

Tomasz CZECH¹, Florian GAMBUŚ¹, Olga GORCZYCA¹,
Michał KOPEĆ¹, Monika MIERZWA-HERSZTEK¹,
Katarzyna URBAŃSKA¹ and Jerzy WIECZOREK^{1*}

SOLUBILITY OF HEAVY METALS IN SOIL FERTILIZED WITH COMPOSTS WITH POLYMER SUPPLEMENTS

ROZPUSZCZALNOŚĆ METALI CIĘŻKICH W GLEBACH NAWOŻONYCH KOMPOSTAMI Z DODATKIEM TWORZYW POLIMEROWYCH

Abstract: Application of composts from municipal waste for fertilization, due to their high content of organic matter and nutrients, generally positively affects crop yield and soil properties. Their production is based on biodegradable fractions of municipal waste, often originating from non-selective collection and therefore they may contain some quantities of pollutants, both organic and mineral, such as heavy metals, which may negatively affect the soil fertility.

In the pot experiment was investigated the effect of composts with an admixture of polymer materials modified with starch as biocomponent, on heavy metal solubility in the tested substrata on which oats and mustard were cultivated. Composts were applied to two soils with natural heavy metal contents, as well as to the soil and post-flotation sediment from zinc and lead ores processing polluted with heavy metals. The 5 composts used for fertilization were prepared from a substrate composed of wheat and rape straw and waste from pea cleaning with an eight percent admixture of polymer foils differing with the starch proportion and density. Speciation analysis of selected heavy metals was conducted using sequential extraction method by Zeien and Brümmer.

On the basis of conducted analysis it was established that the contents of individual forms of metals to the highest degree depended on the analysed element and applied substratum, whereas a supplement of composts with 8 % admixture of various polymer foils as a rule had no significant effect on the distribution of metal contents in the analysed fractions. The biggest amounts of cadmium in soil were assessed in the exchangeably bound fraction, in manganese oxides bonds and in the residual fraction, most strongly bound to solid soil phase. In the post-flotation sediment the biggest quantities of cadmium were assessed in the residual fraction and bound to crystalline iron oxides. The highest amounts of copper were bound to organic matter and natural minerals. In comparison with mineral fertilization, application of composts with polymer supplement decreased the content of copper mobile forms. Nickel, except the post-flotation sediment, occurred in the analysed substrata mainly in hardly available forms. Much greater nickel mobility was revealed in the

¹ Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31-120 Kraków, Poland, phone: +48 12 662 43 49, fax: +48 12 662 43 41, email: rrwieczo@cyf-kr.edu.pl

* Corresponding author: rrwieczo@cyf-kr.edu.pl

post-floatation waste, where this metal, beside the residual fraction, occurred in considerable quantities in the mobile and exchangeable fractions.

Keywords: heavy metals, sequential extraction, soil, post-floatation sediment, compost, polymer

Introduction

Due to a considerable content of organic matter and nutrients, application of composts from municipal waste as fertilizer materials generally positively affects the crop yield and soil properties. Beside soil enrichment in nutrients, organic matter supplied to the soil improves its sorption properties, increases retention capacities of light soils and loosens heavy soil structure. Their production is based on greatly diversified materials. Most frequently these are the residue of biomass processing, mixed municipal waste or biodegradable fractions of municipal waste separated from them [1]. Frequently municipal waste come from a non-selective collection and therefore may contain some amounts of pollutants, both organic and mineral, such as heavy metals which are factors posing a serious hazard to the purity of the soil environment [2]. For this reason, heavy metal contents in composts may be a factor preventing the compost use for fertilization [1, 3]. In order to reduce the risk of excessive heavy metal accumulation in the environment, The Minister of Agriculture and Rural Development issued an executive regulation implementing the law on fertilizers and fertilization [4], which specified the maximum, allowable heavy metal contents in marketed organic fertilizers, also including composts. Total heavy metal content in composts allows to determine their usefulness for agricultural purposes. However, the problem with using this kind of fertilizer materials concerns not only the amount of heavy metals supplied to the soil, but also the rate at which they become mobilized [5, 6]. Information about total metal content does not allow to estimate their mobility and bioavailability after compost application to the soil. The assessment of the directions and rate of transformations which heavy metal undergo in soil may be conducted by means of sequential analysis which allows to determine the content of individual element forms and assess the hazard for the biosphere resulting from their presence.

The aim of the research was determining the changes in heavy metal solubility after application of composts with a supplement of polymer materials modified with starch on Cd, Cu and Ni solubility in three different substrata, on which oat was cultivated and white mustard as consecutive crop.

Materials and methods

The research was conducted in 2012 on the basis of a pot experiment in a vegetation hall, using five composts on three substrata, which were light and medium soils with natural heavy metal contents and soil and post-floatation sediment from zinc and lead ore processing, polluted with heavy metals. On each substratum seven fertilizer treatments were maintained: control – without fertilization (1), mineral NPK treatment (2), and objects where composts were added (3–7) (Table 1). All objects were maintained in three replications.

Table 1

The content of selected mineral components in composts used in the experiment

Share of components in composts	N	P	K	Cd	Cr	Cu	Ni	Pb	Zn
	[g · kg ⁻¹ d.m.]			[mg · kg ⁻¹ d.m.]					
Compost 1 (C1): Biomass as a mixture of wheat straw, rape straw, pea waste 1:1:0.5	8.8	3.9	14.6	2.0	14.3	17.6	8.6	4.2	175.8
Compost 2 (C2): Biomass* + 8 % foil B37 (polyethylene C – 47.5 %, thermoplastic corn starch – 45 %, compatibilizer 7.5 %)	5.8	3.3	12.2	1.1	13.0	7.4	6.8	2.7	148.9
Compost 3 (C3): Biomass* + 8 % foil B36 (polyethylene C – 65 %, thermoplastic corn starch – 30 %, compatibilizer 5 %)	5.3	3.5	12.2	1.0	12.7	5.6	6.7	2.3	138.0
Compost 4 (C4): Biomass* + 8 % foil B22 (polyethylene C – 65 %, thermoplastic corn starch – 30 %, compatibilizer – copolymer 5 %)	7.0	2.9	9.6	0.8	10.9	5.4	5.8	2.2	117.0
Compost 5 (C5): Biomass* + 8 % foil B22 (polyethylene C – 65 %, thermoplastic corn starch – 30 %, compatibilizer – copolymer 5 %) + microbiological vaccine	8.5	3.2	10.0	0.8	11.0	5.6	6.0	2.8	118.4

* as in C1.

Light soil revealed neutral pH, medium soil slightly acid and the post-floatation sediment slightly alkaline. In comparison with the light soil, medium soil was between two to three times more abundant in organic C, N, P and K and contained only slightly bigger quantities of heavy metals. Macroelements content in the post-floatation sediment was on a very low level, reaching only from several to a dozen or so percent of their content in soils, whereas the contents of analysed heavy metals were from two (copper and nickel) to over sixty (cadmium) times higher than in soils.

The composts used for the experiment were made from a mixture of wheat and rape straw and waste from pea cleaning with an eight percent admixture of polymer foils differing with starch proportion (Table 1). Obtained composts revealed a relatively small diversification of minerals. The highest contents of heavy metals were registered in the compost to which no polymer materials were added (C1). Contents of three analysed metals in the other composts were generally on a similar level. The materials were characterized by about twice lower cadmium and copper contents, and only slightly lower content of nickel in comparison with compost 1 (Table 1). Organic fertilizers were used in doses containing 0.2 g N per 1 kg of substratum. On organic fertilizer treatments the amounts of phosphorus and potassium have been aligned to the mineral salts level allowing to maintain the optimal N : P₂O₅ : K₂O ratio (1 : 0.3 : 1.37). The amount of macroelements supplied to the object fertilized exclusively with mineral fertilizers was by half lower than on compost treatments.

Oats were sown on 14 May into pots filled with 3 kg d.m. of analysed substrata mixed with the admixtures, according to the experimental design presented in Table 1. The crop was harvested after 63 days of vegetation and then white mustard was sown and gathered after 72 days of cultivation. When the experiment was completed, the soil was sampled and subjected to speciation analysis of selected heavy metals by means of sequential extraction method according to Zeien and Brummer [7]. The element content in the extracts was assessed using atomic emission spectrometer ICP-OES. Subsequent extractions identified seven fractions of heavy metals:

- F1 – mobile – active fraction (using 1 mol · dm⁻³ NH₄NO₃),
- F2 – exchangeable – auxiliary fraction (using 1 mol · dm⁻³ NH₄OAc, pH = 6.0),
- F3 – fraction of bonds bound to MNO_{xc} (1 mol · dm⁻³ NH₂OH-HCl + NH₄OAc, pH=6.0),
- F4 – fraction of organic bonds (0.25 mol · dm⁻³ NH₄EDTA, pH = 4.6),
- F5 – fraction of amorphous bonds FeO_x (0.2 mol · dm⁻³ ammonium oxalate, pH = 3.25),
- F6 – fraction of strongly crystalline bonds FeO_x (0.2 mol · dm⁻³ ammonium oxalate + 1 mol · dm⁻³ ascorbic acid, pH = 3.25),
- F7 – residual fraction (concentrated HNO₃ and HClO₄).

Statistical computations and graphic presentation of the results were prepared using Statistica w. 10 PL and Microsoft Office Excell 2003 calculation sheet. The significance of differences between means was tested on the basis of one-way ANOVA and Tukey's test, identifying homogenous groups.

Results and discussion

Irrespective of the proportion of individual components in the initial mass, the composts used in the investigations met the requirements of the Regulation of the Minister of Agriculture and Rural Development [4] in view of allowable pollution with heavy metals. Total content of cadmium ranged from 16 to 40 % of the allowable value, *ie* $5 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$, whereas nickel constituted only from 9.7 to 14.3 % (Ni quantity cannot exceed $60 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$), and copper content is not limited.

Application of various fertilizer variants has a relatively slight effect on cadmium content in the individual fractions and their share in total metal content (Table 2, Fig. 1).

Table 2

Content of different cadmium forms in substrata after experiment [$\text{mg} \cdot \text{kg}^{-1} \text{ d.m.}$]

Treatment	Content							
	F1*	F2	F3	F4	F5	F6	F7	Total**
Light soil								
Control	0.08 ^{c***}	0.39 ^a	0.20 ^b	0.08 ^b	0.16 ^a	0.09 ^b	0.22 ^a	1.22 ^b
Mineral fertilizers	0.00 ^a	0.36 ^a	0.13 ^{ab}	0.00 ^a	0.17 ^a	0.00 ^a	0.18 ^a	0.84 ^a
Compost 1	0.00 ^a	0.32 ^a	0.12 ^a	0.07 ^b	0.17 ^a	0.00 ^a	0.15 ^a	0.82 ^a
Compost 2	0.00 ^a	0.38 ^a	0.10 ^a	0.00 ^a	0.15 ^a	0.00 ^a	0.18 ^a	0.82 ^a
Compost 3	0.00 ^a	0.29 ^a	0.12 ^{ab}	0.07 ^b	0.14 ^a	0.00 ^a	0.15 ^a	0.77 ^a
Compost 4	0.00 ^a	0.32 ^a	0.12 ^{ab}	0.08 ^b	0.13 ^a	0.00 ^a	0.14 ^a	0.80 ^a
Compost 5	0.05 ^b	0.29 ^a	0.15 ^{ab}	0.00 ^a	0.18 ^a	0.00 ^a	0.15 ^a	0.82 ^a
Medium soil								
Control	0.00 ^a	0.33 ^a	0.14 ^a	0.00 ^a	0.10 ^a	0.00 ^a	0.16 ^a	0.73 ^a
Mineral fertilizers	0.00 ^a	0.37 ^{ab}	0.14 ^a	0.00 ^a	0.19 ^a	0.00 ^a	0.18 ^a	0.87 ^{ab}
Compost 1	0.00 ^a	0.35 ^{ab}	0.16 ^a	0.00 ^a	0.18 ^a	0.00 ^a	0.16 ^a	0.86 ^{ab}
Compost 2	0.00 ^a	0.34 ^a	0.12 ^a	0.00 ^a	0.18 ^a	0.00 ^a	0.16 ^a	0.79 ^{ab}
Compost 3	0.00 ^a	0.46 ^b	0.14 ^a	0.00 ^a	0.17 ^a	0.00 ^a	0.18 ^a	0.94 ^b
Compost 4	0.00 ^a	0.35 ^{ab}	0.12 ^a	0.00 ^a	0.15 ^a	0.00 ^a	0.16 ^a	0.77 ^{ab}
Compost 5	0.00 ^a	0.35 ^{ab}	0.11 ^a	0.00 ^a	0.17 ^a	0.00 ^a	0.14 ^a	0.77 ^{ab}
Post-flotation sediment								
Control	7.71 ^a	13.18 ^c	2.03 ^a	1.49 ^a	0.00 ^a	1.26 ^a	33.99 ^c	59.66 ^c
Mineral fertilizers	7.06 ^a	12.84 ^{bc}	2.11 ^a	1.36 ^a	0.00 ^a	1.19 ^a	30.87 ^c	55.42 ^{bc}
Compost 1	7.58 ^a	11.87 ^{abc}	2.07 ^a	1.52 ^a	0.00 ^a	1.17 ^a	25.39 ^b	49.59 ^a
Compost 2	7.24 ^a	12.29 ^{abc}	2.08 ^a	1.57 ^a	0.00 ^a	1.24 ^a	22.61 ^{ab}	47.02 ^a
Compost 3	7.21 ^a	12.75 ^a	2.33 ^a	1.63 ^a	0.00 ^a	1.23 ^a	21.05 ^{ab}	46.20 ^a
Compost 4	7.67 ^a	11.45 ^a	2.04 ^a	1.44 ^a	0.00 ^a	1.23 ^a	20.21 ^a	44.04 ^a
Compost 5	7.48 ^a	11.74 ^{ab}	2.24 ^a	1.57 ^a	0.98 ^b	1.28 ^a	20.05 ^a	45.35 ^a

* F1 – mobile (active) fraction, F2 – exchangeable fraction, F3 – bound to MnO_x fraction, F4 – organically bound fraction, F5 – bound to amorphous FeO_x fraction, F6 – bound to crystalline FeO_x fraction, F7 – residual fraction; ** Sum of fractions F1–F7; *** Means marked by the same letters in columns did not differ significantly at $\alpha \leq 0.05$ according to the t-Tukey test.

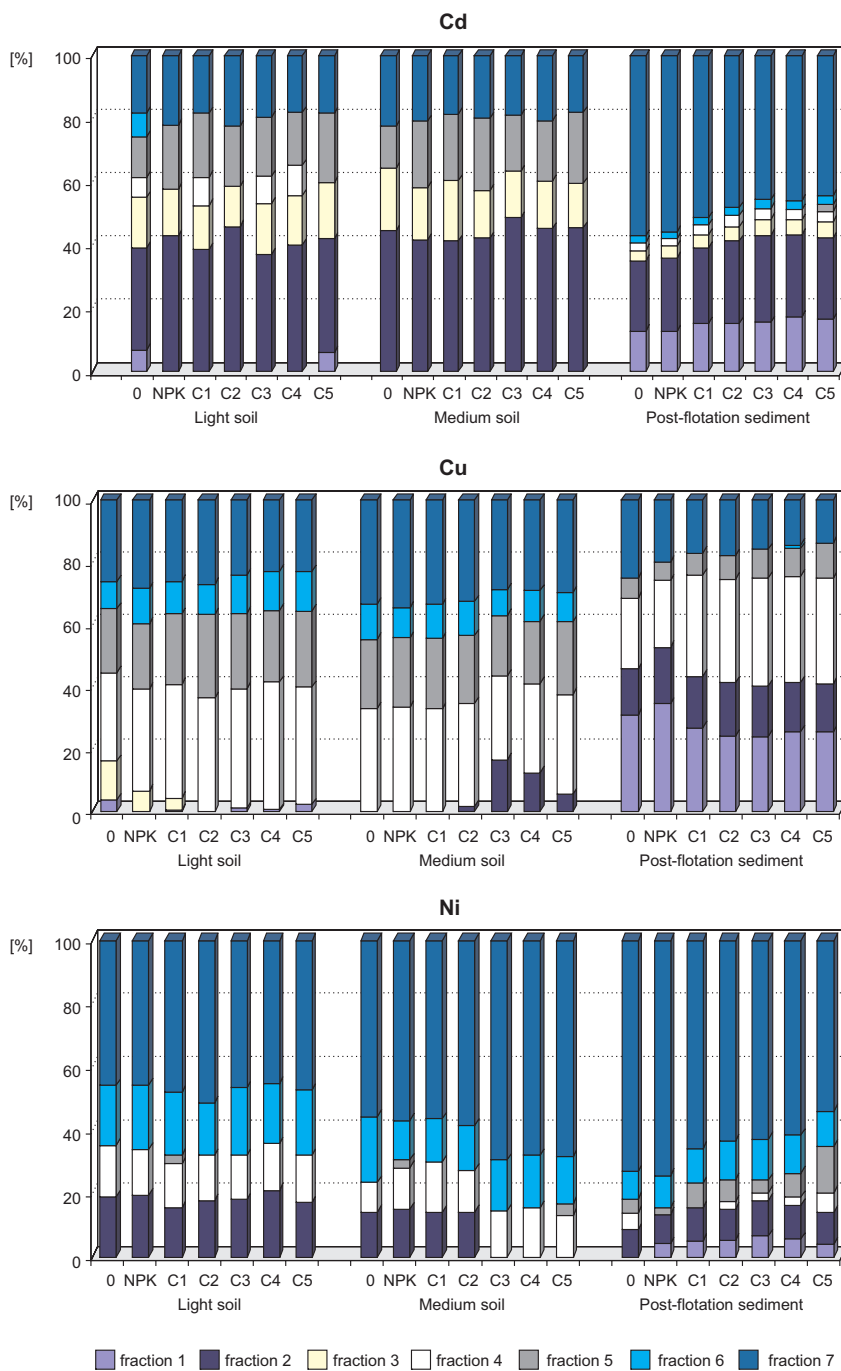


Fig. 1. Share [%] of different cadmium, copper and nickel forms in total content of metals in substrata after experiment

Only in light soil cadmium contents in: mobile (F1), bound to manganese oxides (F3) and crystalline iron oxides (F6) fractions from the non-fertilized object, and from post-floatation sediment in the residual fraction (F7), from the control and exclusively mineral treatments (1 and 2) were significantly higher than the amounts assessed in the soil from the other objects.

It was assessed that supplying composts to post-floatation sediment contributed to a reduction of residual fraction share in total amount of cadmium in comparison with mineral treatment and control (Fig. 1). The experiment confirmed the findings of other authors [8, 9] that the most mobile forms have a significant share in total cadmium content.

Summary amount of cadmium in mobile (F1), exchangeable (F2) and bound to manganese oxides (F3) fractions constituted on average 56.1 % of its total content in the light soil, 60.5 % in medium soil and 44.5 % in post-floatation sediment. However, it is worth noticing that in soils it was present mainly in the exchangeable form and bound to manganese oxides, whereas in the post-floatation sediment in mobile and exchangeable forms. Regardless of applied fertilization the dominating form of cadmium was its exchangeable form (on average 42.6 %), whereas residual fraction prevailed in post-floatation sediment revealing a very high content of this metal (on average 49.7 %).

In soil, copper is usually strongly bound to organic substance and clay minerals. On the basis of the research on the forms of copper occurrence in soil [9–12] it was established that generally the biggest amounts of this metal are bound to organic matter and amorphous iron oxides.

Fractional distribution of copper in both soils was approximate, however is significantly differed from the one determined in the post-floatation sediment (Table 3, Fig. 1). The greatest quantities of copper in soil were bound to organic matter (F4), amorphous iron oxides (F5) and to internal crystalline network of natural minerals (F7), whereas in the post-floatation sediment Cu occurred mainly in mobile and exchangeable forms (F1 and F2) and mostly in bonds with the sediment organic fraction (F4). Fertilization with different materials only slightly diversified copper content in the individual fractions. Fertilization of light soil and post-floatation sediment with composts significantly increased copper amount in organic fraction (F4) in relation to the mineral treatment and non-fertilized control. On the other hand, medium soil enrichment with composts containing polymer supplements caused that copper appeared in exchangeable form, unlike the other fertilizer combinations where no copper was found in this form.

Fertilization with composts with foil admixture also influenced a diversification among objects of single copper fractions in light soil. In the soil of these objects no copper was found in bonds with manganese oxides, whereas in soil fertilized with compost without polymer admixture, receiving mineral fertilizers or non-fertilized, copper content in this fraction ranged from 0.34 to 1.12 mg · kg⁻¹ d.m.

A relatively considerable mobility of nickel in soil is connected with the presence of its mobile chelates, which are readily soluble, irrespectively of the pH. However, solubility of this metal bonds depends mainly on soil pH [11, 13].

Table 3

Content of different copper forms in substrates after experiment [mg · kg⁻¹ d.m.]

Treatment	Content							
	F1*	F2	F3	F4	F5	F6	F7	Total**
Light soil								
Control	0.32 ^{c***}	0.00 ^a	1.12 ^d	2.55 ^a	1.84 ^{ab}	0.78 ^a	2.34 ^{ab}	8.96 ^b
Mineral fertilizers	0.00 ^a	0.00 ^a	0.58 ^c	2.89 ^{ab}	1.85 ^{ab}	1.00 ^a	2.50 ^b	8.83 ^b
Compost 1	0.04 ^{ab}	0.00 ^a	0.34 ^b	3.19 ^b	1.98 ^{ab}	0.92 ^a	2.26 ^{ab}	8.72 ^{ab}
Compost 2	0.00 ^a	0.00 ^a	0.00 ^a	3.07 ^b	2.28 ^b	0.82 ^a	2.27 ^{ab}	8.45 ^{ab}
Compost 3	0.08 ^{ab}	0.00 ^a	0.00 ^a	3.22 ^b	2.02 ^{ab}	1.02 ^a	2.01 ^{ab}	8.36 ^{ab}
Compost 4	0.05 ^{ab}	0.00 ^a	0.00 ^a	3.05 ^b	1.72 ^a	0.95 ^a	1.69 ^a	7.45 ^a
Compost 5	0.19 ^{bc}	0.00 ^a	0.00 ^a	3.24 ^b	2.11 ^{ab}	1.08 ^a	1.97 ^{ab}	8.60 ^{ab}
Medium soil								
Control	0.00 ^a	0.00 ^a	0.00 ^a	2.49 ^a	1.66 ^a	0.85 ^a	2.51 ^a	7.52 ^a
Mineral fertilizers	0.00 ^a	0.00 ^a	0.00 ^a	2.62 ^a	1.75 ^a	0.76 ^a	2.70 ^a	7.82 ^a
Compost 1	0.00 ^a	0.00 ^a	0.00 ^a	2.36 ^a	1.62 ^a	0.79 ^a	2.40 ^a	7.17 ^a
Compost 2	0.00 ^a	0.11 ^a	0.00 ^a	2.40 ^a	1.59 ^a	0.80 ^a	2.37 ^a	7.27 ^a
Compost 3	0.00 ^a	1.38 ^d	0.00 ^a	2.25 ^a	1.61 ^a	0.69 ^a	2.39 ^a	8.32 ^a
Compost 4	0.00 ^a	0.95 ^c	0.00 ^a	2.19 ^a	1.54 ^a	0.75 ^a	2.22 ^a	7.65 ^a
Compost 5	0.00 ^a	0.42 ^b	0.00 ^a	2.47 ^a	1.79 ^a	0.72 ^a	2.28 ^a	7.69 ^a
Post-flotation sediment								
Control	4.96 ^{bc}	2.33 ^a	0.00 ^a	3.63 ^{ab}	1.03 ^a	0.00 ^a	3.98 ^c	15.92 ^b
Mineral fertilizers	5.43 ^c	2.87 ^a	0.00 ^a	3.40 ^a	0.93 ^a	0.00 ^a	3.12 ^b	15.76 ^{ab}
Compost 1	4.12 ^{ab}	2.51 ^a	0.00 ^a	4.99 ^b	1.08 ^a	0.00 ^a	2.60 ^{ab}	15.31 ^{ab}
Compost 2	3.39 ^a	2.42 ^a	0.00 ^a	4.69 ^{abc}	1.07 ^a	0.00 ^a	2.49 ^{ab}	14.06 ^a
Compost 3	3.37 ^a	2.28 ^a	0.00 ^a	4.88 ^{bc}	1.29 ^{ab}	0.00 ^a	2.21 ^a	14.03 ^a
Compost 4	3.61 ^a	2.24 ^a	0.00 ^a	4.85 ^{bc}	1.26 ^{ab}	0.16 ^b	2.02 ^a	14.15 ^{ab}
Compost 5	3.55 ^a	2.17 ^a	0.00 ^a	4.75 ^{bc}	1.60 ^b	0.00 ^a	1.92 ^a	13.98 ^a

* See Table 2; ** see Table 2; *** see Table 2.

Like in case of the previously discussed elements, application of diversified fertilization usually did not cause significant differences in the content of individual nickel fractions (Table 4). Regardless of the fertilization nickel in the studied substrata occurred mainly in the hardly available forms (F6, F7) but in the post floatation sediment in the fraction most readily available to plants, *ie* mobile and exchangeable. Also in the research conducted by Filipek-Mazur et al [11] the biggest amounts of nickel were assessed in the soil in residual fraction.

Table 4

Content of different nickel forms in substrates after experiment [$\text{mg} \cdot \text{kg}^{-1}$ d.m.]

Treatment	Content							
	F1*	F2	F3	F4	F5	F6	F7	Total**
Light soil								
Control	0.00 ^{a***}	0.81 ^a	0.00 ^a	0.69 ^a	0.00 ^a	0.80 ^a	1.95 ^a	4.25 ^a
Mineral fertilizers	0.00 ^a	0.81 ^a	0.00 ^a	0.61 ^a	0.00 ^a	0.86 ^a	1.92 ^a	4.19 ^a
Compost 1	0.00 ^a	0.67 ^a	0.00 ^a	0.58 ^a	0.13 ^a	0.84 ^a	2.06 ^a	4.29 ^a
Compost 2	0.00 ^a	0.75 ^a	0.00 ^a	0.60 ^a	0.00 ^a	0.71 ^a	2.17 ^a	4.24 ^a
Compost 3	0.00 ^a	0.77 ^a	0.00 ^a	0.59 ^a	0.00 ^a	0.91 ^a	1.97 ^a	4.23 ^a
Compost 4	0.00 ^a	0.84 ^a	0.00 ^a	0.59 ^a	0.00 ^a	0.76 ^a	1.81 ^a	4.01 ^a
Compost 5	0.00 ^a	0.75 ^a	0.00 ^a	0.64 ^a	0.00 ^a	0.90 ^a	2.05 ^a	4.34 ^a
Medium soil								
Control	0.00 ^a	0.91 ^b	0.00 ^a	0.60 ^a	0.00 ^a	1.33 ^b	3.57 ^a	6.42 ^c
Mineral fertilizers	0.00 ^a	1.03 ^b	0.00 ^a	0.90 ^{bc}	0.16 ^a	0.85 ^a	3.90 ^a	6.84 ^c
Compost 1	0.00 ^a	0.93 ^b	0.00 ^a	1.05 ^c	0.00 ^a	0.89 ^a	3.72 ^a	6.59 ^c
Compost 2	0.00 ^a	0.90 ^b	0.00 ^a	0.82 ^{abc}	0.00 ^a	0.89 ^a	3.68 ^a	6.28 ^{bc}
Compost 3	0.00 ^a	0.00 ^a	0.00 ^a	0.76 ^{ab}	0.00 ^a	0.83 ^a	3.58 ^a	5.16 ^a
Compost 4	0.00 ^a	0.00 ^a	0.00 ^a	0.80 ^{abc}	0.00 ^a	0.84 ^a	3.49 ^a	5.14 ^a
Compost 5	0.00 ^a	0.00 ^a	0.00 ^a	0.70 ^{ab}	0.20 ^a	0.77 ^a	3.61 ^a	5.27 ^{ab}
Post-floatation sediment								
Control	0.00 ^a	0.84 ^a	0.00 ^a	0.51 ^c	0.42 ^{bc}	0.84 ^a	7.07 ^b	9.68 ^c
Mineral fertilizers	0.39 ^{bc}	0.87 ^a	0.00 ^a	0.00 ^a	0.19 ^a	0.93 ^a	6.86 ^b	9.24 ^{bc}
Compost 1	0.41 ^{bc}	0.84 ^a	0.00 ^a	0.00 ^a	0.61 ^c	0.89 ^a	5.27 ^a	8.03 ^a
Compost 2	0.42 ^{bc}	0.78 ^a	0.00 ^a	0.19 ^b	0.55 ^c	0.96 ^a	5.04 ^a	7.95 ^a
Compost 3	0.49 ^c	0.85 ^a	0.00 ^a	0.18 ^b	0.28 ^{ab}	0.97 ^a	4.65 ^a	7.40 ^a
Compost 4	0.43 ^{bc}	0.80 ^a	0.00 ^a	0.19 ^b	0.58 ^c	0.90 ^a	4.60 ^a	7.48 ^a
Compost 5	0.34 ^b	0.83 ^a	0.00 ^a	0.53 ^c	1.21 ^d	0.93 ^a	4.50 ^a	8.34 ^{ab}

* See Table 2; ** see Table 2; *** see Table 2.

It is worth noticing that in both soils nickel bound to soil humus (F4) constituted a relatively big share in the metal total content. Analysis the results obtained from research conducted on the post-floatation sediment revealed that fertilization with composts contributed to a significant decrease in nickel content in the residual fraction (F7) with simultaneous increasing the number of its organic bonds (F7) in the substratum in comparison with mineral fertilization (object 2).

Conclusions

1. The contents of analysed metal forms to the greatest extent depended on the studied element and used substratum, whereas compost supplement with 8 % admixture

of various polymer foils generally had no marked effect on the distribution of metal content in the researched fractions.

2. The greatest quantities of cadmium in soils were assessed in fraction bound exchangeably, bonds with manganese oxides and residual, whereas in the post-floatation sediment in the residual fraction and bound to crystalline iron oxides.

3. Copper to the highest degree was bound to organic matter and natural minerals. Application of composts with polymer materials supplement decreased the content of mobile copper forms in comparison with mineral fertilization.

4. Nickel in the tested substrata, except for the post floatation sediment was found mainly in hardly available forms. Far greater nickel mobility was demonstrated in post floatation sediment, where considerable amounts of the metal, beside the residual fraction occurred also in mobile and exchangeable fractions.

5. No explicit effect of the kind of polymer used in composting on cadmium, copper or nickel solubility was observed.

References

- [1] Ciesielczuk T, Kusza G. *Ochr Środ Zasob Natural.* 2009;41:347-354.
- [2] Cao L, Shen G, Lu Y. *Environ Geol.* 2008;54:1531-1536. DOI: 10.1007/s00254-007-0934-0.
- [3] Ozimek A, Koncewicz-Baran M, Gondek K. *Acta Agrophys.* 2012;19(4):787-802.
- [4] Rozporządzenie Minister Rolnictwa i Rozwoju Wsi z dnia 18 czerwca 2008 roku w sprawie wykonania niektórych przepisów ustawy o nawozach i nawożeniu. *DzU* 2008, Nr 119, poz 765.
- [5] Gondek K. *Pol J Environ Stud.* 2009;18(3):359-368.
- [6] Jasiewicz Cz, Baran A. *Zesz Probl Post Nauk Roln.* 2009;541:147-156.
- [7] Zeien H, Brümmer GW. *Dtsch Bodenkundl Geselsch.* 1989;59(1):505.
- [8] Filipek-Mazur B, Gondek K. *Acta Agrophys.* 2001;51:209-214.
- [9] Ge Y, Murray P, Hendershot WH. *Environ Pollut.* 2000;107(1):137-144. DOI: 10.1016/s0269-7491(99)00119-0.
- [10] Brazauskienė DM, Paulauskas V, Sabienė N. *J Soils Sediments.* 2008;8:184-192. DOI: 10.1007/s11368-008-0004-6.
- [11] Filipek-Mazur B, Mazur K, Gondek K. *Acta Agrophys.* 2001;51:201-208.
- [12] Wójcik-Kapusta A, Niemczuk B. *J Elementol.* 2009;14(4):815-824. DOI: 10.5601/jelem.2009.14.4.815-824.
- [13] Domańska J. *Ochr Środ Zasob Natural.* 2009; 40:236-245.

ROZPUSZCZALNOŚĆ METALI CIĘŻKICH W GLEBACH NAWOŻONYCH KOMPOSTAMI Z DODATKIEM TWORZYW POLIMEROWYCH

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Stosowanie kompostów z odpadów komunalnych do celów nawozowych, z uwagi na dużą zawartość materii organicznej oraz składników pokarmowych, na ogół korzystnie wpływa na plon roślin i właściwości gleby. Do ich produkcji są wykorzystywane biodegradowalne frakcje odpadów komunalnych, bardzo często pochodzące ze zbiórki nieselektywnej i w związku z tym mogą zawierać pewne ilości zanieczyszczeń, zarówno organicznych, jak i mineralnych, np. metale ciężkie, które mogą negatywnie oddziaływać na żyzność gleby.

W oparciu o doświadczenie wazonowe badano wpływ kompostów z domieszką materiałów polimerowych modyfikowanych skrobią jako biokomponentem na rozpuszczalność metali ciężkich w testowanych podłożach, na których uprawiano owies i gorczycę. Komposty zastosowano do dwóch gleb o naturalnej zawartości

metali ciężkich oraz gleby i osadu poflotacyjnego z przeróbki rud cynkowo-ołowiowych zanieczyszczonych metalami ciężkimi. Do nawożenia zastosowano 5 kompostów, do wytworzenia których wykorzystano substrat złożony ze słomy pszennej, rzepakowej i odpadów z czyszczenia grochu z ośmioprocentowym dodatkiem folii polimerowych różniących się między sobą udziałem skrobi oraz gęstością. Analizę specyficzną wybranych metali ciężkich wykonano metodą sekwencyjnej ekstrakcji według Zeiena i Brümmera.

Na podstawie przeprowadzonych badań stwierdzono, że zawartość poszczególnych form metali w największym stopniu zależała od analizowanego pierwiastka oraz zastosowanego podłoża. Natomiast dodatek kompostów z 8% domieszką różnych folii polimerowych z reguły nie miał istotnego wpływu na rozkład zawartości metali w badanych frakcjach. Najwięcej kadmu w glebach oznaczono we frakcji związanej wymiennie, w formie połączeń z tlenkami manganu oraz rezydualnej, najsilniej związanej ze stałą fazą gleby. W odpadzie poflotacyjnym najwięcej kadmu oznaczono we frakcji rezydualnej oraz związanej z krystalicznymi tlenkami żelaza. Największe ilości miedzi były związane z materią organiczną oraz minerałami pierwotnymi. Stosowanie kompostów z dodatkiem materiałów polimerowych zmniejszyło zawartość ruchliwych form miedzi w porównaniu z nawożeniem mineralnym. Nikiel w badanych podłożach, poza odpadem poflotacyjnym, znajdował się głównie w formach trudnodostępnych. Znacznie większą mobilność niklu wykazano w odpadzie poflotacyjnym, w którym metal ten, oprócz frakcji rezydualnej, w znacznej ilości występował we frakcjach: ruchliwej oraz wymiennej.

Słowa kluczowe: metale ciężkie, sekwencyjna ekstrakcja, gleba, osad poflotacyjny, kompost, tworzywa polimerowe

