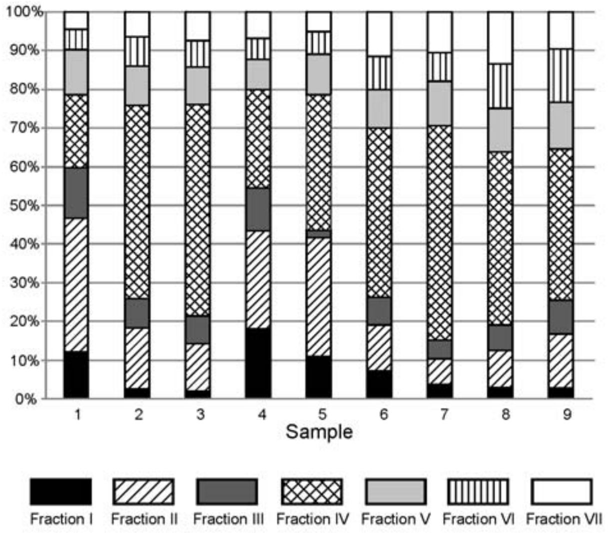

Fig. 3. Amounts of copper in individual fractions expressed as percentages of total copper according to the Zeien-Brümmer method.

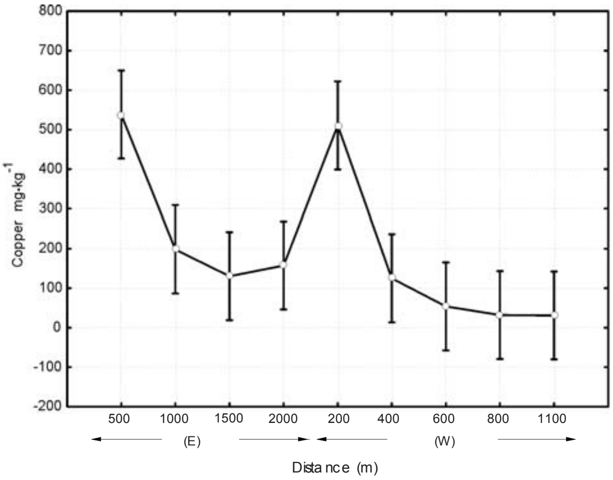

Fig. 4. Mean copper content and 95% confidence interval for samples taken at different distances from emitter.

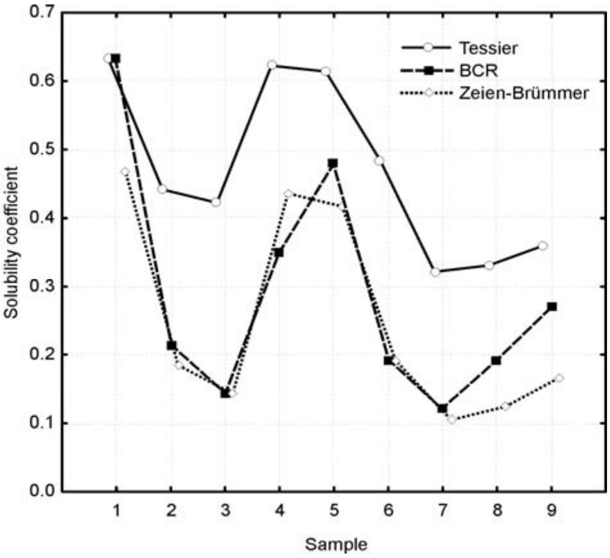

Fig. 5. Means for solubility coefficients determined by 3 methods for samples taken in 9 different places.

shows that both the distance from emitters as well as the applied analytical method exerted a highly significant impact on values of this index. This is also visible in Fig. 5. Results obtained using the Tessier et al. method differ from the results obtained with the assistance of the remaining methods for which solubility indices are similar.

Conclusions

The above-presented results made it possible to put forward the following generalizations:

- Sequential extraction carried out using three methods confirmed the existence of significant differences of copper content in individual fractions.
- Nevertheless, mean copper values in individual fractions as well as confidence intervals exhibited greater similarity between Tessier et al. and Zeien-Brümmer methods.
- In all the applied methods, Cu quantities in the fraction associated with Fe and Mn oxides were similar. The Cu fraction associated with organic matter between Tessier et al. and BCR was also similar.
- The performed analysis of solubility indices indicated that the results obtained by the Tessier et al. method differed significantly from the results recorded using the BCR and Zeien-Brümmer methods.

References

1. ALLOVAY B., DAVIES B.E. Heavy Metal Content of Plants Growing on Soils Contaminated by Lead Mining, J. Agric. Sci. Camb. **76**, 321, **1971**.
2. DROZD J., KOWALIŃSKI S., LICZNAR M. Zonal Contamination of Soil With Copper, Zinc and Sulphur and Soil Cover Changes Under the Erosion Effect in the Copper Metalurgy Works Influence Region, Warszawa, Soil Sci. Ann. **XXXV**, (1), 33, **1984**.
3. KUO S., HEILMAN P.E., BAKER A.S. Distribution and Forms of Copper, Zinc, Cadmium, Iron and Manganese in Soils Near a Copper Smelter, Soil Sci. **135**, (2)101, **1983**.
4. PILC L., ROSADA J., SIEPAK J. The Influence of Dust Emission from the „Głogów" Copper Foundry in Heavy Metal Concentrations in Agrocenoses, Pol. J. Environ. Stud. **8**, (2), 107, **1999**.
5. KABATA-PENDIAS A., PENDIAS H. Trace Elements in Soils and Plants, 2nd Edition. CRC Press. Inc. Boca Raton, Florida, **365**, **1992**.
6. MOCEK A. Possibilities of the Rational Cultivation of Chemically Contaminated Soils in the Industrial Sanitary Protection Zones, Agric. Univ. Ann. **185**, 98, **1989** [In Polish].
7. SYCZEWSKI P, SIEPAK J., NIEDZIELSKI P., SOBCZYŃSKI T. Research on Heavy Metals in Poland, Pol. J. Environ. Stud. **18**, (5), 755, **2009**.
8. BYRDZIAK K.H., JĘDRZEJEWSKI J., KIEDAL Z., MIZERA A., NIERZEWSKA M. Environment protection – bulletin 2002-2004. KGHM Polska Miedź S.A. Ed. KGHM Cuprum sp. z o.o. – CBR in Wrocław and Department of Ecological Politics KGHM in Lublin, Lublin-Wrocław, **2005** [In Polish].
9. GWOREK B., MOCEK A. Comparison of Sequential Extraction Methods with Reference to Zinc Fractions in Contaminated Soils, Pol. J. Environ. Stud. **12**, (1), 41, **2003**.
10. GWOREK B., KONDZIELSKI I., MOCEK A. Speciation of Lead in Industrially Polluted Soils – comparison of Two Extraction Methods. Environ. Eng.-Pawłowski, dudzińska and Pawłowski (Eds.), London, **2007**.
11. SOBCZYŃSKI T., SIEPAK J. Speciation of Heavy Metals in Bottom Sediments of Lakes in the Area of Wielkopolska National Park, Pol. J. Environ. Stud. **10**, (6), 463, **2001**.
12. TESSIER A., CAMPBELL P.B.C., BISSON M. Sequential Extraction Procedure for the Speciation of Particular Trace Metals. Anal. Chem., **51**, (7), 844, **1979**.
13. MOSSOP K.F., DAVIDSON CH.M. Comparison of Original and Modified BCR Sequential Extraction Procedures for the Fractionation of Copper, Iron, Lead, Manganese and Zinc in Soils and Sediments; Anal. Chimica Acta, **478**, 111, **2003**.
14. BRUMMER G.W. Heavy Metal Species, Mobility and Availability in soils, [In:] Importance of Chemical "speciation" in Environmental Processes. Springer, Heidelberg, pp. 399-414, **1986**.
15. MOCEK A., DRZYMAŁA S. Genesis, Analysis and Classification of Soils. Poznan Univ. of Life Scien. **418**, **2010** [In Polish].
16. FAO, ISRIC, ISSS. World Reference Base for Soil Resources Report. **1998**.
17. POLISH SOCIETY OF SOIL SCIENCE. Particle Size Distribution and Textural Classes of Soils and Mineral Materials – Classification of Polish Society of Soil Science 2008. Soil Sci. Ann. **LX**, (2), 5, **2009** [In Polish].
18. SOIL SURVEY STAFF. USDA-NRCS. Soil Taxonomy. A Basic System of Soil Classification for MAKING and Interpreting Soil Surveys. Agric. Handb. 436, U.S. Gov. Printing Office, Washington D.C., **1999.**
19. TERELAK H., STUCZYŃSKI T., PIOTROWSKA M. Heavy Metals in Agricultural Soils in Poland. Pol. J. Sci. **30**, (2), **1997**.
20. LAW GAZETTE. Regulation of the Minister of Environment regarding standards of soil quality and standards of land quality. **5**, 1359, **2002** [In Polish].
21. GWOREK B., MOCEK A., KONDZIELSKI I. Speciation of Copper in Industrially Polluted Soils – a Comparison of Two Sequential Extraction Methods, Pol. J. Environ. Stud. **15**, (2A), 295, **2006**.
22. CHODAK T., SZERSZEŃ L., KOLLENDER-SZYCH A. The Influence of Copper Industry on the Properties and Mineral Composition of Various Size Fractions in Soils. Proc. of 10th Conference on Clay Mineralogy and Petrology. Ostrava (1986) pp. 335-342, **1988**.
23. KARCZEWSKA A. Heavy Metals in Soils contaminated by Copper Smelters – Forms and Solubility. Agric. Univer. of Wrocław, **CLXXXIV**, 432, **2002** [In Polish].
24. KOWALIŃSKI S., DROZD J., LICZNAR M. The Influence of the Distance of a Copper Smelter on the Physico-chemical Properties and Organic Compounds of Soils. Pol. J. Soil Sci. **12**, (1), **1979**.
25. McLAREN R.C., CRAWFORD D.V. Studies on Soil Copper. I. The Fractionation of Copper in Soils. J. of Soil Sci., **24**, 443, **1973**.