

KRZYSZTOF PAKUŁA*, DOROTA KALEMBASA*

FRACTIONS OF CHROMIUM AND LEAD IN FOREST LUVISOLS OF SOUTH PODLASIE LOWLAND

The aim of this work was to separate the fractions of chromium and lead in forest Luvisols by means of three extraction methods (Tessier's at al. method modified by the authors, Zeien's and Brümmer's method, and Hedley's method modified by Tiessen and Moir) and to compare the content of these metals separated in four selected fractions: easily soluble, exchangeable, organic and residual. The results of the sequential fractionation have shown different amounts of Cr and Pb in selected fractions in the genetic horizons of the soils investigated. The highest amount of both metals was found in easily soluble and exchangeable fractions (Zeien's and Brümmer's method); in organic matter fraction (Hedley's method) and in residual fraction (Tessier's at al. method). In general, the statistical evaluation of the results demonstrated that the amounts of Cr and Pb in easily soluble, exchangeable, organic matter and residual fractions showed significant correlation with some properties of the forest Luvisols analyzed.

1. INTRODUCTION

The total content of heavy metals is made up by their different forms (fractions), which can be related to chemical species, as well as to their different solubility and mobility in soil environment. Sequential extraction of elements is used to identify these fractions. The methods of sequential fractionation enable us to determine the quantity of compounds of these metals in soil and to estimate more precisely their availability and toxicity to trophic chain components. The geochemistry (solubility, mobility and availability) of chromium and lead depend on: the value of pH, the content and type of iron and manganese compounds as well as the content of organic matter and clay minerals [1], [2]. The aim of this work was to investigate the fractions of chromium and lead separated by means of three extraction methods and to compare the content of these metals in four selected fractions.

* Department of Soil Science and Plant Nutrition, University of Podlasie, ul. Prusa 14, 08-110 Siedlce, Poland. E-mail: kalembasa@ap.siedlce.pl

2. MATERIAL AND METHODS

The study was conducted on Luvisols formed from boulder glacial deposits (heavy loam, sandy loam and loamy sands), localized in an old forest land of the South Podlasie Lowland in the middle-east of Poland. The soil samples were taken from a particular genetic horizon of the soils, air dried and then the following properties of the soils were determined: granulometric composition, by areometric method (according to Polish Norm PN-R-04033); pH in 1 mol KCl · dm⁻³, potentiometrically; cation exchangeable capacity (CEC) was calculated on the basis of hydrolytic acidity (Hh) and base exchangeable capacity (BEC) determined by Kappen's method; the amount of organic carbon (C_{org}), according to oxidation–reduction method [3]; the total content of chromium and lead (Cr_t and Pb_t), by ICP-AES method, after mineralization in the mixture of concentrated HCl and HNO₃ (3:1) in microwave system.

Table 1

Methods of sequential extraction of chromium and lead

Fraction	Extraction reagent
Tessier's at al. method (in our own modification)	
F1 easily soluble	H ₂ O
F2 exchangeable	1 mol NH ₄ Cl · dm ⁻³
F3 bonded to carbonates	1 mol CH ₃ COOH · dm ⁻³
F4 bonded to Fe-Mn oxides	0.2 mol (NH ₄) ₂ C ₂ O ₄ · dm ⁻³ + 0.2 mol H ₂ C ₂ O ₄ · dm ⁻³
F _{org} bonded to organic matter	0.1 mol NaOH · dm ⁻³
F _{resid} residual*	
Zeien's and Brümmer's method	
F1 easily soluble	1 mol NH ₄ NO ₃ · dm ⁻³
F2 exchangeable	1 mol CH ₃ COONH ₄ · dm ⁻³
F3 bonded to MnO _x	1 mol NH ₂ OH · HCl · dm ⁻³ + 1 mol CH ₃ COONH ₄ · dm ⁻³
F _{org} bonded to organic matter	0.025 mol C ₁₀ H ₂₂ N ₄ O ₈ · dm ⁻³
F5 bonded to amorphous FeO _x	0.2 mol (NH ₄) ₂ C ₂ O ₄ · dm ⁻³ + 0.2 mol H ₂ C ₂ O ₄ · dm ⁻³
F6 bonded to crystalline FeO _x	0.2 mol (NH ₄) ₂ C ₂ O ₄ · dm ⁻³ + 0.2 mol H ₂ C ₂ O ₄ · dm ⁻³ + 0.1 mol C ₆ H ₈ O ₆ · dm ⁻³
F _{resid} residual*	
Hedley's method modified by Tiessen and Moir	
F1 easily soluble	H ₂ O
F2 exchangeable	0.5 mol NaHCO ₃ · dm ⁻³
F _{org} bonded to organic matter	0.1 mol NaOH · dm ⁻³
F4 bonded to carbonates	1 mol HCl · dm ⁻³
F5 bonded to stable organic-mineral and mineral compounds	concentrated HCl
F _{resid} residual*	

* Calculated as the difference between the total amount of heavy metals and the sum of fractions determined above.

The sequential extraction of chromium and lead was carried out, using three different analytical procedures: the method of TESSIER's et al. [4] modified by the authors (the modification involved checking a few extraction solutions and recommending the use of one of them during the stages of analysis performed by the ICP-AES method); ZEIN's and BRÜMMER's method [5] and Hedley's method modified by TIESSEN and MOIR [6] (in this paper it is named Hedley's method) (table 1). Particular fractions of chromium and lead were determined in the extracts by ICP-AES method. The suitability of the sequential extraction methods was compared with that of the external standard method. In the checking procedure, also the control samples were taken into consideration together with the application of proper chemical reagents.

In order to compare the sequential extraction schemes, four fractions of metals were selected: easily soluble (water soluble) (F1), exchangeable (F2), bonded to organic matter (organic fraction – F_{org}), and residual (fraction of very stable organic–mineral and mineral compounds in soils – F_{resid}). The selection of these fractions was based on the possibility of their direct use at each step of the procedures applied. In these four fractions, trace metals were bonded to compounds of soil with different bonds, from the most mobile (fractions F1 and F2), through potentially mobile (F_{org}) to very stable in the compounds of residual fraction (F_{resid}). The percentage contribution of the four fractions of Cr and Pb were shown as a mean for three soil profiles for each sequential extraction procedure.

The interaction between the total content of Cr and Pb and their separated fractions as well as some properties of soils was evaluated using linear correlation (r) and the critical values at $\alpha = 0.01$ and $\alpha = 0.05$.

3. RESULTS AND DISCUSSION

Some physical, physicochemical and chemical properties of the soils investigated were characteristic of the forest Luvisols formed from boulder deposits of the Middle Polish Glacial (table 2). In the Luvisols tested, the total content of Cr ranged from 7.94 to 25.1 $\text{mg} \cdot \text{kg}^{-1}$ and that of Pb varied from 9.86 to 12.2 $\text{mg} \cdot \text{kg}^{-1}$. Taking into account the total mean content of the metals of interest, the genetic horizons of these soils could be presented in the following descending order: IIBt > IIC > Ah > Ol > Eet. The distribution of chromium and lead in the soil profiles was probably the result of lessivage soil formation process (in mineral horizons) and biological accumulation (in organic horizons). The total content of chromium and lead in the soils investigated was below the values of geochemical background for boulder loams in Poland [7]. The distribution of chromium and lead in the Luvisols profiles under analysis was similar to that in the other forest Luvisols [8]–[10]. Both chromium and lead were found in the forest soil profiles due to their occurrence in parent rock of the soils (C)

as well as due to environmental contamination and biological accumulation in the soil surface horizons (Ol and Ah) [1], [11].

Table 2

Some properties (ranges for three soil profiles) of forest Luvisols

Genetic horizon	Sand 2–0.05	Silt 0.05–0.002	Clay < 0.002	pH _{KCl}	CEC*	C _{org}	Cr _t	Pb _t
	% fraction of diameter in mm					g · kg ⁻¹	mg · kg ⁻¹	
Ol	–	–	–	4.81–5.16	545–700	443–472	6.95–9.75	9.17–11.9
Ah	69–76	19–25	5–8	3.08–3.36	75.2–107	12.0–20.3	7.29–9.21	8.47–15.1
Eet	69–80	17–24	3–6	3.55–3.65	43.6–54.0	2.30–5.00	6.55–8.47	7.93–11.1
IIBt	37–53	24–33	23–32	3.32–3.48	146–187	1.60–2.00	21.7–28.3	10.8–14.6
IIC	35–53	28–42	16–26	6.81–7.43	238–388	1.30–1.60	18.1–22.8	9.56–12.8

* mmol(+)kg⁻¹; CEC – Cation Exchangeable Capacity.

Table 3

Mean percentage contribution of chromium and lead fractions
to their total content in soils investigated

Genetic horizon	Cr				Pb			
	Fractions				Fractions			
	F1	F2	F _{org}	F _{resid}	F1	F2	F _{org}	F _{resid}
Tessier's et al. method								
Ol	1.17	1.71	13.3	58.1	2.50	3.77	28.3	48.3
Ah	0.69	1.66	6.47	65.8	0.93	3.27	23.8	51.6
Eet	0.40	0.77	1.71	70.6	0.52	2.10	10.1	63.2
IIBt	0.26	0.53	1.32	82.4	0.24	1.00	2.96	72.1
IIC	0.15	0.27	0.55	89.9	0.17	0.76	1.31	80.1
Zeien's and Brümmer's method								
Ol	1.83	3.07	10.0	51.2	3.23	5.65	21.7	46.2
Ah	1.03	2.30	5.13	58.0	1.63	4.70	19.7	46.4
Eet	0.58	1.27	1.43	63.8	0.88	2.91	8.33	59.7
IIBt	0.34	0.83	0.93	73.1	0.28	1.25	2.17	64.4
IIC	0.17	0.39	0.45	80.9	0.20	0.66	0.98	71.2
Hedley's method modified by Tiessen and Moir								
Ol	1.19	2.07	16.9	42.6	2.47	4.93	32.0	36.8
Ah	0.71	1.91	7.85	47.1	0.94	3.60	26.1	38.0
Eet	0.44	1.11	2.00	49.3	0.52	2.57	11.6	42.1
IIBt	0.27	0.61	1.83	61.0	0.23	0.95	3.15	54.6
IIC	0.14	0.34	0.66	68.6	0.15	0.87	1.89	62.8

Fractions: F1 – easy soluble, F2 – exchangeable, F_{org} – bonded to organic matter, F_{resid} – residual.

In the forest Luvisols investigated, different amounts of chromium and lead were found in the fractions separated by the three sequential extraction methods (table 3). The mean percentage contribution of the four selected fractions of these elements to their total content in the soil horizons can be presented in the following descending orders:

- for Cr in Ol: residual > bonded to organic matter > exchangeable > easily soluble
(42.6–58.1%) (10.0–16.9%) (1.71–3.07%) (1.17–1.83%);
in Ah: residual > bonded to organic matter > exchangeable > easily soluble
(47.1–65.8%) (5.13–7.85%) (1.66–2.30%) (0.69–1.03%);
in Eet, IIBt, IIC: residual > bonded to organic matter > exchangeable > easily soluble
(49.3–89.9%) (0.45–2.00%) (0.39–1.27%) (0.14–0.58%);
- for Pb in Ol: residual > bonded to organic matter > exchangeable > easily soluble
(36.8–48.3%) (21.7–32.0%) (3.77–5.65%) (2.47–3.23%);
in Ah: residual > bonded to organic matter > exchangeable > easily soluble
(38.0–51.6%) (19.7–26.2%) (3.27–4.70%) (0.93–1.63 %);
in Eet, IIBt, IIC: residual > bonded to organic matter > exchangeable > easily soluble
(42.1–80.1%) (0.70–11.6 %) (0.76–2.91%) (0.15–0.88%).

In the soils analyzed, the residual fraction (F_{resid}) of chromium and lead prevailed. The highest amounts of Zn and Cu in this fraction were determined, using Tessier's et al. method (mean: 73.3% for Cr and 63.0% for Pb) and the lowest ones, using the method of Hedley (53.7 and 46.8%, respectively). The concentration of those metals in the residual fraction increased with the depth of soil profiles, independently of the extraction method applied. CZEKAŁA [11] and FILIPEK-MAZUR [12] reported that the contribution of chromium to the residual fraction ranged from about 60.0 to 90.0% in the uncontaminated soils. KABAŁA and SINGH [13] claimed that the amount of lead in the stable mineral compounds (F_{resid}) ranged from 84.0 to 88.0%.

The highest concentrations of chromium and lead in the fraction bonded to organic matter (F_{org}) were determined in the soil organic horizons Ol (on average from 5.85% for Cr and 15.0% for Pb (Hedley's method) to 3.41% and 10.5% (Zeien's and Brümmer's method), respectively). The organic (Ol) and humus (Ah) horizons of the acid forest soils [1] were dominated by lead in organic fraction.

The lowest concentrations of both metals in the forest soils under analysis were found in their easily soluble (F1) and exchangeable (F2) fractions (table 3). The highest amounts of chromium and lead in these fractions were determined using Zeien's and Brümmer's procedure (on average from 0.79 to 1.57% for Cr and from 1.25 to 3.09% for Pb) and the lowest ones, by means of Tessier's et al. method and Hedley's method (0.53–1.21% and 0.87–2.62%), respectively). The concentrations of Cr and Pb in an easily soluble, exchangeable and bonded to organic matter fractions decreased with the depth of soil profiles independently of the extraction method applied. The higher the acidity of soil and environmental pollution, the higher the amounts of Cr and Pb in the most mobile fractions (F1 and F2) and the higher their availability and toxicity to trophic chain components [11], [12], [14]. KABAŁA and SINGH [13] reported that the contribution of lead to these fractions

was below 3.0% in uncontaminated soils, but in polluted soils the contribution of this metal to the exchangeable fraction increased to 45.0%.

Table 4

Coefficients of correlation between fractions of chromium and some parameters of soils

	F1	F2	F _{org}	F _{resid}	Cr _t	pH _{KCl}	C _{org}	CEC	Ø<0.002
Tessier's et al. method									
F1	1	0.920**	0.989**	-0.926**	-0.699**	-0.125	0.882**	0.633**	-0.719**
F2		1	0.890**	-0.934**	-0.760**	-0.342	0.633**	0.445*	-0.746**
F _{org}			1	-0.862**	-0.612**	-0.024	0.912**	0.712**	-0.639**
F _{resid}				1	0.854**	0.459*	-0.685**	-0.334	0.848**
Zeien's and Brümmer's method									
F1	1	0.981**	0.991**	-0.931**	-0.700**	-0.118	0.887**	0.638**	-0.721**
F2		1	0.964**	-0.968**	-0.752**	-0.255	0.781**	0.496*	-0.756**
F _{org}			1	-0.881**	-0.631**	-0.034	0.902**	0.696**	-0.656**
F _{resid}				1	0.831**	0.452*	-0.688**	-0.341	0.825**
Hedley's method modified by Tiessen and Moir									
F1	1	0.937**	0.980**	-0.885**	-0.718**	-0.152	0.872**	0.611**	-0.736**
F2		1	0.875**	-0.943**	-0.824**	-0.349	0.649**	0.335	-0.810**
F _{org}			1	-0.774**	-0.592**	-0.016	0.922**	0.727**	-0.622**
F _{resid}				1	0.873**	0.486*	-0.595**	-0.220	0.860**

Significant at: ** $\alpha = 0.01$; * $\alpha = 0.05$; CEC – Cation Exchangeable Capacity.

Table 5

Coefficients of correlation between fractions of lead and some parameters of soils

	F1	F2	F _{org}	F _{resid}	Pb _t	pH _{KCl}	C _{org}	CEC	Ø < 0.002
Tessier's et al. method									
F1	1	0.864**	0.878**	-0.824**	-0.463*	0.032	0.958**	0.759**	-0.655**
F2		1	0.993**	-0.988**	-0.610**	-0.289	0.686**	0.476*	-0.843**
F _{org}			1	-0.976**	-0.541*	-0.243	0.706**	0.424	-0.794**
F _{resid}				1	0.545*	0.445*	-0.634**	-0.297	0.808**
Zeien's and Brümmer's method									
F1	1	0.944**	0.919**	-0.873**	-0.528*	-0.047	0.902**	0.668**	-0.735**
F2		1	0.993**	-0.973**	-0.607**	-0.262	0.710**	0.497*	-0.839**
F _{org}			1	-0.984**	-0.548*	-0.279	0.663**	0.472*	-0.803**
F _{resid}				1	0.468*	0.461*	-0.597**	-0.278	0.759**
Hedley's method modified by Tiessen and Moir									
F1	1	0.928**	0.896**	-0.730**	-0.477*	0.026	0.953**	0.749**	-0.669**
F2		1	0.984**	-0.919**	-0.631**	-0.217	0.775**	0.475*	-0.842**
F _{org}			1	-0.899**	-0.556*	-0.225	0.720**	0.445*	-0.802**
F _{resid}				1	0.640**	0.539*	-0.514*	-0.132	0.856**

Significance at: ** $\alpha = 0.01$; * $\alpha = 0.05$; CEC – Cation Exchangeable Capacity.

For the Luvisols analyzed, the authors found the coefficients (positive and negative) of statistically significant correlations between most of the variables measured for chromium and lead, independently of the extraction method applied (tables 4 and 5). The statistically significant correlations ($\alpha = 0.05$ and $\alpha = 0.01$) were found between the amount of Cr and Pb in the four fractions and the total content of these metals (Cr_t and Pb_t), the content of organic carbon (C_{org}), the soil fractions with the particles diameter < 0.002 mm, and the values of cation exchangeable capacity (CEC) (with the exception of the residual fraction). The values of soil pH were significantly correlated with the residual ($\alpha = 0.05$) fractions of chromium and lead.

4. CONCLUSIONS

1. In the forest Luvisols investigated, the total content of chromium and lead was below the values of the geochemical background for Polish boulder glacial deposits. Taking account of the total mean content of the metals analyzed, the genetic horizons of the soils could be arranged in the following descending order: IIBt > IIC > Ah > OI > Eet.

2. The sequential fractionation analysis of chromium and lead compounds according to Tessier's et al. method, Zeien's and Brümmer's method, and Hedley's method modified by Tiessen and Moir showed different amounts of both metals in the selected fractions of the soils analyzed. In general, the highest amounts of these metals were determined in the residual fraction, and the lowest – in the easily soluble ones.

3. The highest amounts of chromium and lead in the easily soluble and exchangeable fractions were determined in organic horizons (OI); the organic fraction – in biological accumulation horizons (OI and Ah), and the residual fraction – in parent rock horizons (C) of forest soils.

4. The highest amounts of chromium and lead in the easily soluble and the exchangeable fractions were determined according to the procedure of Zeien and Brümmer, in the organic fraction – by Hedley's method, and in the residual fraction – by Tessier's et al. method.

5. The statistical evaluation of the results suggested that the concentrations of chromium and lead in separated fractions were significantly correlated with some properties of the forest Luvisols (the content of chromium and lead, C_{org} , clay fraction, CEC).

REFERENCES

- [1] KABATA-PENDIAS A., PENDIAS H., *Biogeochemia pierwiastków śladowych*, Wydawnictwo Naukowe PWN, Warszawa, 1999.
- [2] HLAVAY J., PROHASKA T., WEISZ M., WENZEL W.W., STINGEDER G.J., *Determination of trace elements bound to soils and sediment fractions (IUPAC technical report)*, Pure Appl. Chem., 2004, 76, 2, 415–442.

- [3] KALEMBASA S., KALEMBASA D., *The quick method for the determination of C:N ratio in mineral soils*, Polish J. Soil Sci., 1992, 25, 1, 41–46.
- [4] TESSIER A., CAMPBELL P.G.C., BISSON M., *Sequential extraction procedure for the speciation of particulate trace metals*, Anal. Chem., 1979, 51, 844–851.
- [5] ZEIEN H., BRÜMMER, G.W., *Chemische Extraktion zur Bestimmung von Schwermetallbindungsformen in Böden*, Mitteilg. Dtsch. Bodenkundl. Gesellsch., 1989, 59, 505–510.
- [6] TIESSEN H., MOIR J.O., *Characterization of available P by sequential extraction*, [in:] Carter M.R. (ed.), *Soil Sampling and Methods of Analysis*, Canadian Society of Soil Science, Lewis Publishers, 1993, 75–86.
- [7] CZARNOWSKA K., *Ogólna zawartość metali ciężkich w skałach macierzystych jako tło geochemiczne gleb*, Roczn. Glebozn., 1996, 47, supl., 43–50.
- [8] KWASOWSKI W., CHOJNICKI J., OKOŁOWICZ M., KOZANECKA T., *Metale ciężkie w glebach powierzchni wzorcowych (GPW) w Puszczy Białej*, Roczn. Glebozn., 2000, 51, 3/4, 85–95.
- [9] UZIĄK S., MELKE J., KLIMOWICZ Z., *Wpływ użytkowania na zawartość metali ciężkich w glebach „Ściany Wschodniej”*, Acta Agrophysica, 2001, 48, 127–132.
- [10] BROŻEK S., ZWYDAK M., *Atlas gleb leśnych Polski*, Wydawnictwo Centrum Informacyjnego Lasów Państwowych (CILP), Warszawa, 2003.
- [11] CZEKAŁA J., *Chrom w glebie i roślinie – występowanie, sorpcja i pobieranie w zależności od jego formy i dawki, właściwości środowiska i nawożenia*, Wydawnictwo AR w Poznaniu, 1997, 274, 1–90.
- [12] FILIPEK-MAZUR B., *Występowanie i toksyczność metali ciężkich w środowisku*, [w:] Kalembsa S. (ed.), *Diagnostyka gleb i roślin w rolnictwie zrównoważonym*, Wydawnictwo AP w Siedlcach, 2004, 54, 116–130.
- [13] KABAŁA C., SINGH B.R., *Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter*, J. Environ. Qual., 2001, 30, 485–492.
- [14] KARCZEWSKA A., *Metale ciężkie w glebach zanieczyszczonych emisjami hut miedzi – formy i rozpuszczalność*, Zeszyty Naukowe AR we Wrocławiu, 2002, 432, 1–159.

FRAKCJE CHROMU I OŁOWIU W LEŚNYCH GLEBACH PŁOWYCH NA TERENIE NIZINY POŁUDNIOWOPODLASKIEJ

Celem pracy było wydzielenie frakcji chromu i ołowiu z leśnych gleb płowych za pomocą trzech metod ekstrakcji sekwencyjnej (zmodyfikowanej metody Tessiera, metody Zeiena i Brümmera oraz metody Hedleya w modyfikacji Tiessena i Moira), a także porównanie zawartości tych metali w czterech wybranych frakcjach: łatwo rozpuszczalnej, wymiennej, organicznej i rezydualnej. Najwięcej chromu i ołowiu stwierdzono we frakcjach łatwo rozpuszczalnej i wymiennej, wydzielonych za pomocą metody Zeiena i Brümmera, we frakcji organicznej wydzielonej metodą Hedleya oraz w stabilnych połączeniach frakcji rezydualnej wydzielonej metodą Tessiera. Obliczenia statystyczne wykazały, że cztery badane frakcje chromu i ołowiu były na ogół wysoko istotnie i istotnie skorelowane ze sobą oraz z wybranymi parametrami analizowanych gleb.