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CONTENT OF HEAVY METALS AND THEIR FRACTIONS IN SOIL IN RESULT OF RESIDUAL EFFECT OF WASTE MATERIALS

ZAWARTOŚĆ METALI CIĘŻKICH I ICH FRAKCJI W GLEBIE W WYNIKU NASTĘPCZEGO ODDZIAŁYWANIA MATERIAŁÓW ODPADOWYCH

Abstract: Analysed was the effect of various material supplements, *ie* municipal sewage sludge and various doses of ash-sludge and ash-peat mixtures on total content of heavy metals (Cr, Zn, Pb, Cu, Cd and Ni) and their fractions. Five fractions of heavy metals were determined in soil by means of Tessier's method after competed three-year pot experiment on maize as the test plant.

Application of ash-sludge and ash-peat mixtures to the soil influenced the increase in heavy metal content in soil but the amount of these metals did not exceed the standards established for arable soils. The pot experiment with maize revealed that the residual fraction played the main role in Cr, Zn and Pb accumulation, fraction bound to organic matter in Cu and Ni accumulation, whereas exchangeable and residual fraction in Cd accumulation. Heavy metal mobility (the sum of two first fractions) in the analysed ash-sludge and ash-peat mixtures supplied to the soil, irrespectively of applied extractant, was diversified and did not exceed the following values of total content: Cr – 0.39 %; Zn – 20 %, Pb – 13 %, Cu 10 %, Cd – 69 % and Ni – 4 %. The investigations have shown that cadmium was the best available to maize whereas chromium the least.

Keywords: municipal sewage sludge, peat, furnace ash, soil, heavy metals, speciation

Introduction

Systematically increasing volume of generated wastes and regulations limiting their storage make waste management a very important ecological, technical and economic

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problem [1–3]. Environmental management of municipal sewage sludge and furnace ashes meets with growing approval owing to their physicochemical properties [4–5].

Municipal sewage sludge after their processing should return to the natural environment because of their content of organic matter and biogenic components. Their environmental application is recommended, particularly for reclamation purposes [2, 6–7]. Environmental management of municipal sewage sludge is usually limited because of their abnormal contents of heavy metals [8]. In case of the abnormal heavy metal content in sewage sludge, their thermal disposal is recommended [1].

Due to their considerable de-acidifying properties, furnace ashes have recently been used for the environment protection and in municipal economy for neutralising acid sewage, which allows for their rational utilisation, at the same time limiting their stored amounts [9]. Furnace ashes are not hazardous wastes, so their environmental utilisation is possible, including reclamation of landfills [10, 11]. However, beside a high content of soil de-acidifying compounds, also trace elements are present in ashes and may pose ecological hazard [12].

When municipal sewage sludge are mixed with furnace ashes, we will obtain a ash-sludge mixture which may be used for reclamation of a landfill site. Owing to its new physicochemical properties, composed ash-sludge mixture may contain heavy metals in various forms [4, 6]. Therefore, an attempt was made at an assessment of heavy metal mobility from these wastes after their mixing and application to the soil.

Material and methods

The research on the effect of municipal sewage sludge, furnace ashes, peat and their mixtures on physicochemical soil properties was conducted after the 3-year pot experiment was completed. The test plant in the pot experiment was maize. The effect of the materials mentioned above on macroelement, microelement and heavy metal content in maize was discussed in earlier publications [13–15].

Present paper examined the effect of various material supplements, *ie* municipal sewage sludge, furnace ash and various doses of ash-sludge mixtures on the total content of heavy metals (Cr, Zn, Pb, Cu, Cd and Ni) and their fractions.

In case of abnormal concentrations of heavy metals in sewage sludge, the waste maybe replaced by peat, which does not pose any ecological hazard and at the same time is characterized by similar physicochemical properties [16, 17]. Therefore, also an ash-peat mixture was made to compare the availability and heavy metal mobility from sewage sludge and furnace ash. The ash-peat mixture will also allow to assess potential heavy metal release from furnace ash to which organic matter was added as peat.

Five heavy metal fractions were determined in soil by means of Tessier's method [18] after completed three year pot experiment with maize as the test plant.

Very acid soil used for the experiment had a loamy silt texture (Table 1) containing 26 % of sand, 69 % of silt and 5 % of clay. Regarding the agronomic category, the furnace ash applied in the experiment corresponded to medium loam and regarding the texture to sandy loam [19].

Characteristic of physicochemical materials used in experiment

Parameter	Unit	Soil	Sewage sludge	Ash	Peat
Texture		Silt loam	—	Sandy loam	—
pH$_{(KCl)}$	[-]	4.60	6.67	9.85	4.82
pH$_{(H_2O)}$		4.73	6.82	10.06	5.26
Hydrolytic acidity	[mmol(+) $\cdot$ kg^{-1}]	70.68	161.96	3.63	831.94
Base exchange capacity		42.45	887.03	260.25	317.09
Organic C	[g $\cdot$ kg^{-1}]	18.48	219.16	23.69	370.50
Total N		1.92	35.25	0.53	11.49
Available P	[mg $\cdot$ kg^{-1} d.m.]	57.43	611.40	41.18	269.75
Available K		72.42	247.60	140.33	117.97
Available Mg		109.75	885.49	989.86	999.86
Total Cr		39.33	48.95	33.85	11.55
Total Pb		40.40	59.25	18.65	2.75
Total Cu		8.28	272.25	74.50	1.18
Total Zn		70.25	1182.50	93.75	9.28
Total Cd		0.43	5.10	0.28	0.05
Total Ni		30.08	23.03	39.98	7.30

The experiment was conducted in four replications, in polyethylene pots of 6 kg volume, filled with ash-sludge and ash-peat mixtures in the amount of 1–30 % of the total soil mass. The experimental design comprised also objects obtaining solely the individual components of the mixtures (Table 2). In all pots annual constant NPK fertilization with 0.3 gN, 0.08 gP and 0.2 gK $\cdot$ kg^{-1} of soil in the form of NH_4NO_3, KH_2PO_4 and KCl was applied each year. The mineral fertilizers, as solutions, were applied in the first year, two weeks before plant sowing and were thoroughly mixed with soil. In the second and third year of the experiment the fertilizers were applied in early spring before maize vegetation started. During vegetation the plants were watered with bi-distilled water and the soil moisture was maintained on the level of 60 % maximum water capacity.

When the experiment was finished, total heavy metal content was assessed in the soil after the samples dissolving in a mixture of nitric and perchloric acids (3:2, *v/v*) [20] and the metal fractions by Tessier's method [18].

Speciation of heavy metals

The content of various metal fractions in the analysed substrata was determined by means of metal sequential extraction scheme by Tessier et al [18]. Five fractions of heavy metals (Cr, Zn, Pb, Cu, Cd and Ni) were identified:

1. Exchangeable metals, exchangeable fraction (FI) – air dried and homogenized material was extracted with 8 cm^3 1.0 M Mg Cl$_2$, at pH = 7, by shaking for 1 hour at 25 ^{o}C;

2. Metals bound to carbonates, carbonate fraction (FII) – the exchangeable form residue extracted by 8 cm^3 1.0 M CH$_3$COONa, at pH = 5, by shaking constantly for 5 hours at 25 ^{o}C;

3. Metals bound with iron and manganese oxides, oxide fraction (FIII) – carbonate residue extracted for 5 hours in 20 cm^3 of 0.04 M NH$_2$OH·HCl dissolved in 25 % CH$_3$COOH (*v/v*) at 96 ^{o}C, mixing from time to time;

4. Metals bound to organic matter, organic fraction (FIV) – Fe-Mn oxide residue extracted by 3 cm^3 of 0.02 M NHO$_3$ + 5 cm^3 of 30 % H$_2$O$_2$ (*v/v*) for 2 hours at 85 ^{o}C, mixing from time to time, then 3 cm^3 of 30 % H$_2$O$_2$ was added at 85 ^{o}C and all was mixed from time to time. Finally it was shaken with 5 cm^3 3.2 M CH$_3$COONH$_4$ in 20 % HNO$_3$ (*v/v*) for 0.5 hour at 25 ^{o}C;

5. Metal residue bound to silicates, residual fraction (FV) – residue after organic form was hot decomposed with 10 cm^3 of 40 % HF and 2 cm^3 of 70 % HClO$_4$, after slight drying 1 cm^3 of HClO$_4$ was added and heated until white fumes appeared. The residue was dissolved in HCl (1:1, *v/v*) and diluted to 100 cm^3.

Extraction of one-gram samples of the substratum was conducted in 50 cm^3 polyethylene extraction thimbles. After each extraction the samples were centrifuged, 3000 xg for 30 min, The extraction residue was rinsed with 8 cm^3 of H$_2$O, centrifuged again as above and the supernatant was removed. In the filtrates of each replication (pot), Cr, Zn, Pb, Cu, Cd and Ni contents present in individual fractions were assessed by means of ICP-AES method and expressed in percent in relation to its total content.

Statistical computations were conducted using Microsoft Excel 7.0 calculation sheet and Statistica v.7.0. Statistical assessment of individual sources of variability was made using analysis of variance procedure. The significance of differences between the compared means of the analysed features (parameters, indices) was stated on the basis of T Tukey's test at significance level for pot experiments $\alpha \leq 0.01$.

Results

Total content

The soil used for the experiment was characterized by the natural content of Pb, Cu and Cd but elevated concentrations of Cr, Zn and Ni (Table 1) [21]. Assessed heavy metal content was below these elements permissible levels in soils classified for fertilization with sewage sludge [8]. A comparison of heavy metal content in furnace ash to limit numbers suggested by IUNG [21] showed a low content of these elements, except copper (Table 1). Therefore, the content of heavy metals in the ash, as compared with the soil, did not constitute a potential source of metals supplied to the soil. Applied sewage sludge contained higher amounts of heavy metals in comparison with furnace ash, however their content did not exceed permissible values conditioning their environmental utilisation [8].

Table 2

Content of Cr and Zn in soil after experiment [mg · kg⁻¹] and share of heavy metal fractions [%]

Objects*	Cr						Zn					
	Total [mg · kg⁻¹]	Fraction [%]					Total [mg · kg⁻¹]	Fraction [%]				
		FI	FII	FIII	FIV	FV		FI	FII	FIII	FIV	FV
1. Control	34.81	0.12	0.14	0.63	16.51	82.59	52.00	6.82	10.92	18.06	23.25	40.94
2. Sludge	46.06	0.11	0.19	0.88	39.42	59.39	1107.50	6.55	10.23	15.65	33.75	33.82
3. Ash	31.75	0.03	10.51	11.34	12.39	65.74	85.25	0.19	2.16	5.48	17.68	74.49
4. Peat	9.16	0.22	0.08	0.98	13.14	85.58	7.06	2.75	7.41	14.15	61.11	14.57
5. AS	34.23	0.08	0.52	4.96	20.25	74.18	549.25	1.37	3.86	5.62	14.93	74.21
6. AP	22.05	0.07	0.59	4.57	29.17	65.60	44.74	0.53	1.04	2.08	40.02	56.33
7. AS 1 %	33.98	0.09	0.15	0.71	17.07	81.97	51.80	7.87	11.82	22.51	28.92	28.87
8. AS 2 %	34.06	0.11	0.16	0.92	20.25	78.57	55.45	6.41	10.47	18.01	30.22	34.89
9. AS 5 %	35.18	0.12	0.19	0.88	21.66	77.16	66.80	5.04	5.54	12.75	27.73	48.94
10. AS 10 %	36.49	0.13	0.18	1.01	25.84	72.83	80.25	3.08	4.64	10.26	27.92	54.10
11. AS 20 %	37.08	0.14	0.20	1.02	26.68	71.96	106.68	0.57	2.49	6.65	26.24	64.04
12. AS 30 %	38.46	0.15	0.22	1.10	30.74	67.79	120.25	0.31	1.06	3.96	25.35	69.33
13. AP 1 %	34.85	0.10	0.14	0.64	19.08	79.04	60.13	7.05	10.04	18.55	26.26	38.10

444 Jacek Antonkiewicz et al

Table 2 contd.

Objects*	Cr						Zn					
	Total [mg · kg⁻¹]	Fraction [%]					Total [mg · kg⁻¹]	Fraction [%]				
		FI	FII	FIII	FIV	FV		FI	FII	FIII	FIV	FV
14. AP 2 %	34.39	0.10	0.14	0.69	20.19	77.88	59.18	6.16	9.25	17.61	29.60	37.38
15. AP 5 %	34.32	0.11	0.18	0.82	23.35	74.54	57.75	5.91	5.88	15.29	37.54	35.38
16. AP 10 %	33.67	0.09	0.19	0.90	23.29	74.53	55.00	0.72	6.13	14.12	47.23	31.80
17. AP 20 %	32.09	0.13	0.22	1.01	26.93	70.72	54.25	0.55	4.91	11.23	57.25	26.06
18. AP 30 %	31.57	0.14	0.25	1.10	29.49	68.02	52.23	0.37	2.42	8.66	66.70	21.85
$V\%$**	22.54	34.21	306.42	140.77	29.24	9.21	179.95	84.70	58.88	47.65	42.36	41.49
NRI-LSD$_{(\alpha \leq 0.01)}$	6.83	—	—	—	—	—	30.64	—	—	—	—	—

* Objects: 1 – Control; 2 – Sewage sludge; 3 – Ash; 4 – Peat; 5 – AS Ash-Sludge 1:1; 6 – AP Ash-Peat 1:1; 7 – AS Ash-Sludge 1 %; 8 – AS Ash-Sludge 2 %; 9 – AS Ash-Sludge 5 %; 10 – AS Ash-Sludge 10 %; 11 – AS Ash-Sludge 20 %; 12 – AS Ash-Sludge 30 %; 13 – AP Ash-Peat 1 %; 14 – AP Ash-Peat 2 %; 15 – AP Ash-Peat 5 %; 16 – AP Ash-Peat 10 %; 17 – AP Ash-Peat 20 %; 18 – AP Ash-Peat 30 %; ** Variation coefficient.

Table 3

Content of Pb and Cu in soil after experiment [mg · kg⁻¹], and percentage of heavy metal fractions [%]

Objects*	Pb Total [mg · kg⁻¹]	Pb Fraction [%]					Cu Total [mg · kg⁻¹]	Cu Fraction [%]				
		FI	FII	FIII	FIV	FV		FI	FII	FIII	FIV	FV
1. Control	34.44	5.63	8.06	17.28	29.17	39.86	6.03	2.33	6.72	14.11	50.03	26.81
2. Sludge	56.00	5.91	8.46	12.03	30.67	42.92	258.88	2.45	1.82	4.07	79.42	12.25
3. Ash	14.43	0.33	0.45	9.16	28.30	61.76	71.75	0.39	0.09	4.71	54.99	39.81
4. Peat	2.21	2.06	2.37	8.50	32.32	54.75	0.89	8.70	1.49	9.55	61.03	19.23
5. AS	34.16	0.23	0.30	5.97	24.29	69.20	153.38	4.33	0.75	3.86	59.66	31.40
6. AP	10.10	0.35	1.02	11.28	14.59	72.75	35.00	0.54	0.44	4.04	73.91	21.07
7. AS 1 %	36.51	4.30	6.56	12.91	20.77	55.46	8.10	1.95	4.51	16.03	49.77	27.74
8. AS 2 %	36.58	3.72	6.46	12.58	18.73	58.51	8.21	2.10	6.20	15.05	52.48	24.17
9. AS 5 %	36.00	3.45	5.71	10.51	15.77	64.56	10.70	2.25	5.48	15.06	55.40	21.81
10. AS 10 %	35.91	1.72	2.77	5.29	15.69	74.52	14.36	2.42	5.80	13.18	56.15	22.45
11. AS 20 %	35.89	0.55	2.32	3.91	10.21	83.02	21.20	2.44	7.07	17.55	58.87	14.07
12. AS 30 %	35.38	0.47	1.09	2.47	8.83	87.14	30.23	2.39	6.39	15.72	59.85	15.65
13. AP 1 %	37.89	5.20	7.14	14.85	19.87	52.94	7.84	1.42	4.87	9.68	48.67	35.36
14. AP 2 %	37.08	4.23	6.39	14.18	20.13	55.07	7.85	1.06	4.49	8.27	55.62	30.56
15. AP 5 %	36.66	3.70	5.81	9.91	15.85	64.73	8.30	0.92	2.46	6.29	54.50	35.84
16. AP 10 %	35.49	1.07	2.15	5.93	12.33	78.51	9.18	0.73	1.96	4.71	52.21	40.40
17. AP 20 %	35.19	0.62	1.45	3.76	10.49	83.68	10.41	0.30	1.45	2.63	62.01	33.60
18. AP 30 %	34.68	0.50	1.03	2.49	7.38	88.60	12.54	0.30	1.29	2.45	85.18	10.79
V %***	37.11	83.78	74.19	49.82	41.53	22.25	176.00	95.57	68.91	57.73	17.15	36.11
NRI-LSD$_{(α ≤ 0.01)}$	2.75	—	—	—	—	—	3.34	—	—	—	—	—

* Explanations: see Table 2.

Table 4

Content of Cd and Ni in soil after experiment [mg · kg⁻¹] and share of heavy metal fractions [%]

Objects*	Cd Total [mg·kg⁻¹]	FI	FII	FIII	FIV	FV	Ni Total [mg·kg⁻¹]	FI	FII	FIII	FIV	FV
1. Control	0.34	47.80	5.38	8.96	13.59	24.27	24.99	2.79	0.26	10.42	65.25	21.28
2. Sludge	4.91	19.83	8.35	9.09	10.43	52.31	17.88	6.54	2.07	7.46	64.27	19.67
3. Ash	0.25	3.27	4.90	14.29	26.53	51.02	30.25	0.08	0.05	9.70	65.79	24.37
4. Peat	0.04	25.14	15.69	1.00	25.49	32.68	6.04	3.47	0.59	12.87	59.82	23.25
5. AS	2.13	0.79	1.28	8.38	8.49	81.05	28.78	0.39	0.13	6.55	62.73	30.19
6. AP	0.13	7.21	12.01	12.01	31.23	37.54	20.94	0.23	0.22	11.47	63.56	24.53
7. AS 1 %	0.40	43.17	6.40	6.66	12.13	31.65	24.85	2.17	0.20	10.20	66.23	21.21
8. AS 2 %	0.41	38.57	5.28	5.28	12.88	37.98	24.88	2.02	0.15	8.83	67.93	21.07
9. AS 5 %	0.43	34.41	3.99	4.99	12.97	43.64	25.11	1.72	0.15	6.59	68.06	23.49
10. AS 10 %	0.49	28.38	3.55	4.43	15.13	48.50	25.24	1.40	0.13	5.12	69.44	23.90
11. AS 20 %	0.53	25.15	2.43	2.03	17.14	53.25	25.30	0.94	0.11	3.87	70.58	24.50
12. AS 30 %	0.65	13.04	1.00	1.67	18.47	65.82	25.45	0.64	0.06	2.62	72.23	24.46
13. AP 1 %	0.36	55.70	12.75	10.07	13.09	8.39	25.09	3.12	0.23	11.41	71.01	14.23
14. AP 2 %	0.36	52.53	10.65	10.65	17.30	8.87	24.54	3.20	0.24	7.82	71.36	17.37
15. AP 5 %	0.35	48.85	8.14	13.57	20.95	8.48	24.21	3.09	0.18	7.63	73.92	15.18
16. AP 10 %	0.34	35.54	4.35	18.13	30.64	11.33	24.05	0.82	0.19	5.77	77.00	16.22
17. AP 20 %	0.33	32.53	2.77	19.03	34.86	10.81	24.03	0.75	0.18	4.12	78.30	16.66
18. AP 30 %	0.31	25.31	2.98	26.06	43.56	2.09	23.86	0.20	0.07	2.98	82.43	14.32
V %***	160.56	55.52	67.69	68.96	47.92	66.65	21.51	88.20	159.29	40.98	8.44	21.19
NRI-LSD$_{\alpha \leq 0.01}$	0.17	—	—	—	—	—	2.28	—	—	—	—	—

* Explanations: see Table 2.

The content of Cr, Zn, Pb, Cu and Cd in the applied sewage sludge (object 2), after maize vegetation finished was respectively by 0.32, 21, 0.62, 42 and 14-fold higher in comparison with the control (object 1). Higher content of these heavy metals in sewage sludge affected increase in the metal concentrations in the ash-sludge mixtures added to the soil (objects 7–12).

When ash-sludge mixture was solely applied (object 5), over 10, 25 and 6-fold higher content of Zn, Cu and Cd was assessed in comparison with the control (object 1). On the other hand Cr, Pb and Ni content in ash-sludge mixture was approximate to the content in the control soil.

After three years of maize vegetation increase in Cr, Zn, Cu and Cd content in soil was registered under the influence of ash-sludge mixtures proportion (objects 7–12), whereas Pb and Ni content remained on a similar level (Table 2–4). Insignificant changes in Pb and Ni content in the soil fertilized with ash-sludge mixtures one may explain by low lead content in ash and Ni in sewage sludge (Table 2–4). A significant increase in Cr, Zn, Cu and Cd content in the soil fertilized with ash-sludge mixtures has been explained as due to a their higher content in sewage sludge as compared with their content in soil. Moreover, the source of copper in these objects was also furnace ash. Copper concentration in the furnace ash on which maize was grown was over 11-fold higher as compared with the control soil.

In effect of growing proportions of ash-peat mixtures (objects 13–18) a systematic decline of Cr, Zn, Pb, Cd and Ni content in soil was observed, but a marked increase in Cu content in these substrata. A regular decrease in Cr, Zn, Pb, Cd and Ni concentrations in ash-peat mixtures added to the soil was due to low content of these elements in the used peat. Concentrations of Cr, Zn, Pb, Cu, Cd and Ni in peat (object 4) were over 2.8, 6.4, 14.6, 5.8 and 8.0-fold lower in comparison with the control. Presented research has demonstrated that due to its low content of heavy metals peat used in the ash-peat mixtures could be use as organic matter source in reclaimed substrata.

Heavy metal fractions in soil

Percentage distribution of heavy metals among the separated fractions depended on the analysed element and the kind and dose of the material (Table 2–4). In the control soil after 3 years of maize vegetation, the highest share of Cr, Zn and Pb was revealed in the residual fraction (F V), while Cu and Ni in the fraction bound to organic matter (F IV) and Cd bound to the exchangeable (F I) and residual (F V) fraction (Table 2–4). Among heavy metals in the control soil, the lowest share in the most mobile fractions, *ie* available to plants (fractions F I and F II) was registered for Cr, which did not exceed 0.26 % of total Cr. The biggest share in the most mobile fractions, which exceeded over 50 % of its content, was noted for Cd.

After a 3-year maize cultivation on sewage sludge (object 2) a small quantity of Cr was found also in the mobile fractions and the sum of two first fractions did not exceed 0.30 % of the total content. In object 2, where solely sewage sludge was applied, the biggest amounts of Cr, Zn, Pb and Cd were assessed in the residual fraction (F V),

whereas Ni and Cu in the organic fraction (F IV). Copper was most strongly bound by organic matter in the sludge (about 80 %), whereas the highest concentration of Cd, about 52 % was determined in the residual fraction and exchangeable fraction (about 20 %).

In the object where only ash was used (object 3) metals, such as Cr, Zn, Pb and Cd were present mainly in the residual fraction (F V) and Cd and Ni mainly in the organic fraction (over 54 % and 65 %). The best heavy metal availability from furnace ashes (presence in the mobile fractions, F I and F II sum) was assessed for Cr and Cd. It exceeded 10 and 8 % of the total content, respectively. The other analysed metals, such as Zn, Pb, Cu and Ni in most mobile fractions occurred in ash only in small amounts. The content of Zn, Pb, Cu and Ni in F I and F II fractions constituted over: 2.35 %, 0.78 %, 0.49 % and 0.13 % of the total content, respectively. Investigations have demonstrated that furnace ashes to the least extent accumulated Ni and Cu in the mobile fractions (sum of F I and F II). Organic matter (F IV) present in ash as remains of unburnt coal, contributed most to Pb, Cu, Cd and Ni binding and constituted over 28 %, 54 %, 26 % and 65% of its total content, respectively.

In the object where only peat was applied (object 4), heavy metals such as Zn, Cu and Ni occurred mainly in the organic fraction (F IV), whereas the content of Cr, Cd and Pb was registered mainly in the residual fraction (F V). In peat, the biggest share in the most mobile fractions, *ie* available to plants (sum of F I and F II fractions), exceeding 40 % of the total content was assessed for Cd. A considerable proportion in the mobile fractions was found also for Cu and Zn. It exceeded 10 % of their total content.

Ash-sludge (object 5) and ash-peat (object 6) mixtures accumulated the biggest quantities of Cr, Zn, Pb and Cd in the residual fraction (F V), Cu and Ni in the organic fraction (F IV). No considerable share of Cr, Zn, Pb, Cu or Ni in the mobile fractions (sum of F I and F II) was observed in the mixtures mentioned above. The research has shown that ash-peat mixture was a source of Cd in the most mobile fractions, *ie* available to plants where this element share reached about 20 % of the total content.

Under the influence of increasing proportion of ash-sludge mixtures in soil (objects 7–12) a regular increase in Cr and Cu in the most mobile fractions (F I and F II), in the fraction bound to Fe-Mn oxides and in the organic fraction (F III and F IV) was registered. The latter fraction provided a potential source of these metals for maize. On the other hand, presence of Cr and Cu in the residual fraction (F V, almost unavailable to plants) revealed a declining tendency. For Zn and Pb an opposite dependency was registered, *ie* it was found that ash-sludge mixtures added to the soil (object 7–12) caused a systematic decrease in these metals share in the fractions available to plants (F I–F IV), but increase in their content in the residual fraction. Ash-sludge mixtures applied to the soil affected a decrease in Cd and Ni occurrence in F I–F III fractions, whereas these metals share in the organic (F IV) and residual fraction (F V) was growing systematically.

Ash-peat mixtures applied to the soil (objects 13–18) caused an increase in the share of Cr in the phytoavailable fractions (F I and F II), in the fraction bound to Fe-Mn oxides and organic fractions (F III and F IV), whereas this metal percentage in the

residual fraction was declining regularly. It was observed that increasing shares of ash-peat mixtures in soil (objects 13–18) caused a decrease in the percentage of Zn, Cu and Ni in the best available to plants fractions (F I–F III) and in the residual fraction (F V), whereas an increase in the percentage of these metals in the organic fraction (F IV) was registered. Increasing share of ash-peat mixtures in soil caused a decreased share of Pb in the phytoavailable fractions (F I–F III) and in the oxide and organic fractions (F III and F IV), whereas their increased share in the residual fraction (F V) was noted. Cd percentage in the most mobile fractions (F I and F II) was systematically decreasing under the influence of increasing share of ash-peat mixtures in the soil (objects 13–18).

Summing up, it was found that the residual fraction (F V) had greatest share in Cr, Zn and Pb accumulation, while the fraction bound to organic matter (F IV) in Cu and Ni and Cd accumulation was most affected by the exchangeable (F I) and residual (F V) fractions.

Mobility of heavy metals (the sum of the first two fractions) in the soil with ash-sludge and ash-peat mixtures (objects 7–12 and 13–18) was diversified and did not exceed Cr – 0.39 %, Zn – 20 %, Pb – 13 %, Cu – 10 %, Cd – 69 % and Ni – 4 % of their total contents. Investigations have demonstrated that the cadmium was the best and chromium the least available to maize.

Discussion

Heavy metal content in the soil, sewage sludge, furnace ashes and peat was greatly diversified, as confirmed by the other authors' research [22, 23]. Diversified content of heavy metals in the analysed materials indicates a necessity for analysing these materials prior to their environmental management. Research of Tipping et al [24] confirms also a considerable distribution of heavy metals in natural peats.

In the opinion of many authors total heavy metal content is not the proper indicator of element availability to plants, it does not inform about potential element mobility in the environment [25, 26]. Although the total content of heavy metals is a commonly used indicator of the degree of pollution of the environment elements (soil, sewage sludge, ash, peat), still it does not determine the real risk of their effect upon the natural environment [3, 8].

According to the quoted authors and Swietlik and Trojanowska [27], while determining phytoavailability, the chemical forms of metals are more important than their total content. Identification of heavy metal chemical forms allows not only for a better characteristics of wastes, but also for a more precise assessment of an element phytoavailability after its supply to the soil. Investigations of Bojarska and Bzowski [28, 29] confirmed that furnace ashes are characterised by a small share of heavy metals in the phytoavailable fractions, particularly Pb and Zn in mobile forms, best available to plants.

A small quantity of Cr assessed in sewage sludge in the most mobile fractions was confirmed by the research of Czekala et al [30]. These authors revealed that even tannery sludge – greatly abundant in chromium, shows very small amount of this

element in the water soluble and exchangeable form; its content constituted between 0.05 % and 0.14 % Cr in relation to its total content. Also Piotrowska and Dudka [31] found trace amounts of Cr in the exchangeable fraction extracted from sewage sludges, at the same time revealing that the greatest amount of this element occurred in the "residue" fraction.

Research of many authors confirmed that applied ash-sludge and ash-peat mixtures affect a decrease in heavy metal share in mobile fractions, best available to plants. Decreasing heavy metal availability is connected with the increase in soil pH in result of poorer solubility of minerals and increased absorption by negatively charged colloidal soil particles [29]. Also investigations of Kalembasa and Wysokinski [32] demonstrated that brown and hard coal ash supplement to sewage sludges influences a decrease in Zn and Cu availability to plants. Research conducted by Tipping et al [24] also confirm that application of peats in chemically polluted areas may be used for heavy metal binding.

Conclusions

1. In result of furnace ashes and sewage sludge, peat and their mixtures supply to soil, changes were registered in heavy metals concentrations in the soil.

2. Municipal sewage sludge provided the greatest source of heavy metals present in the best phytoavailable fractions (F I and F II), whereas furnace ash contained the smallest amounts of heavy metals occurring in the fractions available to plants.

3. In result of sewage sludge mixing with furnace ash and peat with furnace ash, a decrease in the quantity of heavy metals occurring in the fractions best available to plants was observed. The higher the share of ash in the ash-sludge mixture, the smaller the share of metals in the phytoavailable forms.

4. Supplying increasing amounts of ash-sludge and ash-peat mixtures to soils generally caused increased Cr concentrations in fractions best available to plants (F I and F II), whereas the share of Zn, Pb, Cu, Cd and Ni in these fractions was declining systematically.

5. A prerequisite for the environmental management of ash-sludge and ash-peat mixtures should be monitoring research conducted on the content of heavy metals in the forms most mobile in the environment.

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ZAWARTOŚĆ METALI CIĘŻKICH I ICH FRAKCJI W GLEBIE W WYNIKU NASTĘPCZEGO ODDZIAŁYWANIA MATERIAŁÓW ODPADOWYCH

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Abstrakt: Badano wpływ dodatku materiałów, tj. komunalnego osadu ściekowego, popiołu paleniskowego i torfu oraz różnych dawek mieszanin popiołowo-osadowych i popiołowo-torfowych na całkowitą zawartość metali ciężkich (Cr, Zn, Pb, Cu, Cd, Ni) oraz ich frakcje. Oznaczono pięć frakcji metali ciężkich w glebie metodą Tessiera po zakończonym trzyletnim doświadczeniu wazonowym z kukurydzą jako rośliną testową.

Zastosowanie do gleby mieszanin popiołowo-osadowych oraz popiołowo-torfowych spowodowało zwiększenie zawartości metali ciężkich w glebie, ale zawartość tych metali nie przekraczała standardów ustalonych dla gleb uprawnych. W doświadczeniu wazonowym z kukurydzą stwierdzono, że główną rolę w magazynowaniu Cr, Zn i Pb odegrała frakcja rezydualna, a Cu i Ni frakcja związana z materią organiczną, natomiast Cd frakcja wymienna i rezydualna. Mobilność metali ciężkich (suma pierwszych dwóch frakcji) w badanych mieszaninach popiołowo-osadowych i popiołowo-torfowych wprowadzonych do gleby, niezależnie od zastosowanego ekstrahenta była zróżnicowana i w przypadku Cr nie przekraczała 0,39 %, Zn – 20 %, Pb – 13 %, Cu – 10 %, Cd – 69 %, Ni – 4 % zawartości ogólnych. Z badań wynika, że największą dostępnością dla kukurydzy odznaczał się kadm, a najmniejszą chrom.

Słowa kluczowe: komunalne osady ściekowe, torf, popioły paleniskowe, gleba, metale ciężkie, specjacja