

Comparison of Sequential Extraction Methods with Reference to Zinc Fractions in Contaminated Soils

B. Gworek^{1,2*}, A. Mocek³

¹Institute of Environmental Protection, ul. Krucza 5/11, 00-548 Warsaw, Poland

²Department of Soil Environment Sciences, Warsaw Agricultural University, Warsaw, Poland

³Department of Soil Science, Poznań Agricultural University, Poland

Received: 8 July, 2002

Accepted: 26 August, 2002

Abstract

The total amount of zinc extracted from soils in the Legnicko–Głogowski Copper Mining Region using either the McLaren and Crawford or Tessier *et al.* method differed within the limits of 2–35%, while the application of the latter method yielded higher results for 86% of analyzed samples.

Amongst zinc fractions analyzed using the McLaren and Crawford method the fraction of zinc specifically bound and less easily exchangeable dominates in horizons where there is an accumulation of organic matter while in the remaining horizons a residual fraction. Whereas when the Tessier *et al.* method was used the residual fraction dominated in all the genetic horizons of soils under study.

The smallest amounts of zinc, regardless of the method applied, were found in the fraction embracing ions found in the soil solution and those easily exchangeable.

The quantity of mobile zinc (accessible for plants) calculated on the basis of sequential extraction according to McLaren and Crawford procedure amounts to up to 14–54% while the quantity obtained by the Tessier *et al.* method amounts to up to 6–28% of total zinc value. A significant difference was found in accumulation horizons and amounted to 40–54% and 8–28% respectively.

The share of organic substance in zinc binding was smallest when assessed on the basis of sequential analysis according to McLaren and Crawford. While in the case of applying the method by Tessier *et al.* the smallest amounts of zinc were bound to carbonates, sulphates and phosphates.

Keywords:

Introduction

Proper evaluation of the effect of heavy metals on the natural environment is possible on the basis of knowledge about their forms and bindings with soil components found. Sequential extraction could be the source of the above information, enabling identification and quantitative

determination of various forms of the same chemical element. This extraction procedure takes advantage of the solubility mechanisms in water, ionic exchange, oxidation and reduction processes, as well as complexation and digestion of mineral and organic soil components. Separated fractions are defined in a conventional and operational manner, and as such present a certain approximation in describing different forms of metals found.

*Corresponding author

So far, there have been many sequential extraction procedures elaborated that differed by the type and order of extracted fractions. The selection of reagents and extraction conditions, due to their variety, make comparisons of obtained results impossible. One of the first methods of sequential extraction was developed by McLaren and Crawford [1] for copper fractionation in arable soils. The Tessier *et al.* method [2] has gained the highest acknowledgement and broadest application in soil and geological studies, as well as in environmental protection.

The aim of this work was to identify and compare different zinc fractions determined by the sequential extraction method according to the two procedures prepared by McLaren and Crawford [1] and Tessier *et al.* [2].

Materials and methods

The investigated soils were located in the Silesian Luzycka Lowlands within the Legnicko-Glogowski Copper Mining Region. The analysed profiles were situated at the eastern direction within a distance of about 1300-1600 metres from the emission source centre, in the form of stacks of the shaft furnaces of the "Legnica" Copper Smelter. Due to the majority of western winds they are affected mostly by the proluvial material deposits, rich in *inter alia*, heavy metals and sulphur originating from the surrounding areas of the smelter.

The study covered 6 profiles situated in-between two hills (slopes of 8-10%) at the bottom of which deluvial brown soils were found (144-150 m above sea level), next transforming into deluvial humous soils (141-144 m above sea level). Soil samples for laboratory analyses were taken from each genetic horizon, taking into consideration turf accumulation horizons (0-3 cm) in order to determine the heavy metal accumulation in the layer mostly affected by the emission of pollutants released from the smelter. The following parameters were determined in the samples taken, after drying:

- granulometric composition using the Casagrande method, modified by Prószyński (according to Mocek

- et al.* [3]) in samples after separating their skeletal parts;
- soil pH in H₂O and 1M KCl using the potentiometric method (according to Mocek *et al.* [3]),
- Organic carbon using the Tiurin method (according to Mocek *et al.* [3]),
- Cationic sorption capacity using the Metson method (according to Mocek *et al.* [3]),
- Fe and Mn oxides using the Mehra – Jackson method (Mehra and Jackson [4]).

Zinc fractions were determined by both the McLaren and Crawford method [1] and the Tessier *et al.* method [2]. These methods enable the separation of 5 fractions defined operationally; however, differing with respect to the order of fraction separation and the type and concentrations of reagents used (Table .) To separate the first fraction (FI) including ions in the soil solution and easily exchangeable – non-specifically sorbed ions – in both methods the chloride solutions of different concentrations were used. The next fraction in turn (FII) in the sequential extraction procedure, according to McLaren and Crawford, is the fraction of ions specifically sorbed on the surface of oxides and at the edges of clay-like minerals. This fraction is identified only in a few procedures, whereas in the Tessier *et al.* method the second fraction in the order, called the carbonate (FII), describes the metal fraction chemically sorbed mainly by secondary carbonates, sulphates and phosphates, of which calcite and dolomite are of highest significance. The sodium acetate solution of pH 5 used dissolves carbonates and at the same time may cause a release of part of metals specifically sorbed, and having complexation properties may additionally cause a release of metals bound to organic matter. Potassium diphosphorane (V), causing dispersion of organic colloids and at the same time complexing the released cations, was used to fractionate metals bound to organic matter in the McLaren and Crawford method (FIII). Furthermore, diphosphoranes (V) cause partial digestion of different forms of iron oxides. In the Tessier *et al.* method oxidizing reagents (H₂O, HNO₃), which cause decomposition of the

Table 1. Metal fractions in soils and ways of their determination using two methods of sequential extraction.

Fraction No.	Determined metal fraction		Extraction reagent	
	McLaren and Crawford	Tessier et al.	McLaren and Crawford	Tessier et al.
I	Present in soil solution + easily exchangeable (non-specifically bound)		0.05 M CaCl ₂	1 M MgCl ₂
II	Specifically adsorbed and less exchangeable	Bound to carbonates	2.5% CH ₃ COOH	1 M CH ₃ COONa + CH ₃ COOH
III	Specifically bound to organic matter	Bound to Fe-Mn oxides	0.1 M K ₄ P ₂ O ₇	0.04 M NH ₂ OH•HCl in 25% CH ₃ COOH
IV	Occluded in oxides	Specifically bound to organic matter	1.0 M C ₂ H ₂ O ₄ + 0.175 M (NH ₄) ₂ C ₂ O ₄	0.02 M HNO ₃ + H ₂ O ₂ and 3.2 M CH ₃ COONH ₄ in 20% HNO ₃
V	Residual		30% HF + concentrated HClO ₄	HCl + HNO ₃ (3 : 1)

organic matter and thus a release of metals bound to it, are used to determine metal fractions bound to organic matter (FIV). Reagents used to separate this fraction also cause the decomposition of the sulphide fraction. The metal fraction, called the oxide fraction in the McLaren and Crawford method (FIV) is extracted in the oxalate buffer. This reagent affects the amorphous and micro-crystalline iron oxides and does not digest the crystalline forms. In the Tessier *et al.* method the metal oxide fraction (FIII) is released by hydroxylamine in hydrochloric acid. This reagent is considered to be specific for the extraction of metals co-occluded in manganese oxides and amorphous iron oxides. This method of extraction may also partly release heavy metals bound to organic matter. The residual fraction (FV) is usually digested in both methods in the hydrofluoric and chloric (VII) acids or in *aqua regia*.

A correlation coefficient was calculated in order to determine the relation between the zinc fractions and selected soil properties.

Results and Discussion

Deluvial humous and brown soils, selected for examination, have been formed from dusty loess-like deposits [5]. The soil properties listed in Table 2, indicate the ability of soils, *inter alia*, to bind heavy metals as well as to transform them from easily soluble forms to hardly available, and also play a decisive role in the reverse phenomenon [6,7,8,9]. The first group of phenomena covers processes leading to a decrease in solubility and mobility of elements, that is ionic sorption by mineral and organic sorption complex, precipitation of insoluble compounds from the solution and biological accumulation. The opposite group of phenomena includes processes increasing the mobility of the elements, that is desorption, solubility and mineralization of organic compounds [2,10,11,12].

The results of sequential extraction carried out using the McLaren and Crawford method are presented in Table 3, and using the Tessier *et al.* method in Table 4. The sum of extracted 5 fractions (FI – FV) have been considered in this work to be the total amount of zinc. The amount of extracted zinc using both methods varied within the limits of 2% to 35%. For the majority of soil samples tested by the Tessier *et al.* method a higher quantity of zinc was extracted compared to the McLaren and Crawford method, especially originating from the brown horizon (Bbr), where the difference amounted to 30 and 35%. For the material originating from mineral and organic horizons the differences in the zinc extracted varied within the limits of 2-15%, and 2-29% for the parent rock. Despite applying full decomposition in the McLaren and Crawford method to determine residual fraction (FV) and acid digestion in the case of the Tessier *et al.* method, higher results were obtained in the latter method for 86% of analyzed soil samples.

Furthermore, the amount of zinc bound to organic matter extracted by the Tessier *et al.* method (FIV) in 72% of examined soil samples was higher compared to the

amount extracted using the McLaren and Crawford method (FIII). Most likely the reason for the lower contents of zinc in this fraction determined by the McLaren and Crawford method is the salt used for extraction (sodium pyrophosphate), which after hydrolysis causes dissolving of the organic compounds only, which are soluble in the alkaline environment (pH 10), and after their dissociation an ionic exchange takes place between potassium ions and specifically bound metal ions. Whereas the determination of zinc fractions in the Tessier *et al.* method is based on mineralization of the organic matter. Therefore, it is most likely that the amount of zinc determined in this fraction by the Tessier *et al.* method is higher than in the McLaren and Crawford method. This is especially the case for accumulation horizons of organic matter. Whereas in the parents rock (C) and brown horizons (Bbr), a higher amount of zinc might be the effect of decomposition of sulphides [5]. The calculated correlation coefficients indicate significant dependence between the amount of zinc in this fraction and the organic matter (Table 5.).

Similarly, the amount of zinc bound to the fraction of iron and manganese oxides determined by the Tessier *et al.* method (FIII) was higher in 77% of analyzed soil samples compared to the results obtained by the McLaren and Crawford method (FIV). It is most likely that the higher amount of zinc extracted in the hydroxylamine solution (Tessier *et al.* method) partially released the amount of zinc bound to organic matter, especially as this fraction is determined prior to mineralization of organic matter. However, the oxalate buffer used not only in the McLaren and Crawford method is considered to be a specific reagent affecting the amorphous and microcrystalline iron oxides (despite the fact that it does not digest crystalline forms) no significant dependence was observed between the amount of iron and manganese oxides and the amount of zinc in a given fraction. No such dependence was also observed using the Tessier *et al.* method (Table 5.).

The amount of zinc present in the soil solution and easily exchangeable (non-specifically bound) - FI - determined by the Tessier *et al.* method was higher in 82% of analysed soil samples than by the McLaren and Crawford method. This fact is most likely the effect of magnesium chloride applied for zinc extraction in the Tessier *et al.* method. Magnesium ions having a more similar ionic radius (0.78 nm according to Goldschmidt) to zinc ions (0.83 nm) than calcium ions (1.06 nm), as well as more similar electronegativity to zinc. Regardless, the applied concentration of salt, most likely contributed to the extraction of greater amounts of zinc. Thus, there is possibly a positive correlation between the zinc contents in this fraction and the amount of colloidal clay and organic matter (Table 5.).

Amongst the analyzed zinc fractions determined by the McLaren and Crawford method zinc fraction specifically bound and less exchangeable (FII) dominates in mineral and organic horizons, also in comparison with the next fraction determined by the Tessier *et al.* method (FII), where not only zinc ions bound to carbonates, sulphates and phosphates are extracted, but also a part of specifically

sorbed zinc (Figure 1-4). This fraction amounts to up to 21 to 54% of total zinc content determined by the McLaren and Crawford method, and at the same time in the accumulation horizons of organic matter it presents 41-54% and it decreases together with the depth to 14-28%. Whereas zinc in the second fraction determined by the Tessier *et al.* method shows from 6 to 28% of its total contents. Also, the percentage share of zinc in this fraction in relation to its total contents decreases with depth. Such a result in the McLaren and Crawford method was obtained by using acetic acid solution of pH 2.5, having higher extraction ability than the ammonium acetate solution of pH 5 applied in the Tessier *et al.* method.

The way of extraction of the zinc fractions by both methods enables, according to Salbu *et al.* [13] the

calculation of the mobility index (MI) for zinc on the basis of the following equation:

$$MI = \frac{FI + FII}{FI + FII + FIII + FIV + FV} \times 100$$

The amount of metal calculated this way is considered to be available for plants by the authors mentioned above. The mobility index of zinc determined by the McLaren and Crawford method in the examined soils varied within the limits of 14 to 54%, and 6-28% in the method by Tessier *et al.* The amount of zinc available for plants determined by the McLaren and Crawford method in the accumulation horizons of examined soils amounts to 40-54% of its total

Table 2. Basic soil properties.

Profile No.	Genetic horizon	Depth cm	C org.	Colloidal clay	Fe-OX	Mn-OX	pH		T CEC
			%		mg · kg ⁻¹ d.w.	H ₂ O	KCl	cmol(+)/kg	
Deluvial humous soils <i>Gleyic Phaeozems</i>									
1	Ad	0 - 3	2.21	9.0	1326.2	132.1	6.50	6.15	20.40
	A	4 - 15	2.36	10.0	1186.5	131.6	6.75	6.45	19.16
	ACgg	16 - 68	1.20	9.0	1238.6	166.4	6.60	6.20	15.35
	Cgg	69 - 100	0.51	11.0	1170.6	94.8	6.90	6.40	14.60
2	Ad	0 - 3	2.26	9.0	1381.3	145.2	6.80	6.40	21.50
	A	4 - 46	1.88	8.0	1460.6	105.1	6.85	6.40	18.32
	Cgg	47 - 98	0.62	9.0	1783.3	120.6	6.90	6.50	12.46
3	Ad	0 - 3	2.64	8.0	1366.4	90.3	6.65	6.20	24.12
	A	4 - 27	2.33	10.0	1429.4	91.5	6.80	6.40	21.76
	AC	28 - 64	0.82	10.0	1356.5	79.9	6.70	6.35	16.15
	Cgg	65 - 100	0.40	11.0	1146.4	278.6	6.80	6.35	12.56
4	Ad	0 - 3	2.48	11.0	1421.1	128.6	6.50	6.00	20.62
	AC	4 - 58	2.10	7.0	1444.3	126.1	6.70	6.20	18.44
	Cgg	59 - 130	0.74	10.0	1232.6	163.5	7.10	6.50	13.16
Deluvial brown soils <i>Eutric Cambisols</i>									
5	Ad	0 - 3	1.41	10.0	1092.2	94.9	6.70	6.10	13.27
	A	4 - 20	1.18	8.0	1110.4	114.0	6.90	6.40	10.86
	Bbr	21 - 48	0.42	18.0	937.6	86.8	6.95	6.50	10.30
	C	49 - 120	0.34	11.0	855.2	87.7	6.90	6.55	8.14
6	Ad	0 - 3	1.34	9.0	1134.3	98.2	6.50	6.00	10.63
	A	4 - 16	1.20	9.0	1215.4	92.4	6.60	6.15	10.24
	Bbr	17 - 45	0.38	21.0	1084.2	83.3	6.65	6.30	8.80
	C	46 - 100	0.27	11.0	967.5	81.5	6.80	6.40	7.35

contents, whereas 23-29% and 14-28% in the brown and parents rock horizons. But the amount of zinc available for plants determined by the Tessier *et al.* method in the accumulation horizons of the tested soils is significantly lower and amounts to up to 8-28% of total contents, and from 6 to 20% in the remaining genetic horizons.

The percentage shares of zinc in the analysed fractions in the major genetic horizons of the examined soils, regardless the type, are found in the following sequences:

· for the accumulation horizon (A):

according to McLaren and Crawford:

FII (39) > FV (23) > FIV (16) > FIII (14) > FI (1)

according to Tessier *et al.*:

FV (36) > FIII (26) > FIV (19) > FII (17) > FI (2)

· for the brown (cambic) horizon (Bbr):

according to McLaren and Crawford:

FV (48) > FII (25) > FIV (15) > FIII (12) > FI (0,01)

according to Tessier *et al.*:

FV (56) > FIII (19) > FIV (14) > FII (8) > FI (3)

· for the parents rock (C):

according to McLaren and Crawford:

FV (51) > FII (12) > FIV (11) > FIII (10) > FI (6)

according to Tessier *et al.*:

FV (66) > FIII (12) > FII (10) = FIV (10) > FI (2)

Regardless of the analytical procedure used, in the majority of cases the share of zinc residual fraction (FV) is the dominating one, whereas the smallest is the share of easily exchangeable zinc fraction (FI) in the examined genetic horizons of soil. Next, according to the McLaren

Table 3. Zinc fractions determined by McLaren and Crawford method in deluvial soils (mg·kg⁻¹ d.w.). Mean for n = 4 and ± sd.

Profile No.	Genetic horizon	Depth cm	Fractions					Σ FI - V
			I	II	III	IV	V	
Deluvial humous soils <i>Gleyic Phaeozems</i>								
1	Ad	0 - 3	0.50 ± 0.08	106.67±12,4	37.93 ± 3.9	74.52 ± 8.3	44.35 ± 5.3	263.97
	A	4 - 15	0.08 ± 0.01	34.16 ± 9.3	6.08 ± 1.7	16.11 ± 3.7	29.43 ± 7.4	85.86
	ACgg	16 - 70	0.09 ± 0.01	23.48 ± 7.4	5.05 ± 1.7	9.53 ± 2.2	28.44 ± 6.8	66.59
	Cgg	71 - 100	0.22 ± 0.03	11.46 ± 2.3	3.12 ± 0.9	3.38 ± 1.1	23.60 ± 3.1	41.78
2	Ad	0 - 3	0.99 ± 0.12	91.62 ± 10.2	26.93 ± 3.8	29.27 ± 2.9	33.52 ± 7.0	182.33
	A	4 - 45	0.23 ± 0.08	75.27 ± 8.1	24.96 ± 3.1	19.02 ± 2.1	28.44 ± 4.0	147.92
	Cgg	46 - 100	0.05 ± 0.01	4.78 ± 0.9	3.05 ± 0.4	4.92 ± 1.7	21.74 ± 3.2	34.54
3	Ad	0 - 3	0.21 ± 0.06	110.47±10.4	49.29 ± 5.2	29.13 ± 4.0	33.52 ± 6.7	222.62
	A	4 - 25	0.06 ± 0.01	93.28 ± 9.6	34.98 ± 7.2	22.12 ± 3.7	32.48 ± 3.2	182.92
	AC	26 - 65	0.15 ± 0.03	14.54 ± 2.1	4.80 ± 1.7	5.87 ± 1.2	26.47 ± 4.3	51.83
	Cgg	66 - 100	0.33 ± 0.06	18.13 ± 3.4	6.90 ± 2.0	10.25 ± 2.3	26.47 ± 3.9	62.08
4	Ad	0 - 3	0.25 ± 0.04	112.06±11.2	61.15 ± 7.3	42.41 ± 5.8	33.52 ± 7.0	249.39
	AC	4 - 60	0.67 ± 0.11	35.25 ± 6.1	10.23 ± 2.0	11.88 ± 3.0	20.83 ± 4.7	78.86
	Cgg	61 - 130	0.17 ± 0.02	12.64 ± 1.8	4.36 ± 1.2	11.86 ± 2.1	21.74 ± 3.9	50.77
Deluvial brown soils <i>Eutric Cambisols</i>								
5	Ad	0 - 3	12.44 ± 2.56	42.69 ± 5.3	11.41 ± 3.0	19.30 ± 3.0	33.52 ± 5.4	119.36
	A	4 - 20	26.77 ± 4.43	29.42 ± 4.2	9.45 ± 3.2	12.58 ± 2.7	25.50 ± 3.7	103.72
	Bbr	21 - 50	0.26 ± 0.07	12.74 ± 3.1	5.11 ± 1.9	4.98 ± 1.2	22.66 ± 3.2	45.75
	C	51 - 100	0.53 ± 0.12	8.70 ± 2.1	2.04 ± 0.8	3.62 ± 1.3	18.15 ± 4.1	33.04
6	Ad	0 - 3	11.40 ± 1.98	34.14 ± 4.7	9.22 ± 2.9	17.22 ± 3.2	30.84 ± 8.2	102.82
	A	4 - 15	10.96 ± 2.01	21.48 ± 3.2	7.47 ± 2.1	16.80 ± 3.4	22.61 ± 7.0	79.32
	Bbr	16 - 45	0.38 ± 0.08	9.63 ± 2.6	5.31 ± 1.7	8.14 ± 2.0	20.46 ± 5.2	43.92
	C	46 - 100	0.11 ± 0.02	6.41 ± 1.9	1.89 ± 0.2	5.36 ± 1.2	16.58 ± 4.9	30.35

and Crawford procedure, comes the specifically bound and less exchangeable zinc fraction (FII), whereas according to the Tessier *et al.* procedure – the fraction bound to iron and manganese oxides (FIII). Spoisito *et al.* [14] emphasize that these oxides are the elements, which play the major role in binding heavy metals. This phenomenon in the accumulation horizons may be partly explained by analysing the composition of industrial dusts, where metals are found in the form of bindings to compounds with high iron share. The third fraction in turn determined by the McLaren and Crawford method

is the fraction occluded in oxides (IV), although its percentage in total content of zinc is similar to the fraction determined by the Tessier *et al.* method.

As it may be observed from the presented sequences above, the share of organic matter in binding zinc (amongst the tested elements) is the smallest in the case of using the McLaren and Crawford sequential analysis procedure. Whereas the study results obtained using the Tessier *et al.* method indicate that to the smallest extent zinc was bound to carbonates, sulphates and phosphates (FII).

Table 4. Zinc fractions determined by Tessier *et al.* method in deluvial soils ($\text{mg}\cdot\text{kg}^{-1}$ d.w.) Mean for $n = 6$ and \pm sd.

Profile No.	Genetic horizon	Depth cm	Fractions					Σ F I - V
			I	II	III	IV	V	
Deluvial humous soils <i>Gleyic Phaeozems</i>								
1	Ad	0 - 3	3.10 ± 1.38	71.23 ± 16.7	100.32 ± 22.4	41.60 ± 9.8	52.30 ± 11.2	268.55
	A	4 - 15	2.67 ± 0.72	21.25 ± 4.9	32.30 ± 8.1	11.05 ± 3.1	16.40 ± 4.0	83.67
	ACgg	16 - 70	1.74 ± 0.31	11.88 ± 2.3	24.42 ± 5.0	7.92 ± 2.0	26.40 ± 5.6	72.36
	Cgg	71 - 100	1.43 ± 0.24	6.72 ± 1.4	5.46 ± 1.6	4.41 ± 1.1	21.30 ± 5.2	39.32
2	Ad	0 - 3	2.05 ± 0.62	27.30 ± 5.3	54.60 ± 9.7	23.40 ± 5.1	54.60 ± 12.3	161.95
	A	4 - 45	1.43 ± 0.21	14.70 ± 2.8	45.57 ± 7.3	13.00 ± 2.8	61.40 ± 11.2	136.10
	Cgg	46 - 100	0.02 ± 0.01	4.08 ± 0.7	4.42 ± 1.1	2.72 ± 0.9	22.70 ± 7.1	33.94
3	Ad	0 - 3	2.56 ± 0.93	46.62 ± 8.3	57.72 ± 12.4	33.00 ± 7.1	81.20 ± 20.3	221.10
	A	4 - 25	0.74 ± 0.18	20.02 ± 4.4	43.68 ± 11.2	16.38 ± 3.4	86.34 ± 24.8	167.16
	AC	26 - 65	0.61 ± 0.14	8.54 ± 1.5	6.83 ± 1.5	4.96 ± 1.2	49.20 ± 9.6	70.14
	Cgg	66 - 100	0.60 ± 0.14	7.40 ± 1.2	6.43 ± 2.0	4.90 ± 0.9	48.36 ± 10.9	67.69
4	Ad	0 - 3	2.43 ± 1.12	45.00 ± 9.3	65.00 ± 11.2	57.50 ± 14.1	86.42 ± 24.0	256.35
	AC	4 - 60	0.91 ± 0.19	7.80 ± 2.4	11.70 ± 3.0	16.38 ± 4.2	43.74 ± 11.2	80.53
	Cgg	61 - 130	0.15 ± 0.03	6.00 ± 1.3	5.77 ± 1.8	4.50 ± 1.6	40.28 ± 9.7	56.70
Deluvial brown soils <i>Eutric Cambisols</i>								
5	Ad	0 - 3	4.14 ± 1.24	19.32 ± 4.4	23.53 ± 5.2	37.20 ± 8.2	53.82 ± 11.8	138.01
	A	4 - 20	2.41 ± 0.91	7.23 ± 1.5	35.92 ± 7.0	22.90 ± 5.1	52.07 ± 14.2	120.53
	Bbr	21 - 50	0.64 ± 0.13	3.24 ± 0.8	14.90 ± 3.1	7.78 ± 2.0	38.24 ± 9.7	64.80
	C	51 - 100	0.46 ± 0.09	2.31 ± 0.5	7.40 ± 1.7	5.54 ± 1.4	30.49 ± 7.4	46.20
6	Ad	0 - 3	5.91 ± 2.01	16.72 ± 4.1	19.60 ± 3.9	33.48 ± 7.3	44.31 ± 11.4	120.02
	A	4 - 15	1.65 ± 0.83	9.88 ± 2.0	13.79 ± 3.1	23.86 ± 5.3	37.04 ± 8.9	86.22
	Bbr	16 - 45	2.91 ± 0.63	6.40 ± 2.1	9.20 ± 2.9	9.89 ± 2.2	39.57 ± 9.7	67.97
	C	46 - 100	1.43 ± 0.29	4.71 ± 1.9	3.29 ± 1.0	5.56 ± 1.9	27.82 ± 6.3	42.81

Conclusions

The total amount of zinc extracted from soils in the Legnicko–GBogowski Copper Mining Region using either McLaren and Crawford or Tessier *et al.* method differed within the limits of 2–35%, while the application of the latter method yielded higher results for 86% of analyzed samples.

Amongst zinc fractions analysed using the McLaren and Crawford the fraction of zinc specifically bound and

less easily exchangeable dominates in horizons where there is the accumulation of organic matter while in the remaining horizons – the residual fraction. Whereas, when Tessier *et al.* was used the residual fraction dominated in all the genetic horizons of soils under study.

The smallest amounts of zinc, regardless of the method applied, were found in the fraction-embracing ions found in the soil solution and those easily exchangeable.

The quantity of zinc (accessible for plants) calculated as mobility index (MI) on the basis of sequential extraction according to McLaren and Crawford amounts to up to

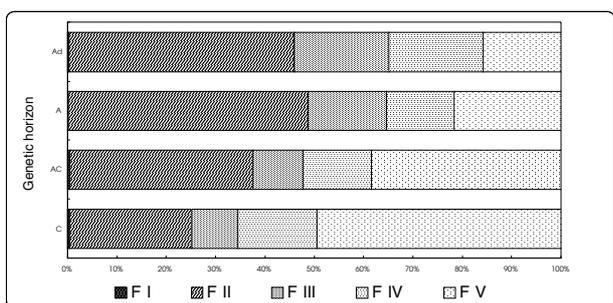


Fig. 1 Percent share of zinc fraction determined by McLaren and Crawford method in genetic horizons of Gleyic Phaeozems.

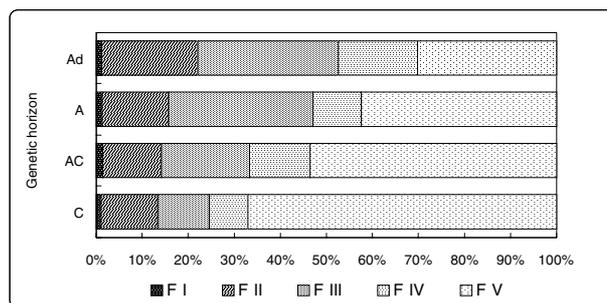


Fig 3 Percent share of zinc fraction determined by Tessier method in genetic horizons of Gleyic Phaeozems.

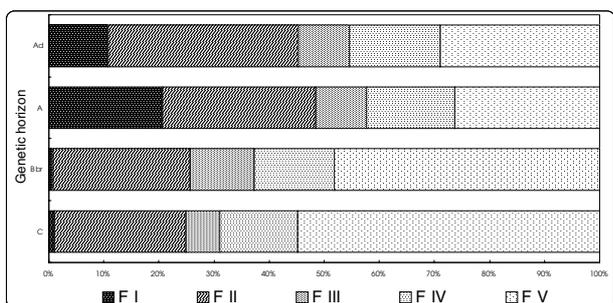


Fig 2 Percent share of zinc fraction determined by McLaren and Crawford method in genetic horizons of Eutric Cambisols.

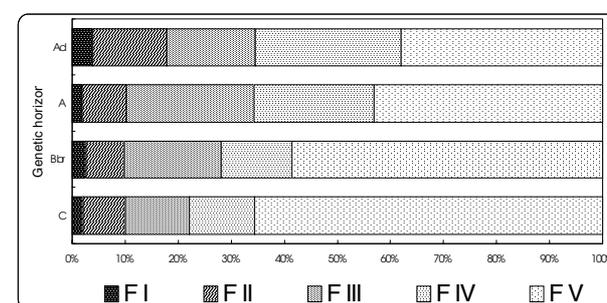


Fig. 4 Percent share of zinc fraction determined by Tessier method in genetic horizons of Eutric Cambisols.

Table 5. Significant correlation between soil basic properties and zinc fractions determined by McLaren and Crawford (M) and Tessier *et al.* (T) methods.

Components of soil and CEC	Method	Fraction				
		FI	FII	FIII	FIV	FV
Colloidal clay	M	-	0.88**)	0.78**)	0.68**)	0.73**)
	T	0.56*)	-	-	-	-
C-org	M	-	0.88**)	0.78**)	0.68**)	0.73**)
	T	0.46*)	0.40*)	-	0.41*)	-
T CEC	M	-	-	0.76**)	0.61**)	0.76**)
	T	-	-	-	-	0.49*)
Fe-OX	M	-	0.43*)	-	-	-
	T	-	-	-	-	0.43*)

*P=0.05

**P=0.01

14–54% while the quantity obtained by Tessier *et al.* amounts to up to 6–28% of total zinc value. A significant difference was found in accumulation horizons and amounted to 40-54% and 8-28% respectively.

The share of organic substance in zinc binding was smallest when assessed on the basis of sequential analysis according to McLaren and Crawford. While in case of applying the method by Tessier *et al.* the smallest amounts of zinc were bound to carbonates, sulphates and phosphates.

References

1. MCLAREN R. G., CRAWFORD D.V. Studies on soil copper. I. The fractionation of Cu in soils. *J. Soil Sci.* **24**, 443, **1973**
2. TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential extraction procedure for the speciation of particular trace metals, *Anal. Chem.* **51**, 844, **1979**
3. MOCEK A., DRZYMAŁA S. MASZNER P. Geneza, analiza i klasyfikacja gleb, 416, **1997**
4. MEHRA O.P., JACKSON M.L. Iron oxide removal from soils clays by dithionite – citrate system buffered with sodium dicarbonate. *Clays and Clay Minerals* **7**, **1960**
5. MOCEK A. Możliwości racjonalnego zagospodarowania gleb chemicznie skażonych w przemysłowych strefach ochrony sanitarnej, *Rocz. AR w Poznaniu, Rozprawy naukowe.*, **185**, 97, **1989**
6. ZEIEN H., BRÜMMER G.W. Ermittlung der Mobilität und Bindungsformen von Schwermetallen in Boden mittels sequentieller Extraktionen, *Mitteln. Dtsch. Bodenkundl. Gesellsch.* **66**, I, 439, **1991**
7. REDDY K.J., WANG L., GLOSS S.P. Solubility and mobility of copper, zinc and lead in acid environments, 141, **1995**
8. ZHANG M. *et al.* Chemical association of Cu, Zn, Mn and Pb in selected sandy citrus soils, *Soil Sci.* **162**, 3,181, **1997**
9. KWAPISZ J. Frakcje cynku, miedzi i ołowiu w glebach o zróżnicowanej zawartości metali ciężkich., *Praca doktorska, SGGW*, **98**, **2000**
10. ALLOWAY B.J. Heavy metals in soils, John Wiley and Sons. New York. 339, **1990**
11. VAN BENSCHOTEN J. *et al.* Metal removal by soil washing for an iron oxide coated sandy soil, *Water Environ. Research.* **66**, (2), 168, **1994**
12. KARCZEWSKA A. Metal species distribution in top- and sub-soil in area affected by copper smelter emissions, *Applied Geochemistry*, **11**, 35, **1996**
13. SALBU B., KREKLING T., OUGHTON D.H. Characterisation of radioactive particles in the environment. *Analyst*, **123**, 843, **1998**
14. SPOSITO G. LUND L.J., CHANG A.C. Trace metal chemistry in air-zone filed soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd and Pb in soil phases, *Soil Sci. Soc. Am. J.* **46**, 260, **1982**