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EVALUATION OF THE EFFECT OF COMBUSTION WASTES ON MIKROELEMENTS CONTENTS IN SOIL AFTER VIRGINIA FANPETALS (*SIDA HERMAPHRODITA* RUSBY) CULTIVATION

OCENA ODDZIAŁYWANIA ODPADÓW PALENISKOWYCH ORAZ KOMPOSTU Z OSADU ŚCIEKOWEGO NA ZAWARTOŚĆ MIKROSKŁADNIKÓW W GLEBIE PO UPRAWIE ŚLAZOWCA PENSYLWAŃSKIEGO

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Streszczenie. Doświadczenie jednoczynnikowe przeprowadzono w latach 2008–2010 w Stacji Oceny Odmian w Szczecinie – Dąbiu. Gleba na której założono doświadczenie wytworzona jest z piasku gliniastego lekkiego (pgl). Pod względem składu granulometrycznego zalicza się ją do kategorii gleb lekkich, kompleksu przydatności rolniczej IV b, żytniego dobrego (5). W doświadczeniu użyto odpadu paleniskowego w postaci popiołu z węgla brunatnego oraz kompostu wyprodukowanego z udziałem komunalnego osadu ściekowego metodą GWDA. W obu odpadach popiele z węgla brunatnego oraz osadzie ściekowym użytym do produkcji kompostu nie stwierdzono przekroczenia norm dla metali ciężkich określonych w przepisach ministerialnych. Schemat badań obejmował sześć obiektów nawozowych. Rośliną testową był ślazowiec pensylwański *(Sida Hermaphrodita Rusby).* Istotne zwiększenie zawartości ogólnej miedzi, manganu i niklu w glebie stwierdzono na obiektach III, IV i VI w porównaniu z obiektami nawożonymi węglanem wapnia lub popiołem z węgla brunatnego w dawce odpowiadającej 1,5 Mg CaO $\cdot$ ha^{-1} (obiekty I i II). Nawożenie organiczne z popiołem z węgla brunatnego przyczyniło się do wzrostu zawartość form kadmu, miedzi, manganu, ołowiu i cynku rozpuszczalnych w mol $\cdot$ dm^{-3} HCl w porównaniu z obiektem nawożonym wyłącznie węglanem wapnia oraz zawartością wyjściową. W stosunku do zawartości wyjściowej zmalała zawartość cynku, a wzrosła kadmu, miedzi, manganu i niklu rozpuszczalnego w 1 mol $\cdot$ dm^{-3} HCl.

Key words: compost, content of assimilable and soluble forms, sewage sludge, soil, total content of microelements, waste.
Słowa kluczowe: gleba, kompost, komunalny osad ściekowy popioły paleniskowe, zawartość ogólna i form rozpuszczalnych mikroskładników.

INTRODUCTION

Waste management consisting in their land-filling is a serious economic and ecological problem. These wastes include, among others, products derived from combustion processes and municipal sewage sludge.

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Combustion wastes possess physicochemical and biological properties that are subject to extreme opinions. Combustion ashes are characterised by many features which may favourably affect soil environment through de-acidification, delivery of nutrients for plants and improvement of the site of their development (Stankowski et al. 2006, Gibczyńska et al. 2007, Rosik-Dulewska 2008, Kowàćik et al. 2011). Wastes from power industry contain micro--components, including heavy metals. In excessively large quantities, they may constitute a serious threat to the soil-plant-animal system (Goswami and Maranta 2007). Numerous chemical analyses being carried out show that the content of heavy metals in combustion wastes ranges as follows: arsenic 0.85–0.93 mg · kg^{-1} D.M, chromium 35.5–272.0 mg · kg^{-1} D.M.; cadmium 0.5–4.6 mg · kg^{-1} D.M.; copper 7.2–670.0 mg · kg^{-1} D.M; nickel 19.0–180.0 mg · kg^{-1} D.M; zinc 46.6–520.0 mg · kg^{-1} D.M and manganese 316–1250 mg · kg^{-1} D.M. (Bahranowski et al. 1999, Maciak 2003). As a general rule, the quantity of heavy metals in ashes does not exceed the values being considered acceptable for soils.

The group of organic wastes include municipal sewage sludge. They are a rich source of organic matter and mineral nutrients being essential for plants. They can be environmentally managed providing they have been subject to stabilisation and hygienisation processes. One of the methods of municipal sewage sludge hygienisation and stabilisation is composting. The composting process is a relatively cheap, environmentally safe and agriculturally profitable technology Wong and Selvan 2006, Cai et al. 2007, Haroun et al. 2007, Zorpas and Loizidou 2008, Hua et al. 2009,). Through composting with structure-forming components, sewage sludge becomes a valuable organic fertiliser. Application of organic waste compost is not only connected with its efficiency as a fertiliser but also with the question whether it can be safely used in environmental and agricultural applications due to the content of heavy metals in it. Inorganic pollutants, which include heavy metals, do not biodegrade during the composting process (Barker and Bryson 2002, Nair et al. 2008, Rosik-Dulewska 2008) contrary to organic substances which decompose to pollutants being less toxic or non-toxic for environment (Marttinen et al. 2004). Jasiewicz et al. (2006) and Antonkiewicz (2007) state that grass fertilisation with sewage sludge composts increases the content of heavy metals in plants. The studies being carried out show that the content of heavy metals in sewage sludge and composts produced from it depend on their material composition, degree of solubility and size of fertiliser dose (Kucharzewski et al. 2004, Jasiewicz et al. 2007). Soil introduction of composts produced from municipal sewage sludge has many positive features being expressed, among others, in increase in the microbial activity of soils or improvement of their physicochemical properties (Whittle and Dyson 2002, Krzywy et al. 2005, Weber et al. 2007). The total content of heavy metals is nether a good parameter of the availability of chemical elements for plants nor a bad one as it does not inform about the potential mobility of metals in environment and their uptake by plants (He et al. 2009). Therefore, one of the most important criteria of environmental use of sewage sludge is the quantity of heavy metals being found in them. Frequently, they are being found in sewage sludge in excessive quantities. This results from high ability to accumulate these chemical elements in soils and plants (Jakubus 2003, 2006).

This study aimed at evaluation of the effect of application of combustion wastes (brown coal ash) and sewage sludge compost on the total content of micro-components and the content of their soluble forms in the soil material, including heavy metals, after a three-year--long cultivation of Virginia fanpetals.

MATERIAL AND METHODS

When achieving the research purpose, a single-factor field experiment being set at the Cultivar Evaluation Station in Szczecin-Dąbie was carried out in 2008–2010. The study design included 6 fertilisation objects. A field experiment was carried out in four replications in a randomized complete block on experimental plots, 33 m^2 each.

The content of microelements in soil, including heavy metals, was determined in average samples from four replications of each fertilisation object after Virginia fanpetals harvest in each year (i.e. in 2008, 2009 and 2010). The stock solution was obtained after previous wet mineralisation of soil material according to the Polish standards PN–ISO 11466/2002 and PN-ISO 11047/2001. The content of 1 mol · dm^{-3} HCl soluble microelements in soil was determined by atomic absorption spectrometry method. The solution for determination of soluble forms was obtained after extraction in 1 mol hydrochloric acid (1 M HCl). The total content of cadmium, copper, nickel, lead and zinc and the content of their forms soluble in 1 mol · dm^{-3} HCl were determined by the method of atomic absorption spectrometry on a Perkin Elmer AAS 300 Atomic Absorption Spectrometer. Physical and chemical properties of soil, brown coal ash and municipal sewage sludge compost being produced by the GWDA method and mineral fertilisation doses being applied were previously published by Krzywy-Gawrońskiej (2012).

Total contents of assimilable and soluble forms of microelements was processed statistically by the analysis of variance method using Statistica® 8.0 PL computer software package. In case of significant differences, the Tukey's test was used at significance level $p = 0.05$.

Due to long description of the fertilisation objects, letter abbreviations have been adopted for municipal sewage sludge compost and brown coal ash, i.e. SSC and BCA, respectively, being used throughout the section below with discussion of study results.

RESULTS AND DISCUSSION

When using sewage sludge or composts produced from it, it is possible to induce contamination of soil environment. In order to prevent such a situation, it is proposed to use ash-sludge mixtures or a combined compost fertilisation with addition of ashes because fly ashes from coal combustion contain generally a smaller quantity of heavy metals than municipal sewage sludge (Baran et al. 2006, Jakubus 2006, Czekała 2008). However, the fact that soil fertilisation with sewage sludge or composts produced from it increases the total content of heavy metals should be taken into account (Berti and Jacobs 1998). On the other hand, the content of heavy metals in soils do not increase when using moderate doses of municipal sewage sludge and composts produced from it, even after a long-term application, but at the same time their physical, chemical and biological properties improve.

According to the specific standards in the Regulation of the Minister of Environment on the soil quality and earth quality standards (DzU 2002, nr 165 poz. 1359), the soil on which the experiment was set up did not contain excessive quantities of heavy metals (Table 1).

Table 1. Total cadmium, copper, manganese, nickiel, lead and zinc contents in soil (mg · kg^{-1} d.m.) after Virginia fanpetals harvest in 2008–2010

Tabela 1. Zawartość kadmu, miedzi, manganu, niklu, ołowiu i cynku w mg · kg^{-1} s.m. w glebie po zbiorze ślazowca pensylwańskiego w latach 2008–2010

Parameters Pierwiastek	Content initial Zawartość początkowa	Study years Lata badań	Fertilisation objects Obiekty nawozowe						Mean Średnia	$LSD_{0.05}$ $NIR_{0,05}$
			I*	II	III	IV	V	VI		
			Total content in mg · kg^{-1} D.M. Zawartość ogólna w mg · kg^{-1} s.m.							
Cadmium Kadm	0.22	2008	0.22	0.23	0.24	0.26	0.24	0.26	0.24	0.009
		2009	0.24	0.25	0.26	0.25	0.25	0.28	0.25	n.s.
		2010	0.25	0.26	0.28	0.29	0.27	0.21	0.26	n.s.
		Mean – Średnia	0.24	0.25	0.26	0.27	0.25	0.25	0.25	n.s.
Copper Miedź	9.50	2008	10.1	10.2	12.0	11.8	12.1	12.5	11.4	0.08
		2009	9.85	9.70	11.4	11.6	11.6	12.0	11.0	0.07
		2010	9.58	9.72	10.7	11.5	10.2	12.6	10.7	0.05
		Mean – Średnia	9.84	9.87	11.4	11.6	11.3	12.4	11.1	n.s.
Manganese Mangan	205.0	2008	216	225	262	256	242	247	241	1.56
		2009	222	218	240	241	234	238	232	1.30
		2010	208	210	218	222	218	226	217	1.86
		Mean – Średnia	215	218	240	239	231	237	230	0.85
Nickiel Nikiel	9.50	2008	10.3	10.2	11.0	11.9	11.2	12.1	11.1	0.07
		2009	10.0	9.95	10.7	11.4	11.0	11.7	10.8	0.13
		2010	9.80	9.85	10.2	11.0	10.0	11.2	10.4	0.39
		Mean – Średnia	10.0	10.0	10.7	11.4	10.7	11.7	10.8	0.12
Lead Ołów	19.2	2008	20.1	20.0	21.4	21.8	20.9	21.2	20.9	0.10
		2009	19.7	19.8	21.4	21.4	20.5	21.0	20.6	0.09
		2010	19.5	19.6	20.8	20.8	20.0	20.9	20.3	0.10
		Mean – Średnia	19.8	19.8	21.2	21.3	20.5	21.0	20.6	0.09
Zinc Cynk	24.0	2008	24.9	25.8	27.2	27.9	26.3	28.0	26.7	0.09
		2009	24.6	25.4	26.8	26.8	25.9	27.7	26.2	n.s.
		2010	24.2	24.6	25.6	25.9	24.8	26.0	25.2	n.s.
		Mean – Średnia	24.6	25.3	26.5	26.9	25.7	27.2	26.0	n.s.

***Description of fertilisation objects: I** – Carbonate lime ($CaCO_3$) at a dose corresponding to 1.5 Mg CaO · ha^{-1}, **II** – High-calcium brown coal ash at a dose corresponding to 1.5 Mg CaO · ha^{-1}, **III** – Municipal sewage sludge compost at a dose corresponding to 250 kg N · ha^{-1}, **IV**- Municipal sewage sludge compost at a dose corresponding to 250 kg N · ha^{-1}+ high-calcium brown coal ash at a dose corresponding to 1.5 Mg CaO ·ha^{-1} in the first year of experiment **V** – High-calcium brown coal ash at a dose corresponding to 1.5 Mg CaO · ha^{-1} in the first year of experiment, with 0.75 Mg CaO · ha^{-1} in next years each, **VI** – Municipal sewage sludge compost at a dose corresponding to 250 kg N · ha^{-1} + high-calcium brown coal ash at a dose corresponding to 1.5 Mg CaO · ha^{-1} in the first year of experiment, with 0.75 Mg CaO · ha^{-1} in next years each; n.s. – not significant.

***Objaśnienia obiektów nawozowych: I** – wapno węglanowe ($CaCO_3$) w dawce odpowiadającej 1,5 Mg CaO · ha^{-1}, **II** – wysokowapniowy popiół z węgla brunatnego w dawce odpowiadającej 1.5 Mg CaO · ha^{-1}, **III** – kompost z komunalnego osadu ściekowego w dawce odpowiadającej 250 kg N · ha^{-1}, **IV** – kompost z komunalnego osadu ściekowego w dawce odpowiadającej 250 kg N · ha^{-1}+wysokowapniowy popiół z węgla brunatnego w dawce odpowiadającej 1,5 Mg CaO · ha^{-1} w pierwszym roku badań, **V**- wysokowapniowy popiół z węgla brunatnego w dawce odpowiadającej 1,5 Mg CaO · ha^{-1} w pierwszym roku, a w latach następnych w dawkach odpowiadających po 0,75 Mg CaO · ha^{-1}, **VI** – kompost z komunalnego osadu ściekowego w dawce odpowiadającej 250 kg N · ha^{-1} + wysokowapniowy popiół z węgla brunatnego w dawce odpowiadającej 1,5 Mg CaO · ha^{-1} w pierwszym roku, a w latach następnych w dawkach odpowiadających 0,75 Mg CaO · ha^{-1}; n.s. – nieistotny.

Statistical analysis of the total content of heavy metals in the first year after application of municipal sewage sludge compost at a dose corresponding to 250 kg N · ha^{-1} without and with BCA addition (fertilisation objects III, IV and VI) showed a significant effect of experimental factors on the content of cadmium, manganese, nickel, lead and zinc in the soil material. A significant increase occurred in the content of these chemical elements in the soil material when compared to the fertilisation objects being fertilised with calcium carbonate or BCA at a dose corresponding to 1.5 Mg CaO · ha^{-1} (fertilisation objects I and II) (Table 1). Differences in the content of heavy metals being analysed in the soil material were not significant as affected by respective fertilisation objects.

It was found that copper, manganese, nickel, lead and zinc contents in soil decreased in 2010 by 6.54%, 11.05%, 6.73%, 2.95% and 5.95%, respectively, when compared to 2008. On the other hand, the cadmium content in soil in 2010 increased by 8.33% when compared to 2008. In the three-year period when the experiment was carried out in the fertilisation objects being fertilised with municipal sewage sludge compost without and with BCA addition, the content of heavy metals was on average higher, for cadmium by 6.12%, copper by 19.8%, manganese by 10.2%, nickel by 13.0%, lead by 6.87% and zinc by 7.69%, when compared to the fertilisation objects where fertilisation with calcium carbonate or brown coal ash had been exclusively applied (fertilisation objects I and II) (Table 1).

Organic fertilisation without and with addition of brown coal ash induced an increase in the total content of cadmium, copper, manganese, nickel, lead and zinc in the soil material when compared to the initial status (Table 1). During three years of experiment in the fertilisation objects with application of calcium carbonate and BCA (fertilisation objects I and II), no significant effect on increase in copper, manganese, nickel, lead and zinc contents in the soil material was observed (Table 1). After three years from SSC application without and with addition of BCA (fertilisation objects III, IV and VI), the total content of heavy metals in soil decreased, except that of cadmium. As reported by no significant increase in the content of lead and cadmium in the soil being fertilised with municipal sewage sludge compost was observed in the study carried out for four years. On the other hand, obtained similar results to those in the presented experiment when studying the soil material fertilised with municipal sewage sludge compost.

In case of the forms of heavy metals soluble in 1 mol $\cdot$ dm^{-3} HCl, a high dynamics of changes in their content in soil was noted during three years of study as affected by experimental factors in relation to the fertilisation objects with exclusive application of calcium carbonate and BCA at a dose corresponding to 1.5 Mg CaO $\cdot$ ha^{-1} (fertilisation objects I and II) and the initial content (Table 2). A significant increase in the content of copper, manganese, nickel and zinc forms soluble in 1 mol $\cdot$ dm^{-3} HCl was observed in the soil material in the fertilisation objects with exclusive application of BCA in the first year of study at a dose corresponding to 1.5 Mg CaO $\cdot$ ha^{-1} and in the subsequent years at a dose of 0.75 Mg CaO $\cdot$ ha^{-1} when compared to fertilisation objects I, II and III.

In the next study years, a largest average increase in the content of copper, manganese, nickel and zinc forms soluble in 1 mol $\cdot$ dm^{-3} HCl was noted in the fertilisation objects with BCA and compost (fertilisation objects V and VI) (Table 2). In 2008, after application of SSC without and with addition of BCA, an increase was observed in the content of analysed heavy metals when compared to their initial content, i.e. by 87.5% for cadmium, by 23.8% for copper, by 52.9% for manganese, by 104.6% for nickel, by 59.9% for lead, and by 10.8% for zinc. The limits of total cadmium, copper, nickel, lead and zinc contents in mg $\cdot$ kg^{-1} D.M. in the soil material after completion of experiment allow it to be rated among groups B and 0 of the degree of soil pollution according to the recommendation by IUNG (Institute of Soil Science and Plant Cultivation – State Research Institute in Puławy and 1995). Therefore, it is possible to state that BCA and municipal sewage sludge compost being applied did not induced soil pollution during the experiment.

Tabela 2. Contents of 1 M HCl soluble cadmium, copper, manganese, nickiel, lead and zinc in soil (mg · kg^{-1} d.m.) after Virginia fanpetals harvest in 2008–2010

Tabela 2. Zawartość form rozpuszczalnych w 1 M HCL kadmu, miedzi, manganu, niklu, ołowiu i cynku w mg · kg^{-1}s.m. w glebie po zbiorze ślazowca pensylwańskiego w latach 2008–2010

Parameters Pierwiastek	Content initial Zawartość początkowa	Study years Lata badań	Fertilisation objects Obiekty nawozowe I*	II	III	IV	V	VI	Mean Średnia	$LSD_{0.05}$ $NIR_{0,05}$
Contents of 1 M HCl soluble of mg · kg^{-1} d.m. Zawartość form rozpuszczalnych w 1 M HCl w mg · kg^{-1} s.m										
Cadmium Kadm	0.08	2008	0.12	0.13	0.15	0.16	0.14	0.17	0.14	0.02
		2009	0.14	0.15	0.17	0.18	0.16	0.19	0.16	n.s.
		2010	0.18	0.16	0.20	0.18	0.21	0.22	0.19	0.01
	Mean –	Średnia	0.14	0.15	0.17	0.17	0.17	0.19	0.17	n.s.
Copper Miedź	4.95	2008	5.52	5.60	5.87	5.95	5.76	6.57	5.87	0.02
		2009	5.38	5.47	5.95	6.12	5.97	6.79	5.94	n.s.
		2010	5.80	5.85	6.00	6.30	6.60	7.20	6.29	0.07
	Mean –	Średnia	5.57	5.64	5.94	6.12	6.11	6.85	6.04	0.06
Manganese Mangan	58.3	2008	79.0	78.1	87.5	91.0	94.2	89.0	86.5	0.11
		2009	77.1	76.5	86.9	89.3	93.2	93.5	86.1	0.13
		2010	85.0	86.7	90.5	97.0	102	95.0	92.7	1.06
	Mean –	Średnia	80.4	80.4	88.3	92.4	96.5	92.5	88.4	0.09
Nickiel Nikiel	1.51	2008	3.01	3.06	2.75	3.15	3.22	3.35	3.09	0.03
		2009	2.97	3.01	2.80	3.24	2.96	3.09	3.01	0.02
		2010	2.90	2.94	3.20	3.35	3.48	3.60	3.24	0.04
	Mean –	Średnia	2.96	3.00	2.91	3.24	3.22	3.35	3.11	0.10
Lead Ołów	7.94	2008	11.5	11.6	12.5	12.7	11.9	12.8	10.2	0,02
		2009	10.9	11.1	11.8	11.9	11.2	12.1	11.2	n.s.
		2010	8.81	8.96	9.06	9.22	9.36	9.45	9.14	n.s.
	Mean –	Średnia	10.4	10.6	11.1	11.3	10.8	11.5	10.9	n.s.
Zinc Cynk	11.7	2008	11.1	11.0	13.2	12.5	13.3	13.4	12.4	0.11
		2009	10.9	10.8	12.5	11.9	12.7	12.6	11.9	0.10
		2010	10.1	10.2	11.0	11.2	11.3	11.4	10.9	0.10
	Mean –	Średnia	10.7	10.7	12.2	11.9	12.4	12.5	11.7	0.07

*Description of fertilisation objects is given in Table 1.
*Objaśnienia obiektów nawozowych zamieszczono pod tabelą 1.

When comparing the last year of study (2010) with 2008, an increase in the content of 1 mol · dm^{-3} HCl-soluble cadmium, copper, manganese and nickel was demonstrated, respectively by 35.7%, 7.14% and 4.85%, and a decrease in that of lead and zinc, respectively by 11.6% and 13.8% (Table 2).

In the third year of study (2010), more copper, manganese, nickel, lead and zinc forms soluble in 1 mol · dm^{-3} HCl were in soil in the fertilisation objects fertilised with SSC with addition of BCA (fertilisation objects IV and VI) and with exclusive application of brown coal ash (fertilisation object V) when compared to other ones. It was observed that the highest content of 1 mol · dm^{-3} HCl-soluble cadmium, copper, nickel, lead and zinc forms in the last study year (2010) was characteristic of the fertilisation object with combined organic fertilisation and BCA (fertilisation object VI). A significant effect of combined organic fertilisation with BCA (fertilisation objects III, IV and VI) on increase in the content of cadmium, copper, manganese and nickel forms soluble in 1 mol · dm^{-3} HCl was observed when compared to the fertilisation object being exclusively fertilised with calcium carbonate (fertilisation object I) and the initial content. In relation to the initial contents, the content of 1 mol · dm^{-3} HCl-soluble zinc decreased, while that of cadmium, manganese, nickel and lead increased (Table 2).

Taking into account the classification of the quantity of heavy metals in soils essential for plants being adopted by chemical and agricultural stations, it was found that copper, zinc and manganese contents determined in 1 mol · dm^{-3} HCl was average (Filipek 2006) (Table 2).

The increase in the cadmium, copper, manganese, nickel and lead contents obtained in this study in the soil being exclusively fertilised with ash in the first study year and every year (fertilisation object V) and with SCC without and with addition of BCA was not high enough to present a threat from heavy metals. A reason for increase in the total content of above-mentioned metals in soil was higher content of these elements in the compost and BCA being applied when compared to the initial content in the soil material.

Similar results were confirmed by the studies where a small increase in the content of elements being analysed had been observed as a result of ash application on the sandy soil (Antonkiewicz 2009). Development of chelate complexes with trace elements, including heavy metals, induces soil detoxification, which may decrease their availability for plants (Jakubus 2009). As a result of soil fertilisation with municipal sewage sludge composts containing large quantities of heavy metals, organometallic complexes develop that decrease their availability for plants (Businelli et al. 2009).

Availability of heavy metals for plants and their movement to deeper horizons of the soil profile is determined by the percentage of soluble forms of these elements in their total content. The percentages of 1 mol · dm^{-3} HCl-soluble heavy metals in soil prior to starting the field experiment and in its subsequent years are summarised in relative numbers (total content equals to 100%).

The average percentage of 1 mol · dm^{-3} HCl-soluble manganese, nickel and lead in their total content slightly differed in the soil from respective fertilisation objects (Table 3). When evaluating the percentage of soluble forms of heavy metals in their total content, it was found that most lead and zinc was in 2008, whereas most cadmium, copper, manganese and nickel was in 2010. The percentage of soluble forms of these elements after three years of the field experiment increased on average by 46.6% for cadmium, 83.5% for nickiel, 5.37% for copper, 35.6% for manganese and 28.3% for lead. On the contrary, a decrease was observed in the case of zinc (by 10.8%).

From among the elements being analysed, the highest percentage of soluble forms in their total content was observed in 2010 for cadmium (70.8%), while the lowest one for nickel (31.3%). The content of heavy metals in municipal sewage sludge, composts produced from it and combustion ashes is connected with their migration to environment. Through their solubility, they become available for plants. It was found in the experiment being carried out that availability of heavy metals decreased after three years of study and it referred principally to nickel, zinc and lead. The fertilisation system being applied contributed to the reduction of solubility of nickel, lead and zinc compounds and induced an increase in the content of cadmium, copper and manganese forms soluble in 1 mol · dm^3 HCl. The studies of other authors, who also conducted them on the light soils being fertilised with ash, suggest a decrease in the zinc content and an increase in that of cadmium, copper and lead (Kabata-Pendias 2004). Antonkiewicz (2009) found an increase in the zinc, copper and nickiel contents in the soil material in light soils as affected by application of increasing combustion ash doses, whereas the lead and cadmium contents decreased.

Table 3. The share of 1 mol · dm^{-3} HCl soluble cadmium, copper, manganese, nickel, lead and zinc in their total content in soil. Data are given in %
Tabela 3. Udział form rozpuszczalnych kadmu, miedzi, manganu, niklu, ołowiu i cynku w 1 mol · dm^{-3} HCl w ogólnej zawartości w glebie. Dane podano w %

Parameters Pierwiastek	Content initial Zawartość początkowa	Study years Lata badań	Fertilisation objects Obiekty nawozowe						Mean Średnia
			I*	II	III	IV	V	VI	
Cadmium Kadm	44.0	2008	54.0	56.0	63.0	62.0	58.0	65.0	60,0
		2009	58.0	60.0	65.0	72.0	64.0	68.0	64.0
		2010	72.0	65.0	71.0	62.0	74.0	80.0	71.0
		Mean – Średnia	61.0	60.0	66.0	65.0	65.0	71.0	65.0
Copper Miedź	52.0	2008	55.0	55.0	50.0	50.0	48.0	53.0	52.0
		2009	55.0	56.0	52.0	53.0	52.0	57.0	54.0
		2010	61.0	60.0	56.0	55.0	65.0	57.0	59.0
		Mean – Średnia	57.0	57.0	53.0	53.0	55.0	56.0	55.0
Manganese Mangan	28.0	2008	37.0	35.0	33.0	36.0	39.0	36.0	36.0
		2009	35.0	35.0	36.0	37.0	40.0	39.0	37.0
		2010	41.0	41.0	42.0	44.0	47.0	42.0	43.0
		Mean – Średnia	37.0	37.0	37.0	39.0	42.0	39.0	39.0
Nickiel Nikiel	16.0	2008	29.0	30.0	25.0	27.0	29.0	28.0	29.0
		2009	30.0	30.0	26.0	28.0	27.0	26.0	28.0
		2010	30.0	30.0	31.0	30.0	35.0	32.0	31.0
		Mean – Średnia	30,0	30.0	27.0	28.0	30.0	29.0	29.0
Lead Ołów	41.0	2008	57.0	58.0	58.0	58.0	57.0	60.0	58.0
		2009	55.0	56.0	55.0	56.0	55.0	58.0	56.0
		2010	45.0	46.0	44.0	44.0	47.0	45.0	45.0
		Mean – Średnia	52.0	53.0	52.0	53.0	53.0	54.0	53.0
Zinc Cynk	49.9	2008	45.0	43.0	49.0	48.0	48.0	48.0	46.0
		2009	44.0	43.0	47.0	47.0	46.0	46.0	45.0
		2010	42.0	41.0	43.0	44.0	45.0	44.0	43.0
		Mean – Średnia	44.0	42.0	46.0	46.0	46.0	46.0	45.0

*Description of fertilisation objects is given in Table 1.
*Objaśnienia obiektów nawozowych zamieszczono pod tabelą 1.

Therefore, an increase in the total content and the content of 1 mol · dm^{-3} HCl-soluble forms of heavy metals in soil depends on the chemical composition of municipal sewage sludge from which the compost had been produced as well as on the type of combustion ash and the content of these elements in both these products (Kabata-Pendias et al. 2004).

Low solubility of heavy metals is being explained by the fact that these elements easily transform into compounds sparingly available for plants in alkaline environment (Mocek et al. 2005). It was found as a result of the study being carried out that introduction of the materials with alkaline properties into soil contributed to a decrease in the solubility of most heavy metals, through which their uptake by plants was reduced.

Copper, being introduced into soil, becomes non-exchangeably bound to organic matter. Therefore, the quantity of bound copper increases together with increase in the content of organic matter and soil reaction, through which the quantity of its form being most available for plants decreases (Gambuś and Wieczorek 1999).

According to Baran et al. (2002, 2006), Czekała (2008), Jakubus (2006, 2009), sewage sludge and composts produced from it being introduced into soil may contribute to the pollution of soil environment. To prevent such a situation, it is proposed to apply ash-sludge mixtures or combined compost fertilisation with addition of ashes because fly ashes from coal combustion contain generally a smaller quantity of heavy metals than municipal sewage sludge. Attention must be also paid to the fact that soil fertilisation with sewage sludge or its composts increases the total content of heavy metals. It was found that application of moderate doses of municipal sewage sludge or its composts does not significantly increase the content of heavy metals in soil, even after their long-term application, whereas its physical, chemical and biological properties are being improved.

CONCLUSIONS

Significant increase in the total copper, manganese, nickiel and lead contents in soil was observed in fertilisation objects III, IV and VI when compared to those being fertilised with calcium carbonate or brown coal ash at a dose corresponding to 1.5 Mg CaO · ha^{-1} (fertilisation objects I and II).

During the three-year experiment, the content of heavy metals in the objects being fertilised with municipal sewage sludge without and with addition of high-calcium brown coal ash was larger on average by 6.12% for cadmium, 19.8% for copper, 10.2% for manganese, 13.0% for nickel, 6.87% for lead and 7.69% for zinc when compared to fertilisation objects I and II.

No significant differences were found in the content of heavy metals being analysed in soil as affected by respective fertilisation objects.

Combined organic fertilisation with brown coal ash contributed to an increase in the content of cadmium, copper, manganese, lead and zinc forms soluble in 1 mol · dm^{-3} HCl when compared to the fertilisation object being exclusively fertilised with calcium carbonate and the initial content. In relation to the initial contents, the content of 1 mol · dm^{-3} HCl-soluble zinc decreased, while that of cadmium, manganese, nickel and lead increased.

As compared to the initial state, the percentage of soluble forms of these chemical elements in soil after three years of the field experiment increased for cadmium, nickel, copper, manganese and lead, while a decrease was observed in case of the zinc content by 10.8%.

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Zorpas A.A., Loizidou M. 2008. Sawdustand natural zeolite as abulking agent improving quality of a composting product from anaerobically stabilized sewage sludge. Bioresour. Technol., 99, 7545–7552.

Abstract. A single-factor field experiment was carried out he Cultivar Evaluation Station in Szczecin-Dąbie in 2008–2010. The soil on which this experiment was set up is formed from light loamy sand (lls). Regarding its granulometric composition, the soil is classified to the category of light soils, of soil quality class IV b and good rye complex (5). In the experiment, a combustion waste in the form of high-calcium brown coal ash was used, as well as a compost produced from municipal sewage sludge by the GWDA method. In both waste products, i.e. in high--calcium brown coal ash and sewage sludge used to produce a compost, the standards for heavy metals specified in the ministerial regulations were not exceeded. The study design included six fertilisation objects. A test plant was virginia fanpetals *(Sida Hermaphrodita* Rusby*).* Significant increase in the total content of copper, manganese and nickel, in soil was observed in fertilisation objects III, IV and V when compared to those being fertilised with calcium carbonate or high-calcium brown coal ash at a dose corresponding to 1.5 Mg CaO · ha^{-1} (fertilisation objects I and II). Organic fertilisation with high-calcium brown coal ash contributed to the increase in the content of mol · dm^{-3} HCl soluble cadmium, copper, manganese, nickiel and zinc forms in soil when compared to the object being fertilised exclusively with calcium carbonate and their initial contents. As compared to the initial value, the content of 1 mol · dm^{-3} HCl soluble zinc decreased, while that of cadmium, copper, manganese, nickel and lead increased.