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PROFILE DIFFERENTIATION OF LEAD AND CHROMIUM FRACTIONS FOUND IN SOILS LOCALIZED ON A MORAINE SLOPE

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Abstract

In order to evaluate a potential threat to soil environment by heavy metals, it is important to separate and determine their fractions by means of sequential extraction.

The research aimed at evaluating the total content of lead and chromium as well as their fractions in soils localized on a moraine slope in the Siedlce Heights (transects A and B). Sequential fractionation of these elements was carried out according to Zeien and Brümmer's method. Chemical analyses revealed varied contents of seven lead and chromium fractions in the soils. The largest amounts of both heavy metals were mostly recorded in the residual fraction (F7), and those of lead also in the organic fraction (F4). The least lead was found in the exchangeable fraction (F2) (it was not detected in easily soluble fraction F1), while the least chromium appeared in the easily soluble (F1) and organic fractions (F4). Statistical processing revealed that the examined lead and chromium fractions generally depended on separated fractions, total contents of these metals, and some properties of analyzed soils.

Key words: sequential extraction, Zeien and Brümmer's method, fractions, lead, chromium, moraine slope.

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PROFILOWE ZRÓŻNICOWANIE ZAWARTOŚCI FRAKCJI OŁOWIU I CHROMU W GLEBACH POŁOŻONYCH NA STOKU MORENOWYM

Abstrakt

Dla oceny potencjalnego zagrożenia środowiska glebowego przez metale ciężkie istotne jest wydzielenie i ilościowe zbadanie ich frakcji na drodze ekstrakcji sekwencyjnej.

Celem pracy było zbadanie ogólnej zawartości ołowiu i chromu oraz ich frakcji w glebach położonych na stoku morenowym Wysoczyzny Siedleckiej (transekt A i B). Frakcjonowanie sekwencyjne tych pierwiastków przeprowadzono według metody Zeiena i Brümmera. Wykazano zróżnicowaną zawartość wydzielonych siedmiu frakcji ołowiu i chromu w badanych glebach. Najwięcej obydwu metali stwierdzono (w przeważającej większości) we frakcji rezydualnej F7, a najwięcej ołowiu we frakcji organicznej (F4). Najmniej ołowiu stwierdzono we frakcji wymiennej F2 (we frakcji łatwo rozpuszczalnej F1 nie został on wykryty), a najmniej chromu we frakcji łatwo rozpuszczalnej (F1) oraz organicznej (F4). Obliczenia statystyczne wykazały, że badane frakcje ołowiu i chromu były przeważnie istotnie zależne od wydzielonych frakcji, ogólnej zawartości tych metali oraz niektórych właściwości analizowanych gleb.

Słowa kluczowe: ekstrakcja sekwencyjna, metoda Zeiena i Brümmera, frakcje, ołów i chrom, stok morenowy.

INTRODUCTION

Behaviour of heavy metals towards in soil environment depends on their properties and chemical form (fraction) as well as on the physical and chemical features of the soil. Methods of sequential chemical extraction of heavy metals consist in the extraction of given element forms (fractions) bound to particular soil components by subsequent treatments of soil samples with different extraction solvents. Such methods allow for determining the percentage of a particular fraction of a given element in its total amount in soil, hence making possible to complete evaluation of its availability and potential toxicity to biotic elements in a trophic chain (KABATA-PENDIAS, 1998). The behavior of heavy metals in soil is predominantly determined by loamy minerals, organic matter content and acidity.

The research aimed at determining the total content of lead and chromium as well as separating fractions of these metals by means of sequential extraction according to Zeien and Brümmer's method in genetic horizons of soils localized on an eroded moraine slope.

MATERIAL AND METHODS

The soil study was carried out on a slope of a hilly terminal moraine (western exposure) formed during the Middle Polish glaciation (the Warta River Stadial) in the Siedlce Heights, in Middle-Polish Lowlands. Six outcrops were made in two transects (at about 700 m distance): transect A – one at the top (podzolized lessive soil – I) and two on the slope (Calcaric Cambisol – II and deluvial humus soil – III); transect B – at the top (regulated soil – IV), on the slope (Haplic Luvisol – V) and at the bottom (deluvial soil – VI). The soil material was collected from particular genetic horizons and subjected to determinations of the percentage of loam fraction Ø < 0.002 mm – areometric method (according to PN-R-04033); pH – potentiometry; soil sorption capacity (CEC) – calculated on the basis of hydrolytic acidity (H_h) and sum of exchangeable basic cations (S) determined by means of Kappen's method (except samples with pH > 7.5); organic carbon content (C_{org}) – oxidation-titrimetric method (KALEMBASA, KALEMBASA 1992); total contents of Pb and Cr – ICP-EAS (Optima 3200 RL device, Perkin Elmer) after combustion at 450°C and extraction with 20% HCl. Lead and chromium fractions were separated by means of Zeien and Brümmer's method (Table 1), which makes it possible to separate metals into seven fractions different with respect to their activity in soil environment. The analysis was performed in three replications. The reference materials (WEPAL Soil Reference Material RTH 912 – Swiss Less Soil, Perkin Elmer) and internal stand-

Table 1

Sequential extraction of heavy metals with Zeien and Brümmer's method

Fraction	Name	Extraction reagent	Extraction time (h)	pH
F1	easily soluble	1 mol $NH_4NO_3 \cdot dm^{-3}$	24	natural
F2	exchangeable	1 mol $CH_3COONH_4 \cdot dm^{-3}$	24	6.00
F3	bound to MnO_x	1 mol $NH_2OH \cdot HCl \cdot dm^{-3}$ +1 mol $CH_3COONH_4 \cdot dm^{-3}$	0.5	6.00
F4	F_{org}bound to organic matter	0.025 mol $C_{10}H_{22}N_4O_8 \cdot dm^{-3}$	1.5	4.60
F5	bound to amorphous FeO_x	0.2 mol $(NH_4)_2C_2O_4 \cdot dm^{-3}$ + 0.2 mol $H_2C_2O_4 \cdot dm^{-3}$	4	3.25
F6	bound to crystalline FeO_x	0.2 ml $(NH_4)_2C_2O_4 \cdot dm^{-3}$ + 0.2 mol $H_2C_2O_4 \cdot dm^{-3}$ + 0.1 mol $C_6H_8O_6 \cdot dm^{-3}$	0.5	3.25
F7	F_{resid} residual	calculation as difference between total content of nickel and sum of the above determined fractions	-	-

proportion soil / solution 1 g : 10 cm^3

ards were used to check the accuracy of determinations. The detection limit (the lowest concentration possible to detect applying a given method at particular probability) for lead is 0.001-0.01 $mg \cdot dm^{-3}$ and for chromium – 0.0001-0.001 $mg \cdot dm^{-3}$.

In order to find dependencies between total content of chromium and lead, their fractions and selected soil properties (fraction Ø < 0.002 mm, C_{org}, CEC, pH_{KCl}), values of Pearson's correlation coefficient were calculated. Significant values ($p = 0.05$) were marked with an asterisk (*) in the tables.

RESULTS AND DISCUSSION

Selected physical and physicochemical properties of the soils on the examined terminal moraine slope are presented in Table 2.

The total content of lead (0.13-9.33 $mg \cdot kg^{-1}$) and chromium (1.21--19.90 $mg \cdot kg^{-1}$) in the soils varied between and within the profiles, reaching (in $mg \cdot kg^{-1}$) 0.13-8.22 Pb and 1.21-16.81 Cr in transect A; 2.50-9.33 Pb and 2.40-19.90 Cr in transect B. In the surface humus horizons, the concentra-

Table 2

Selected properties of investigated soils*

Horizon	Depth (cm)	% fraction of diameter in mm Ø< 0.002	pH_{KCl}	CEC	Org. C
				$mmol(+) \cdot kg^{-1}$	$g \cdot kg^{-1}$
Transect A					
I. Albic luvisol (flat)					
A	0-25	9	4.05	45.71	6.30
Eet,fe	25-40	8	4.46	28.20	1.50
Bt,fe	40-60	7	4.80	85.00	0.70
Bt	60-90	9	7.73	-	0.50
C	90-120	0	8.87	-	0.3
II. Dystric Cambisol (slope)					
A	0-24	4	3.63	66.21	7.30
ABbr(fe)	24-37	5	3.77	56.43	2.60
Bbr1	37-47	24	4.04	123	1.80
Bbr2	47-75	21	4.57	132	1.00
Bbr3	75-100	21	4.95	122	0.94
Bbr4	100-140	10	7.49	-	0.83

cont. Table 2

III. Mollic Fluvisol (slope)					
IA1	0-15	2	6.68	127	17.71
IA2	15-35	2	6.61	126	6.70
IA3	35-46	6	6.42	124	8.10
IIA	46-68	12	6.36	213	9.90
AC	68-78	10	6.25	167	3.90
IC	78-100	1	6.26	128	1.60
IICG	100-125	15	6.32	137	1.10
Transect B					
IV. Anthropic Regosol (flat)					
Aan	0-25	5	4.26	54.70	7.73
AanA	25-50	6	4.60	48.71	2.78
Ees	50-80	4	4.18	37.51	0.78
Bhfe	80-110	8	4.20	66.22	0.77
C	110-150	17	3.87	104	0.96
V. Haplic Luvisol (slope)					
A	0-25	8	3.47	72.40	6.95
Eet	25-50	6	3.95	33.70	0.66
EB	50-80	8	4.38	146	1.21
Bt	80-120	16	3.95	96.91	0.71
C1	120-150	1	4.96	29.00	0.29
C2	150-180	3	5.12	33.92	0.14
VI. Haplic Phaeozem (foot-slope)					
A1	0-40	6	3.47	119	10.40
A2	40-64	10	3.95	135	8.49
AC	64-74	8	4.38	75	1.05
CG	74-90	6	3.95	77	0.74

*information source: Kalembasa, Majchrowska-Safaryan (2007)

tion ranged (in $mg \cdot kg^{-1}$) within 5.60-8.22 of lead and 4.29 -8.67 of chromium in transect A; 4.95-7.46 Pb and 5.82-7.39 Cr in transect B (Tables 3, 4). These levels of the heavy metals did not exceed permissible levels for arable lands (*Decree*.....2002) and were within the range of natural quantities according to IUNG (Kabata-Pendias et al. 1995). The total Pb content in lessive soils (profiles I and V), and Calcaric Cambisol (profile II) was the highest in the humus horizons and enrichment horizon B, which mainly result-

Table 3

The total content of lead and percentage contribution of lead fractions in soils in transects A and B

Horizon	Depth (cm)	Fraction							Total content
		F1	F2	F3	F4	F5	F6	F7	
		% total content							$mg \cdot kg^{-1}$
1	2	3	4	5	6	7	8	9	10
Transect A									
I. Albic luvisol (flat)									
A	0-25	n.d	6.68	13.70	40.91	11.60	6.00	20.90	5.60
Eet,fe	25-40	n.d	8.13	18.41	27.50	10.61	15.50	19.91	1.93
Bt,fe	40-60	n.d	8.48	14.42	19.31	16.60	13.12	28.10	4.62
Bt	60-90	n.d	2.91	24.90	41.00	n.d	12.60	18.32	4.77
C	90-120	n.d	n.d	25.00	20.00	n.d	19.01	35.91	1.00
Mean		n.d	5.24	19.28	35.71	7.76	13.25	24.63	3.78
II. Dystric Cambisol (slope)									
A	0-24	n.d	8.21	8.40	34.71	11.80	2.86	34.01	6.46
ABbr(fe)	24-37	n.d	1.20	14.41	26.50	7.83	14.50	38.50	5.20
Bbr1	37-47	n.d	n.d	9.30	25.51	10.52	8.60	46.52	6.93
Bbr2	47-75	n.d	1.78	13.10	25.53	12.31	8.98	38.31	7.11
Bbr3	75-100	n.d	4.40	14.62	34.00	8.25	12.80	25.82	7.11
Bbr4	100-140	n.d	n.d	21.70	32.21	3.13	6.65	36.33	6.00
Mean		n.d	2.59	13.59	29.74	8.97	9.07	36.61	6.47
III. Mollic Fluvisol (slope)									
IA1	0-15	n.d	4.51	7.62	56.01	14.60	4.67	12.50	8.22
IA2	15-35	n.d	6.36	4.92	52.62	19.61	4.75	12.63	7.26
IA3	35-46	n.d	5.95	3.65	39.70	17.32	8.16	25.30	6.70
IIA	46-68	n.d	n.d	n.d	28.92	14.70	7.35	48.92	7.51

cont. Table 3

1	2	3	4	5	6	7	8	9	10
AC	68-78	n.d	4.42	3.88	25.80	12.33	5.44	48.21	6.31
IC	78-100	n.d	n.d	8.72	36.30	8.93	11.01	35.00	5.24
IICG	100-125	n.d	n.w	15.30	43.42	15.40	7.60	17.70	0.13
Mean		n.d	3.03	6.30	40.40	14.70	7.00	28.60	5.91
Transect B									
IV. Anthropic Regosol (flat)									
Aan	0-25	n.d	n.d	15.61	38.51	14.50	10.31	20.91	6.78
AanA	25-50	n.d	16.70	13.80	22.82	13.30	12.40	21.01	4.44
Ees	50-80	n.d	6.44	13.52	25.80	4.60	9.60	40.02	2.50
Bhfe	80-110	n.d	13.51	7.97	18.83	6.04	19.12	34.60	5.18
C	110-150	n.d	4.00	10.00	18.51	6.48	20.01	45.90	6.67
Mean		n.d	8.12	12.18	24.89	9.18	14.31	31.59	5.11
V. Haplic Luvisol (slope)									
A	0-25	n.d	n.d	16.70	34.50	12.41	22.41	14.01	4.95
Eet	25-50	n.d	n.d	18.00	22.42	8.35	12.61	38.60	3.57
EB	50-80	n.d	n.d	6.44	26.00	12.42	14.00	41.00	9.33
Bt	80-120	n.d	5.30	12.62	14.81	19.60	13.51	34.13	6.30
C1	120-150	n.d	6.70	9.54	30.61	n.d	7.60	46.30	2.84
C2	150-180	n.d	11.20	22.51	37.20	n.d	2.07	26.80	2.70
Mean		n.d	3.86	14.30	27.59	8.80	12.03	33.50	4.94
VI. Haplic Phaeozem (foot-slope)									
A1	0-40	n.d	9.37	10.80	40.70	13.51	11.81	13.40	7.46
A2	40-64	n.d	8.00	14.00	30.21	10.52	16.83	20.52	5.42
AC	64-74	n.d	12.80	12.12	25.41	4.75	6.02	38.91	3.90
CG	74-90	n.d	17.01	8.36	20.50	12.60	11.01	30.50	4.64
mean		n.d	11.00	11.32	29.01	10.35	11.42	25.83	5.35

n.d – not detected

Table 4

The total content of chromium and percentage contribution fractions of this metal in the investigated soils in transect A and B

Horizon	Depth (cm)	Fraction							Total content
		F1	F2	F3	F4	F5	F6	F7	
		% total content							$mg \cdot kg^{-1}$
1	2	3	4	5	6	7	8	9	10
Transect A									
I. Albic luvisol (flat)									
A	0-25	4.96	4.54	28.50	3.40	18.80	20.91	18.90	4.29
Eet,fe	25-40	4.60	7.79	29.11	2.05	12.21	19.81	24.40	4.53
Bt,fe	40-60	2.25	13.90	15.21	2.03	9.72	12.63	45.72	9.21
Bt	60-90	2.68	14.81	13.80	2.10	6.39	16.10	44.11	9.34
C	90-120	1.27	10.90	14.00	2.10	17.00	17.90	30.90	1.21
Mean		3.15	10.38	20.12	2.34	12.80	17.47	32.82	5.72
II. Dystric Cambisol (slope)									
A	0-24	4.84	21.40	22.12	9.95	14.42	14.50	13.71	5.96
ABbr(fe)	24-37	4.43	20.92	17.71	4.09	10.70	19.20	22.80	7.34
Bbr1	37-47	1.98	10.60	9.98	1.82	7.93	12.71	54.90	13.70
Bbr2	47-75	1.92	9.56	9.67	2.45	9.52	13.13	53.50	14.91
Bbr3	75-100	1.47	9.77	9.32	2.25	7.11	18.80	56.32	15.70
Bbr4	100-140	1.93	11.60	8.54	1.09	8.08	12.41	56.33	14.82
Mean		2.70	14.00	12.91	3.61	9.62	15.13	42.90	12.08
III. Mollic Fluvisol (slope)									
IA1	0-15	2.83	16.31	14.80	4.64	9.76	20.61	35.80	8.67
IA2	15-35	3.07	14.92	14.01	3.96	7.69	20.71	35.71	8.65
IA3	35-46	3.01	14.60	12.91	4.60	11.40	19.13	34.30	9.57
IIA	46-68	1.51	9.24	9.18	1.82	11.30	10.70	56.31	15.90
AC	68-78	1.40	9.68	7.60	1.78	7.91	10.70	60.82	16.81

cont. Table 4

1	2	3	4	5	6	7	8	9	10
IC	78-100	1.70	9.75	9.40	1.55	6.62	13.41	57.61	13.90
IICG	100-125	1.92	9.53	9.95	1.82	6.02	11.50	59.30	14.50
Mean		2.20	12.01	11.12	2.88	8.67	15.25	48.55	12.57
Transect B									
IV. Anthropic Regosol (flat)									
Aan	0-25	3.88	21.20	20.31	5.62	13.50	20.40	14.73	5.82
AanA	25-50	3.89	22.31	21.01	4.28	11.01	18.30	19.01	6.21
Ees	50-80	7.60	13.12	10.10	4.93	13.03	22.91	28.30	2.80
Bhfe	80-110	2.90	16.00	13.32	3.30	8.21	13.70	42.60	9.55
C	110-150	1.50	10.20	8.54	2.23	4.20	12.51	60.81	15.00
Mean		3.95	16.56	14.66	4.07	9.98	17.56	33.12	7.87
V. Haplic Luvisol (slope)									
A	0-25	4.23	21.21	19.63	5.05	13.50	16.60	19.71	6.26
Eet	25-50	4.98	20.72	20.80	6.70	8.45	22.40	16.00	5.18
EB	50-80	1.13	7.35	7.79	1.16	6.05	8.64	67.80	19.90
Bt	80-120	1.53	11.80	10.90	0.76	9.04	11.21	54.71	14.41
C1	120-150	4.87	14.00	10.91	2.33	13.30	17.70	36.90	2.40
C2	150-180	6.50	11.51	9.70	2.71	14.11	12.73	42.80	3.00
Mean		3.87	14.43	13.29	3.95	10.71	14.90	39.65	8.52
VI. Haplic Phaeozem (foot-slope)									
A1	0-40	3.30	20.60	17.90	4.47	12.01	14.21	27.41	7.39
A2	40-64	3.13	18.22	16.81	3.58	8.75	15.80	33.70	8.11
AC	64-74	3.32	20.40	20.40	6.49	7.77	19.60	22.03	6.68
CG	74-90	2.99	16.81	14.03	1.50	11.10	17.72	35.70	8.85
Mean		3.18	19.00	17.29	4.01	9.90	16.83	29.70	7.76

ed from the soil-forming processes (lessivage and chemical erosion) shaping these soils. In deluvial soils (profiles III and IV), more Pb was associated with the humus horizons containing more organic matter. The total Cr concentration was associated with the loam fraction and organic matter in the analyzed soil horizons. More chromium was recorded in the soil horizons of transect A (10.50 $mg \cdot kg^{-1}$) than of transect B (8.10 $mg \cdot kg^{-1}$, on average), while the highest content of chromium appeared in deluvial humus soil (profile III – 12.57 $mg \cdot kg^{-1}$) and Calcaric Cambisol (profile II – 12.07 $mg \cdot kg^{-1}$) on the moraine slope, and the lowest amounts were in lessive podzolized soil (profile I – 5.72 $mg \cdot kg^{-1}$) on the hill top.

The spetiation analysis of lead in the soils on the moraine slope, performed by Zeien and Brümmer's method, indicates that the metal was bound to different parts of the soil's solid phase (forms, fractions) – Table 3. The highest lead content was found in forms bound to organic matter (F4): 29.74--40.39% of the total content in soils of transect A, mostly in deluvial humus soil, and 24.89-29.01% in soils of transect B, mainly in deluvial soil, and post-extraction residuals (F7) (residual forms indicating lead in primary and secondary silicates and aluminosilicates) in transect A: 24.63-36.61%, most in Calcaric Cambisol, and in transect B 25.83-33.50%, most in Haplic Luvisol. Lead dominated in the humus soil horizons of both transects (34.50--56.01%), which is consistent with its bio-geochemistry, and in some enrichment horizons B (namely of podzolized lessive soil and Calcaric Cambisol in transect A), which may indicate some dislocation despite the fact that this metal is considered to be less mobile in soil environment, and in mother rock C (deluvial humus soil and Haplic Luvisol), which in turn can imply the lithogenic origin of lead in these soils (KABATA-PENDIAS 1998). Similar or identical amounts of lead were found (in transects) in forms associated with manganese oxides susceptible to oxidation (F3) (6.30-19.28% in transect A and 11.32-14.30% in transect B, but most in the deepest soil horizons), and with crystalline iron oxides (F6) (7.00-13.25% in transect A and 11.41-14.30% in transect B), whose content within the profiles was more differentiated. Similar quantities of Pb (7.76-14.70%) were recorded in bonds with amorphous iron oxides (F5), the compounds that were not detected in lower horizons of lessive soils (profiles I and V), whereas within the profiles lead content was not univocally differentiated. No lead was found in easily soluble forms (F1), while its share in exchangeable forms (F2) ranged from 2.59 to 11.00% of the total content; it was detected in some horizons, indicating its reduced susceptibility to mobilization from the soil's solid phase to a solution. KARCZEWSKA (2002) also claims that lead in mineral soils is present most often in the residual fraction as well as bound to organic matter; its lowest percentage (namely in soils with natural lead content) is made up by the most mobile fractions (easily soluble and exchangeable).

The sequential extraction analysis according to Zeien and Brümmer's method revealed that chromium in the examined soils was present in more varied bindings than lead (Table 4). Particular soil horizons differed in the chromium fraction distribution. As bio-available fractions (F1 and F2), Cr content was much higher than lead, which may indicate better mobility of chromium than lead: higher in soils of transect B than A. Considerably less Cr was recorded in easily soluble fraction F1 (2.20-3.95% of the total content, on average for profiles) than in exchangeable fraction F2 (10.38-19.00%). Chromium dominated in residual forms (29.70-48.55%): more mainly

Table 5

Correlation coefficients between fractions of lead and chromium $(mg \cdot kg^{-1})$ and some properties of investigated soils

Parametr	Element	Fraction						
		F1	F2	F3	F4	F5	F6	F7
Transect A								
Total content	Pb	-	0.33	0.33	0.83*	0.78*	0.61*	0.63*
	Cr	0.44	0.78*	0.61*	0.24	0.81*	0.88*	0.98*
Org. C	Pb	-	0.44	-0.27	-0.76*	0.70*	-0.05	0.09
	Cr	0.13	0.09	0.13	0.53	0.21	-0.02	-0.21
pH_{KCl}	Pb	-	- 0.21	- 0.14	0.03	- 0.21	- 0.11	- 0.31
	Cr	- 0.44	- 0.01	- 0.44	- 0.28	- 0.18	- 0.03	0.12
CEC	Pb	-	-	- 0.49*	0.30	0.66*	0.24	0.48*
	Cr	0.27	0.48*	0.48*	0.51*	0.70*	0.59*	0.60*
Ø<0.002[a]	Pb	-	- 0.17	- 0.12	0.44	0.47*	0.23	0.48*
	Cr	0.46*	0.70*	0.47*	0.38	0.74*	0.79*	0.72*
Transect B								
Total content	Pb	-	- 0.10	0.55*	0.75*	0.85*	0.80*	0.64*
	Cr	0.26	0.69*	0.71*	0.05	0.76*	0.86*	0.96*
Org. C	Pb	-	- 0.07	0.70*	0.81*	0.55*	0.29	- 0.37
	Cr	0.32	0.32	0.31	0.41	0.22	-	- 0.24
pH_{KCl}	Pb	-	0.48	- 0.23	0.27	- 0.06	- 0.45	- 0.34
	Cr	- 0.26	- 0.17	- 0.19	- 0.12	- 0.17	- 0.31	- 0.26
CEC	Pb	-	- 0.07	0.34	0.65*	0.76*	0.72*	0.46
	Cr	0.33	0.70*	0.71*	0.21	0.67*	0.68*	0.70*
Ø<0.02[a]	Pb	-	0.20	0.43	0.59*	0.60*	0.33	0.06
	Cr	0.48	0.54*	0.56*	0.25	0.49*	0.43	0.11

[a] percentage fraction of clay

* significant $p = 0.05$

in the horizons with its higher total content. Czekała (1997) reported that stable chromium bindings in the residual fraction of mineral soils made up 56-86%.

The percentage of chromium in the fractions bound to manganese oxides and hydroxides (F3), amorphous (F5) and crystalline (F6) iron oxides and hydroxides varied between within the analyzed profiles. Higher Cr amounts were found in the form occluded on crystalline iron oxides (14.90-17.56%, on average for profiles) than on amorphous ones (8.67-12.80%). Between 8.54 – 29.11% of chromium was bound to manganese oxides: more in soils of transect A than B; more in surface and sub-surface soil layers and most (13.80-29.11%) in podzolized lessive soil on the top of the slope (profile I). Little chromium was found in forms bound to organic matter (F4), and its quantity ranged at the level of easily soluble fraction (F1). Chromium content in fraction F4 was 2.34-4.07% (mean for profiles); most in anthropogenically regulated soil (profile IV) and deluvial soil (profile VI); most in surface and sub-surface layers. According to Czekała (1997), chromium share in organic fractions in humus horizons of mineral soils was 12.70% of its total amount. Kalembasa et al. (2008) found the following Cr contents in surface soil horizons localized along the ring road around Siedlce: in the fractions separated by means of Zeien and Brümmer's method (percentage of the total content): F1 3.78-6.42; F2 5.43-8.99; F3 1.98-2.75; F4 7.47-15.50; F5 31.00-40.50; F6 6.91-7.66; F7 29.20-32.50.

Significant correlations were recorded between separated Pb and Cr fractions and their total content, sorption capacity CEC (mainly chromium), organic carbon content (mainly lead), as well as loamy fraction (Ø < 0.002 mm) in the studied soils of transects A and B (Table 5). The strongest correlations were observed between lead and chromium in bindings with amorphous iron oxides F5, in stable bindings of residual fraction F7 (transect A) and in the fraction bound to manganese oxides F3 (transect B) versus selected properties of the soils. Kalembasa et al. (2008), when examining the heavy metals fractions along the ring road around Siedlce, achieved similar values of Pearson's correlation coefficients for the analyzed metals.

CONCLUSIONS

1. Total content of lead and chromium in soils on a moraine slope did not exceed concentrations permissible by the Decree of the Ministry for Environment, and ranged within natural levels according to IUNG. These metals were slightly higher in soils of transect A than B.

2. Sequential fractionation of lead and chromium made by Zeien and Brümmer's method revealed their varied concentrations in separated fractions in particular horizons of the soils. The highest levels of the heavy

metals were predominantly recorded in the residual fraction (F7), while lead was also high in the organic fraction (F4). No lead was detected in bioavailable fraction F1, and its very small quantities were detected in fraction F2; both fractions contained much more chromium. More chromium than lead was recorded in the fraction bound to manganese oxides (F3) as well as amorphous (F5) and crystalline iron oxides and hydroxides (F6). The levels of Pb and Cr were not unambiguously differentiated in the fractions of typologically distinct soils of both transects.

3. Percentages of the heavy metals in separated fractions to their total content for soils in transects A and B can be ordered in the following sequences:

transect A Pb: F4> F7> F3> F5> F6> F2> F1 (not detected);
Cr: F7> F6> F3> F2> F5> F4> F1;
transect B Pb: F7> F4> F3> F6> F5> F2> F1 (not detected);
Cr: F7> F2> F6> F3> F5> F4> F1.

4. Statistical processing revealed significant differences between lead and chromium in the separated fractions and, in general, their fractions, total content, organic matter content and loam fraction < 0.002 mm versus CEC of analyzed soils.

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