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## HEAVY METAL FRACTIONS IN SOILS FERTILIZED WITH SEWAGE SLUDGE

The influence of fertilization with municipal sewage sludge on Zn, Cr, Ni, Pb, and Cu content in exchangeable, reducible, oxidizable, and residual fractions (separated by means of the method recommended by the European Community's Bureau of References (BCR)) and their distribution in the profiles of four soil types (Stagnic Luvisols and Cambic Arenosols) that were agriculturally utilized was evaluated. The most metals were found in residual fraction (F4), while the fewest – in exchangeable fraction (F1). The sequential analysis revealed that sewage sludge introduced into the soil increased heavy metal content in exchangeable fraction (F1), reducible fraction associated with Fe and Mn oxides (F2), and oxidizable organic fraction (F3), whereas their content in residual fraction (F4) decreased.

### 1. INTRODUCTION

Municipal sewage sludge introduced into the soil may result in imbalance in geochemical circulation of heavy metals, particularly in the rate of their release from waste materials and their transport to the soil solution [1]–[3]. The ecological and fertilizing influence of sewage sludge on the soil is closely associated with heavy metal forms (fractions) in which they occur. The methods of sequential extraction make it possible to identify these bindings and to estimate qualitatively their availability and potential toxicity for biotic elements of the food chain [1], [4]–[7]. The aim of present research was to evaluate the effects of fertilization with municipal sewage sludge on the amount and distribution of zinc, chromium, nickel, lead, and copper fractions in agriculturally utilized soils.

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## 2. MATERIALS AND METHODS

Our test were carried out on Stagnic Luvisols (2 profiles) and Cambic Arenosols (2 profiles), the arable land localized in the South-Podlasie Lowland. Within a given sub-type, the above soils formed pairs: fertilized (a year after fertilization at the rate of  $15 \text{ t d.m.} \cdot \text{ha}^{-1}$ ) and not fertilized with sewage sludge from mechanical-biological municipal purification plant. In the soil samples taken from a particular genetic soil horizon and air dried, the following properties of the soils were determined: granulometric composition, pH in  $1 \text{ mol KCl} \cdot \text{dm}^{-3}$ , cation exchangeable capacity (CEC), organic carbon ( $C_{\text{org}}$ ) by the methods commonly applied in soil-science laboratories. The total content of Zn, Cr, Ni, Pb, and Cu were assessed by ICP-AES method after soil mineralization in the mixture of concentrated HCl and  $\text{HNO}_3$  (3:1) in a microwave system. The fractions of heavy metals were determined by the sequential extraction procedure recommended by The European Community's Bureau of References (BCR) [8], in which four fractions were separated: F1 – exchangeable, readily soluble in acid medium ( $0.11 \text{ mol CH}_3\text{COOH} \cdot \text{dm}^{-3}$ , pH 3); F2 – reducible associated with Fe and Mn oxides ( $0.5 \text{ mol NH}_2\text{OH} \cdot \text{HCl} \cdot \text{dm}^{-3}$ , pH 2); F3 – oxidizable, associated with organic matter and sulfides ( $8.8 \text{ mol H}_2\text{O}_2 \cdot \text{dm}^{-3}$  plus  $1 \text{ mol CH}_3\text{COONH}_4 \cdot \text{dm}^{-3}$ , pH 2); F4 – residual, calculated as a difference between the total content of a particular heavy metal and the total of: F1, F2, and F3. The content of Zn, Cr, Ni, Pb, and Cu in particular fractions was determined with ICP-AES method.

## 3. RESULTS AND DISCUSSION

The Stagnic Luvisols and Cambic Arenosols were characterized by varied physical, physicochemical and chemical properties (table 1). Soil fertilization with sewage sludge increased pH, sorption capacity (CEC), and organic carbon content ( $C_{\text{org}}$ ), especially in the surface layers of the soils studied. The values of pH, CEC, and  $C_{\text{org}}$  along with total lead and zinc content were recorded to be higher in the sandy levels of Cambic Arenosols than in the upper level of the Stagnic Luvisol profile developed from sandy silt. Regardless of the sub-type, the soils contained slightly higher mean amounts of heavy metals after being fertilized with sewage sludge, which can be presented as the following descending order:  $\text{Zn} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Cu}$ , amounting respectively to ( $\text{mg} \cdot \text{kg}^{-1}$ ): 13.3; 7.87; 6.68; 5.02, and 4.70 (Stagnic Luvisols fertilized with sewage sludge); 12.8; 6.98; 6.36; 4.39, and 2.96 (Stagnic Luvisols not fertilized with sewage sludge); 17.3; 6.60; 6.50; 6.29, and 2.71 (Cambic Arenosols fertilized with sewage sludge); and 16.7; 5.66; 5.42; 5.32, and 2.50 (Cambic Arenosols not fertilized with sewage sludge). Other authors [1], [3], [7], [9], [10] reported similar dependencies in the soils fertilized with sewage sludge. The enrichment of surface genetic levels with heavy metals did not cause any exceeding their permissible values in agriculturally utilized soils [11].

Table 1

Some properties and total content of heavy metals in soils investigated

Soil	Genetic horizon	Depth (cm)	Sand	Silt	Clay	pH <sub>KCl</sub>	C <sub>org</sub>	CEC**	Pb <sub>tot</sub>	Cr <sub>tot</sub>	Cu <sub>tot</sub>	Zn <sub>tot</sub>	Ni <sub>tot</sub>
			2–0.5	0.5–0.002	<0,002								
			% fraction of diameter in mm*			g · kg <sup>-1</sup>							
Stagnic Luvisol <sup>1)</sup>	AEet	0–22	44	50	6	6.43	10.9	81.8	16.5	8.75	5.06	7.64	3.72
	Eet	22–45	61	34	5	6.01	1.67	65.3	12.0	5.66	4.93	4.54	3.68
	EetBt	45–62	75	19	6	5.33	0.33	72.7	7.93	5.76	5.08	4.06	4.18
	Bt1	62–70	76	16	8	4.56	0.48	82.7	12.8	8.71	9.64	4.24	4.81
	Bt2	70–115	69	17	14	4.69	0.49	95.0	15.9	10.1	8.07	4.79	6.02
	C	115–150	70	16	14	4.46	0.43	93.2	14.8	8.22	7.77	4.86	6.08
Stagnic Luvisol <sup>2)</sup>	AEet	0–27	45	50	5	5.40	10.8	79.1	15.8	8.54	4.58	7.38	2.47
	Eet	27–52	53	42	5	5.15	1.00	64.6	8.78	5.21	4.31	3.15	2.91
	EetBt	52–75	63	23	4	5.11	0.41	70.5	10.7	5.06	4.71	3.07	3.13
	Bt1	73–80	74	17	9	4.38	0.45	87.4	14.4	7.55	10.1	4.38	2.99
	Bt2	80–120	68	19	13	4.22	0.31	73.5	13.5	7.72	7.36	3.98	3.09
	C	120–150	66	19	15	4.35	0.39	90.4	13.3	7.82	7.11	4.35	3.19
Cambic Arenosol <sup>1)</sup>	Ap	0–27	88	9	3	7.05	11.0	117	23.9	3.76	2.99	8.12	2.20
	Bv	27–55	89	8	3	5.53	1.46	48.6	18.0	3.73	2.77	7.52	1.14
	BvC	55–85	89	8	3	5.85	0.51	52.4	7.92	3.01	2.43	4.15	0.64
	C	85–95	90	6	4	6.35	0.31	52.7	17.8	5.22	6.19	5.55	2.03
	IIC1	95–130	66	19	15	7.17	0.26	94.9	17.6	9.52	9.87	5.66	5.06
	IIC2	130–150	69	17	14	7.31	0.23	106	18.5	14.4	14.6	6.75	5.21
Cambic Arenosol <sup>2)</sup>	Ap	0–25	86	11	3	5.78	8.61	58.9	18.4	3.03	2.38	7.46	1.53
	Bv	25–40	88	9	3	5.32	1.32	44.7	15.4	3.30	2.19	4.35	0.94
	BvC	40–60	88	8	4	5.99	0.48	48.9	12.5	2.99	2.58	4.05	0.74
	C	60–95	86	10	4	6.27	0.32	61.4	15.9	4.12	5.77	4.53	2.13
	IIC1	95–130	68	16	16	6.64	0.28	104	18.9	10.2	9.69	5.03	4.79
	IIC2	130–150	66	21	13	6.91	0.24	119	19.3	10.3	9.88	6.49	4.84

1) – fertilized with sewage sludge.

2) – not fertilized with sewage sludge.

\* – According to Polish Standard: PN-R-04033.

\*\* CEC – Cation Exchangeable Capacity in mmol(+) · Kg<sup>-1</sup>.

The chemical soil analysis revealed differentiated content of zinc, chromium, nickel, lead, and copper in four separated fractions of the soils (table 2). The fewest metals were separated in exchangeable fraction (F1): 0.75–12.2% (fertilized soils) and 0.37–8.68% (not fertilized soils), the excess of which may be toxic to plant and animal organisms. The largest amounts of metals were recorded in residual fraction (F4): 35.07–76.60% (fertilized soils) and 48.32–84.34% (not fertilized soils). This confirmed the dominating role of stable mineral compounds in trace elements' circulation within the soil environment [4], [5]. Mean per cent (table 2) of separated Zn, Cr, Ni, Pb, and Cu fractions in Cambic Arenosols as well as Cr and Cu fractions in Stagnic Luvisols can be arranged according to the following descending order: F4 > F3 > F2 > F1 (fertilized and not fertilized), while the proportion of the four fractions of Zn, Ni, and Pb in Stagnic Luvisols (fertilized and not fertilized) can be presented as follows: F4 > F2 > F3 > F1. BRAZAUSKIENE et al. [4] and ŁUKOWSKI [10] found a similar sequence for sewage-fertilized soil developed from loamy deposits.

Table 2

Percentage contribution of zinc, chromium, nickel, lead and copper fractions to soils investigated

Soil	Genetic horizon	Depth (cm)	Zn				Cr				Ni				Pb				Cu			
			F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
Stagnic Luvisol <sup>1)</sup>	AEt	0-22	6.26	30.95	31.2	31.59	3.51	15.17	33.19	48.14	3.97	9.48	26.48	60.07	1.37	24.73	56.74	17.16	6.87	16.94	53.36	22.82
	Eet	22-45	5.93	32.00	16.17	45.9	3.25	14.12	18.61	64.01	2.45	10.63	10.18	76.73	0.87	25.74	36.41	36.28	6.54	14.62	24.38	54.46
	EetBt	45-62	4.62	33.42	11.2	50.77	3.21	11.94	8.49	76.36	1.65	10.26	9.92	78.17	0.78	27.02	25.87	46.32	4.50	13.08	18.21	64.21
	Bt1	62-70	2.71	33.98	9.22	54.09	1.27	6.89	4.85	86.99	1.61	10.74	6.05	81.6	0.73	31.27	20.96	47.04	3.10	8.99	10.47	77.44
	Bt2	70-115	1.36	35.41	5.65	57.57	0.84	6.25	3.81	89.10	0.67	12.19	4.65	82.49	0.38	34.32	14.78	50.52	0.96	7.77	9.84	81.42
Average		1.22	35.54	5.32	57.91	0.68	6.19	3.78	89.34	0.55	12.84	4.05	82.55	0.34	35.02	13.75	50.89	0.91	7.06	9.68	82.34	
Stagnic Luvisol <sup>2)</sup>	AEt	0-27	3.68	33.55	13.1	49.64	2.13	10.1	12.1	75.66	1.82	11.5	10.1	76.6	0.75	29.68	28.09	41.37	3.81	11.4	20.99	63.78
	Eet	27-52	4.87	19.58	20.52	55.03	2.60	9.05	18.51	69.84	2.82	8.29	19.27	69.62	0.96	23.18	39.04	36.82	4.33	14.41	41.28	39.98
	EetBt	52-75	3.27	28.0	11.85	56.89	1.94	8.81	10.65	78.59	1.92	9.32	9.39	79.36	0.44	24.64	30.34	44.58	3.85	11.80	17.79	66.56
	Bt1	73-80	2.82	30.0	9.35	57.83	1.86	7.93	6.47	83.74	1.70	9.80	7.55	80.96	0.29	25.67	23.97	50.07	3.67	10.64	10.89	74.79
	Bt2	80-120	2.52	32.36	6.91	58.21	1.17	6.20	3.50	89.13	1.00	10.96	5.59	82.46	0.23	31.53	18.13	50.11	1.84	7.72	7.11	83.33
Average		0.91	34.67	3.93	60.49	0.49	5.43	1.92	92.16	0.54	12.07	3.91	83.48	0.13	34.92	8.92	56.03	0.52	5.09	4.12	90.28	
Cambic Arenosol <sup>2)</sup>	Ap	0-27	2.54	30.03	9.27	58.16	1.42	7.09	7.15	84.34	1.41	10.5	8.20	79.9	0.37	29.22	21.43	48.99	2.45	9.09	14.18	74.29
	Bv	27-55	4.48	22.8	49.1	23.7	23.6	23.9	31.3	21.1	5.10	19.7	37.9	37.3	n.d.*	29.5	51.0	19.5	5.20	15.0	58.7	21.1
	BvC	55-85	4.43	23.3	48.0	24.3	16.7	25.4	34.9	23.0	4.70	19.7	32.9	42.8	n.d.*	29.4	51.0	19.6	4.60	14.1	43.8	37.5
	C	85-95	5.34	25.7	32.6	36.3	16.1	25.9	36.9	21.1	4.10	20.9	30.5	44.5	16.45	27.5	31.3	24.8	3.20	11.0	33.4	52.3
	IIC1	95-130	2.62	26.4	17.0	54.0	7.55	18.4	21.7	52.5	3.30	21.0	21.4	54.4	9.29	25.2	38.6	26.8	2.12	10.2	19.6	68.0
Average		2.00	27.3	9.90	60.8	4.60	11.4	15.1	68.9	1.57	23.1	14.2	55.2	3.87	17.6	21.5	57.1	0.454	8.51	19.0	72.0	
Cambic Arenosol <sup>2)</sup>	Ap	0-25	3.49	25.32	27.8	43.45	12.2	19.2	25.9	42.77	3.37	21.8	25.6	48.4	5.59	24.41	34.93	35.07	2.66	11.3	32.1	53.95
	Bv	25-40	2.28	18.5	44.5	34.7	15.8	20.2	39.6	20.1	2.10	8.30	21.5	68.1	n.d.*	13.2	48.7	38.1	1.77	12.7	44.7	40.9
	BvC	40-60	2.23	19.2	30.4	48.2	9.37	20.5	30.9	39.5	1.50	9.80	16.1	72.6	n.d.*	7.70	48.3	40.5	1.28	11.8	40.9	46.0
	C	60-95	1.52	17.6	22.6	58.2	13.0	19.0	33.0	33.5	1.00	11.1	15.2	72.7	12.8	12.0	27.7	47.5	0.64	10.4	28.5	60.5
	IIC1	95-130	1.28	21.3	12.4	65.0	7.63	10.3	21.5	51.8	0.62	11.9	11.6	74.9	6.89	12.9	32.0	48.2	0.20	10.6	19.5	69.6
Average		0.84	23.9	7.49	67.8	3.14	10.3	15.3	71.3	0.44	6.61	5.50	87.5	5.15	9.94	16.2	68.8	0.20	8.40	12.0	79.4	
IIC2	130-150	0.80	22.1	6.77	70.4	3.13	9.23	12.9	73.7	0.46	7.00	5.40	87.2	2.45	5.95	13.9	77.8	0.18	7.62	11.6	80.6	
Average		1.49	20.43	20.7	57.38	8.68	14.9	25.5	48.32	1.02	9.12	12.6	77.17	4.55	10.28	31.13	53.48	0.73	10.3	26.2	62.83	

<sup>1)</sup> Fertilized with sewage sludge.<sup>2)</sup> Not fertilized with sewage sludge.

\* n.d. – not determined.

Fractions: F1 – exchangeable, F2 – reducible (bounded to Fe-Mn oxide), F3 – oxidizable (bounded to organic matter), F4 – residual.

Table 3

Values of coefficient of correlation between fractions of heavy metals and some properties of soils

Parameter	Stagnic Luvisol <sup>1)</sup>				Stagnic Luvisol <sup>2)</sup>				Cambic Arenosol <sup>1)</sup>				Cambic Arenosol <sup>2)</sup>			
	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
Zn <sub>tot</sub>	-0.317	0.137	0.152	-0.103	0.149	-0.258	0.232	-0.099	-0.343	-0.404	0.165	-0.098	-0.328	0.682	-0.199	0.115
C <sub>org</sub>	0.628	-0.753	0.944*	-0.726	0.778	-0.796	0.881*	-0.751	0.404	-0.753	0.863*	0.835*	0.681	-0.451	-0.847*	-0.873*
CEC	-0.569	0.429	-0.219	0.263	-0.634	0.477	-0.507	0.670	-0.361	-0.043	-0.149	0.188	-0.717	0.719	-0.701	0.658
< 0.002	-0.923*	0.880*	-0.665	0.896*	-0.859*	0.851*	-0.769	0.869*	-0.824*	0.888*	-0.797	0.715	-0.819*	0.862*	-0.740	0.694
C <sub>tot</sub>	-0.645	-0.568	-0.150	0.298	-0.246	-0.393	0.051	0.063	-0.735	-0.709	-0.837*	0.854*	-0.781	-0.796	-0.887*	0.919*
C <sub>org</sub>	0.560	0.662	0.924*	-0.860*	0.700	0.592	0.883*	-0.827*	0.779	0.403	0.851*	-0.519	0.714	0.555	0.816*	-0.699
CEC	-0.631	-0.597	-0.291	0.404	-0.728	-0.718	-0.495	0.591	0.001	-0.494	-0.471	0.340	-0.802	-0.803	-0.841	0.761
< 0.002	-0.925*	-0.849*	-0.637	0.732	-0.903*	-0.934*	-0.723	0.799	-0.883*	-0.942*	-0.876*	0.895*	-0.836*	-0.841*	-0.835*	0.878*
N <sub>tot</sub>	-0.769	0.642	-0.599	0.538	-0.695	0.660	-0.582	0.560	-0.796	0.755	-0.688	0.906*	-0.720	-0.622	-0.741	0.961*
C <sub>org</sub>	0.874*	0.389	0.960*	-0.980*	0.848	-0.686	0.942*	-0.967*	0.915*	-0.465	0.901*	-0.753	0.860*	-0.153	0.849*	-0.600
CEC	-0.274	0.516	-0.179	0.129	-0.642	0.741	-0.376	0.297	-0.303	0.439	-0.132	0.011	-0.656	-0.782	-0.742	0.725
< 0.002	-0.880*	0.968*	-0.604	0.541	-0.863	0.930*	-0.672	0.604	-0.939*	0.869*	-0.858*	0.952*	-0.907*	0.832*	-0.881*	0.963*
Pb <sub>tot</sub>	0.526	-0.157	0.607	-0.726	0.768	-0.242	0.459	-0.611	-0.794	-0.466	0.402	0.137	-0.788	-0.328	0.086	0.231
C <sub>org</sub>	0.846*	-0.598	0.903*	-0.957*	0.950*	-0.581	0.841*	-0.835*	-0.474	-0.510	0.911*	-0.269	-0.581	0.109	0.856*	-0.461
CEC	-0.255	0.872*	-0.305	0.194	-0.353	0.823*	-0.701	0.566	-0.514	-0.980*	-0.138	0.652	-0.306	-0.863*	-0.721	0.779
< 0.002	-0.817*	0.945*	-0.886*	0.612	-0.834*	0.928*	-0.841*	0.776	-0.891*	-0.948*	-0.820*	0.979*	-0.834*	-0.867*	-0.848*	0.928*
C <sub>uot</sub>	-0.795	-0.763	-0.753	0.842*	-0.666	-0.798	-0.761	0.932*	-0.798	-0.667	-0.566	0.808	-0.637	-0.761	-0.720	0.724
C <sub>org</sub>	0.638	0.723	0.963*	-0.915*	0.565	0.709	0.949*	-0.897*	0.687	0.752	0.850*	-0.729	0.747	0.684	0.816*	-0.722
CEC	-0.831*	-0.544	-0.211	0.312	-0.822*	-0.730	-0.350	0.480	-0.189	-0.849*	0.142	-0.085	-0.613	-0.879*	-0.798	0.807
< 0.002	-0.930*	-0.864*	-0.586	0.694	-0.967*	-0.912*	-0.631	0.738	-0.875*	-0.876*	-0.671	0.831*	-0.842*	-0.889*	-0.711	0.821*

\* Significance at  $\alpha = 0.05$ ;  $n = 6$ .

1) Fertilized with sewage sludge.

2) Not fertilized with sewage sludge.

Fractions: F1 – exchangeable, F2 – reducible (bounded to Fe-Mn oxide), F3 – oxidizable (bounded to organic matter), F4 – residual.

The sequence analysis revealed that in the sewage sludge-fertilized soil the heavy metal concentration in exchangeable (F1), reducible (F2), and oxidizable (F3) fractions increased, while in residual one (F4) decreased. The results obtained are consistent with literature data [1], [2], [4], [6], [7], [9]. MAŃKO and TERELAK [10] recorded the decrease of Zn, Ni, Pb, and Cu concentration in exchangeable fraction of surface soil horizons fertilized with sewage sludge, and their increasing proportion in stable compounds of residual fraction.

Much higher mean per cent of Zn, Cr, Ni, Pb, and Cu in fraction F4 (63.78; 75.66; 76.6; 41.37, and 49.64%, respectively), Zn, Pb, and Cu in fraction F2 (33.55; 29.68; and 11.4%, respectively), as well as Zn and Cu in fraction F1 (3.68, and 3.81%, respectively) was recorded in Stagnic Luvisols fertilized with sewage sludge than that in fertilized Cambic Arenosols. In Cambic Arenosols fertilized with sewage sludge, much higher levels of heavy metals were found in fraction F3 (Zn, 27.80; Cr, 25.90; Ni, 25.60; Pb, 34.93; Cu, 32.10%) and in fraction F2 (Cr, 19.2; Ni, 21.8%), as well as Cr, Ni, and Pb in exchangeable F1 forms (12.2; 3.37; 5.59%, respectively) as compared to Stagnic Luvisols.

In humus horizons, KIM and McBRIDE [1] separated the largest amount of Zn, Pb, and Ni in reducible fraction (F2): 52.5; 58.4; 47.6%, respectively, while the smallest – in exchangeable fraction (F1): 8.55; 2.08; 6.58%, respectively. In the soil amended with the sewage sludge, NYAMANANGARA [2] recorded the proportion of Zn and Cu in fraction F1 as large as 22.0% each, in organic fraction – 21.0 and 41.0%, respectively, and in residual fraction – 45.0 and 34.0%, respectively. BRAZAUSKIENE et al. [4] separated the most zinc, copper, and lead from sandy soils in the following fractions: F2, F3 and F4, respectively, while the least in: F3, F2 and F1, respectively. KUBOVA et al. [6] recorded the highest concentration of zinc in fraction F1 (44.7%), whereas the lowest, in fraction F4 (15.0%); the most copper in fraction F3 (42.9%), and the least in fraction F1 (5.24%). WALTER and CUEVAS [7], examining the nickel speciation, separated 11–13% of reducible fraction, 16–29% of organic fraction, and 59–71% of residual fraction of the metal in the surface horizons of fertilized soils. FILIPEK-MAZUR [13] reported that in the horizons of cultivated soils, chromium occurred mainly in stable organic-mineral and mineral compounds (F4) – 50.64%, as well as it is occluded on manganese and iron oxides (F2) – 47.65%, while its lowest content could be found in soluble and exchangeable fraction – 0.29%.

Statistical analysis (table 3) revealed that heavy metal content in residual fraction significantly depended on organic carbon content (Stagnic Luvisols) and clay fraction ( $\phi < 0.002$  mm) (Cambic Arenosols). Total content of Zn and Cu (Stagnic Luvisols) as well as Cr and Ni (Cambic Arenosols) had a significant influence on the proportion of F4 fraction in the soils examined. Regardless of the soil sub-type, per cent of the metals in organic fraction (F3) considerably depended on  $C_{org}$  and total content of the metal in Stagnic Luvisols (Cr, Cu) as well as on clay fraction in Cambic Arenosols (Pb, Cr, Ni). Exchangeable (F1) and reducible (F2) fractions of

the analyzed elements significantly depended on the content the particles of < 0.002 mm diameter. Exchangeable fraction of Pb (Stagnic Luvisols) and Ni (Cambic Arenosols) depended on  $C_{\text{org}}$  content, while Cu content in that fraction was correlated with the sorption capacity. The sorption capacity (CEC) of Cambic Arenosols considerably affected the Cu and Pb per cent in fraction F2. Other authors [1], [4], [5], [7] also reported a significant influence of soil properties ( $C_{\text{org}}$  content, < 0.002 mm fraction) and geochemical properties of particular heavy metals on their speciation within the soil environment.

#### 4. CONCLUSIONS

1. In middle-eastern Poland, mean total heavy metal content in the soils of Stagnic Luvisol and Cambic Arenosols type fertilized with sewage sludge was high. The metals could be arranged in the following descending order: Zn > Cr > Ni > Pb > Cu. Concentrations of these metals in the soils tested did not exceed permissible values ranging within the natural levels.

2. Sequential fractionation of Zn, Cr, Ni, Pb, and Cu by BCR method indicated their varied contents in separated fractions of the soils. The most metals were found in stable compounds of residual fraction (F4), while the fewest in exchangeable one (F1).

3. Sequential analysis revealed that sewage sludge introduced into the soil, regardless of the soil subtype, increased the heavy metal content in exchangeable (F1), reducible (F2), and oxidizable (F3) fractions, especially in the surface horizons; however, it decreased the proportion of residual fraction (F4).

4. Statistical analysis proved that separated fractions of Zn, Cr, Ni, Pb, and Cu were in majority significantly dependent on organic carbon content and clay fraction and to a lesser degree on a total content of a given metal and soil sorption capacity.

#### REFERENCES

- [1] KIM B., MCBRIDE M.B., *A test of sequential extractions for determining metal speciation in sewage sludge-amended soils*, Environmental Pollution, 2006, 144, 475–482.
- [2] NYAMANGARA J., *Use of sequential extraction to evaluate zinc and copper in a soil amended with sewage sludge and inorganic metal salts*, Agriculture, Ecosystems and Environment, 1998, 69, 135–141.
- [3] SINGH R.P., AGRAWAL M., *Effects of sewage sludge amendment on heavy metal accumulation and consequent responses of Beta vulgaris plants*, Chemosphere, 2007, 67, 2229–2240.
- [4] BRAZAUSKIENE D.M., PAULAUSKAS V., SABIENE N., *Speciation of Zn, Cu, and Pb in the soil depending on soil texture and fertilization with sewage sludge compost*, J. Soils Sediments, 2008, 8, 184–192.
- [5] 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.

- [6] KUBOVA J., STREŠKO V., BUJDOŠ M., MATUŠ P., MEDVED J., *Fractionation of various elements in CRMs and in polluted soils*, Anal. Bioanal. Chem., 2004, 379, 108–114.
- [7] WALTER I., CUEVAS G., *Chemical fractionation of heavy metals in a soil amended with repeated sewage sludge application*, The Science of the Total Environment, 1999, 226, 113–119.
- [8] RAURET G., LÓPEZ-SÁNCHEZ J.F., SAHUQUILLO A., RUGIO R., DAVIDSON C., URE A., QUEVAUILLER PH., *Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials*, J. Environ. Monit., 1999, 1, 57–61.
- [9] ŁUKOWSKI A., *Wpływ nawożenia obornikiem i osadem ściekowym z mleczarni na zawartość Pb, Cu i Zn we frakcjach gleby o kategorii agronomicznej glina lekka*, [in:] *Obieg pierwiastków w przyrodzie*, Wyd. IOŚ, Warszawa, 2005, 142–146.
- [10] MAŃKO P., TERELAK H., *Wpływ osadu ściekowego z oczyszczalni komunalnej na mobilność metali ciężkich (Zn, Cd, Pb, Cu, Ni) w glebie gliniastej*, Zesz. Nauk. AR Szczecin, 1999, 200, 231–234.
- [11] Rozporządzenie Ministra Środowiska z dnia 9 września 2002 roku w sprawie standardów jakości gleby oraz standardów jakości ziemi. DzU nr 165, poz. 1359.
- [12] FILIPEK-MAZUR B., *Występowanie i toksyczność metali ciężkich w środowisku*, [in:] *Diagnostyka gleb i roślin w rolnictwie zrównoważonym*, Wyd. AP w Siedlcach, 2004, Monografie, 54, 116–130.

#### FRAKCJE METALI CIĘŻKICH W GLEBACH NAWOŻONYCH OSADAMI ŚCIEKOWYMI

Badano wpływ nawożenia komunalnym osadem ściekowym na ilość Zn, Cr, Ni, Pb i Cu we frakcji wymiennej, redukcyjnej, utleniającej oraz rezydualnej, wydzielonych za pomocą metody rekomendowanej przez European Community's Bureau of References (BCR) oraz ich rozmieszczenie w profilach czterech gleb (płowe opadowo-glejowe i rdzawe właściwe) użytkowanych rolniczo. Najwięcej metali stwierdzono we frakcji rezydualnej (F4), a najmniej we frakcji wymiennej (F1). Analiza sekwencyjna wykazała, że wprowadzenie do gleby osadu ściekowego zwiększyło zawartość metali ciężkich we frakcji wymiennej (F1), redukcyjnej związanej z tlenkami Fe i Mn (F2) i utleniającej – organicznej (F3), a zmniejszył się ich udział we frakcji rezydualnej (F4).