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Małgorzata KONCEWICZ-BARAN[1] and Krzysztof GONDEK[1]

ZINC, CADMIUM AND LEAD BINDING BY HUMUS IN SOIL FERTILIZED WITH COMPOSTS

WIĄZANIE CYNKU, KADMU I OŁOWIU PRZEZ PRÓCHNICĘ W GLEBIE NAWOŻONEJ KOMPOSTAMI

Abstract: Binding heavy metals by humus compounds decreases these elements availability to plants, their leaching from soil and causes their partial detoxication. Organic matter supplied to the soil with composts may significantly affect heavy metal availability to plants, therefore the investigations conducted on the basis of a two-year pot experiment aimed at determining the effect of fertilization with composts prepared from plant and other biodegradable wastes and from mixed municipal wastes on zinc, cadmium and lead binding by soil humus. In order to compare the analyzed features, the treatments on which swine manure and nitrogen, phosphorus and potassium in mineral forms were applied, were used. The contents of Zn, Cd and Pb in combination with humus compounds were extracted from the soil by means of 0.025 mol · dm^{-3} NH_4EDTA solution using sequential chemical extraction developed by Zeien and Brümmer. In the obtained extracts the contents of Zn, Cd and Pb were assessed using the ICP-AES method.

Significantly lower acidification was assessed in the soil fertilized with manure and composts than in the soil with a supplement of mineral salts or in unfertilized soil, both after the first and second year of the experiment. Compost fertilization caused an increase in organic carbon content in soil in comparison with organic C assessed in the soil with added mineral salts. The highest total contents of Zn and Pb were determined in the soil with an admixture of municipal waste compost. The contents of lead and zinc bound to humus compounds revealed a positive relationship with organic carbon content and were the highest in the soil receiving organic materials. The biggest contents of cadmium total forms after the first year of the research were assessed in the soil of treatments where the composts and swine manure were used, whereas after the second year contents of Cd in soil did not differ significantly depending on the applied fertilization. An admixture of manure or composts to the soil did not affect significantly the changes of cadmium contents in the combinations with humus compounds.

Keywords: zinc, cadmium, lead, humus, soil, compost

Soil humus compounds may form simple or chelated complex compounds with heavy metal ions. Metal ions may also fulfill the function of bridges in the complexes of humus compounds with clay minerals. Durability of the complexes to a great extend

[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 46, fax: +48 12 662 43 41, email: koncewicz_m@wp.pl

depends on the soil pH and the kind of metal ion. Heavy metal binding by humus compounds decreases these elements availability to plants, their leaching into the deeper soil profile layers and causes their partial detoxication [1].

In view of growing organic matter deficit in the soils of Poland, caused by among others diminished amount of applied farmyard manure, alternative sources of organic materials are being sought, which would improve organic matter balance in soil. Composts produced from waste organic materials may provide a valuable and cheap source of organic matter, although one must remember that these materials may be also burdened with undesirable substances, including heavy metals [2–4]. Organic matter supplied to the soil with composts may significantly affect heavy metal availability to plants, therefore the research conducted on the basis of a two-year pot experiment aimed at determining the influence of fertilization with composts prepared from plant and other biodegradable wastes and from mixed municipal wastes on zinc, cadmium and lead binding by soil humus.

Material and methods

The pot experiment, conducted in 2006–2007, comprised 5 treatments in four replications according to the following design: 0 – soil without fertilization, M – soil with mineral salts supplement, SM – soil with swine manure supplement, CI – soil with added compost prepared from plant and other biodegradable wastes, CII – soil with a supplement of mixed municipal waste compost. The experiment was set up on soil with granulometric composition of clay containing 26 % of particles < 0.02 mm in diameter. Selected properties of the soil material were presented in Table 1.

Table 1

Some properties of soil used for the experiment

Determination	Unit	Value
pH KCl	[-]	5.69
Hydrolytic acidity	[mmol(+) · kg^{-1} d.m.]	23.9
Organic C	[g · kg^{-1} d.m.]	15.9
Content of available forms		
P	[mg · kg^{-1} d.m.]	328
K		373
Total content		
Zn	[mg · kg^{-1} d.m.]	104.3
Cd		1.14
Pb		30.2

Two different composts were applied in the experiment: compost from plant and other biodegradable wastes (compost I – CI) originating from the composting plant

situated in Krakow-Plaszow, where the wastes are composted using Mut-Kyberferm technology, and compost from mixed municipal wastes (compost II – CII) originating from a composting plant in Katowice operating in Mut-Dano system. The reference materials for the analyzed features in the presented experiment were swine manure and mineral fertilization. Basic chemical properties were assessed in the organic materials using methods developed by Baran and Turski [5]. Chemical composition of organic materials was given in Table 2.

Table 2

Some properties of farmyard manure and composts used in the experiment

Determination	Unit	SM	CI	CII
Dry matter	[g · kg^{-1}]	224.8	475.9	563.4
Organic matter	[g · kg^{-1} d.m.]	823.3	515.8	246.1
pH H_2O	[-]	8.06	7.30	7.18
Electrolytic conductivity	[mS · cm^{-1}]	4.57	3.80	1.41
Total content				
N	[g · kg^{-1} d.m.]	27.31	35.61	6.78
P		13.09	7.17	2.29
K		23.65	25.57	11.16
Ca		2.01	22.57	34.31
Total content				
Zn	[mg · kg^{-1} d.m.]	636.9	282.5	1835.5
Cd		0.61	1.51	6.28
Pb		4.28	14.66	343.67

The swine manure and composts were applied once in the first year of the experiment and their doses were established on the basis of their nitrogen contents. In the first year of the research, nitrogen dose supplied to the soil with the manure and composts was 1.00 g N per pot (8.60 kg of air-dried soil material). Phosphorus and potassium on all treatments (except the unfertilized object) were supplemented to the equal level introduced with the composts and manure, respectively to 0.48 g P · pot^{-1} and 1.64 g K · pot^{-1}. The supplementary phosphorus dose was introduced in a water solution of $Ca(H_2PO_4) \cdot H_2O$ and potassium as a water KCl solution. On the treatment where only mineral salts were used as fertilizers, nitrogen was supplied as NH_4NO_3 while phosphorus and potassium as water solutions of $Ca(H_2PO_4) \cdot H_2O$ and KCl. The quantities of elements supplied to the soil with the swine manure (SM), compost prepared from plant and other biodegradable materials (CI) and compost prepared from mixed municipal wastes (CII) were the following: zinc – 23.31 mg, 7.93 mg and 270.71 mg Zn · pot^{-1}, cadmium: 0.02 mg, 0.04 mg and 0.92 mg Cd · pot^{-1} and lead: 0.15 mg, 0.41 and 50.68 mg Pb · pot^{-1}, respectively. In the second year of the research all treatments, except the unfertilized soil, received supplementary fertilization with

nitrogen, phosphorus and potassium applied as water solutions of the following salts: NH_4NO_3, $Ca(H_2PO_4) \cdot H_2O$ and KCl. The amounts of supplied elements were respectively: 0.70 g N, 0.10 g P and 1.60 g K $\cdot$ pot^{-1}.

Each year of the experiment maize, cv. 'San' (FAO 240), was cultivated. The maize (designed for green fodder) was always harvested at 7–9 leaves stage. Each year after the crop harvest soil material samples were collected. After drying and grounding in a porcelain mortar the soil material was sifted through a sieve with 1 mm mesh. In the soil samples pH was determined by potentiometer in a suspension of soil and 1 mol $\cdot$ dm^{-3} KCl solution. Organic carbon content was assessed after the sample wet mineralization in potassium dichromate(VI) using Tiurin's method. Total contents of zinc, cadmium and lead in the soil material were assessed after incineration of the sample organic material in a muffle furnace (at 500 ^oC for 8h) and the remains mineralization in concentrated HNO_3 and $HClO_4$ acids (2:1) (v/v). Heavy metal fraction bound to the soil humus compounds (Zn-NH_4EDTA, Cd-NH_4EDTA and Pb-NH_4EDTA) were separated using sequential chemical extraction developed by Zeien and Brümmer [6] by means of 0.025 mol $\cdot$ dm^{-3} NH_4EDTA solution. The contents of zinc, cadmium and lead were assessed in the obtained solutions using ICP-AES method on JY 238 Ultrace apparatus and obtained results were converted into absolutely dry soil mass (105 ^oC for 12 h).

The analysis of experimental material was conducted in four replications, whereas the initial materials (organic materials and soil material) in two replications and a plant reference material – NCS DC73348 (China National Analysis Center for Iron & Steel) or soil reference material– *Agro*MAT AG-2 (SCP Science) was added to each analyzed series. The result was considered reliable if the relative standard error did not exceed 5 %.

Two factor ANOVA (factors: fertilization and year) in a completely randomized design using F-Fisher test was conducted for the obtained results. Significance of differences between arithmetic means was estimated on the basis of homogenous groups determined by Duncan test at a significance level $p < 0.05$. Using nonparametric rank Spearman's test the value of correlation coefficient (r) was computed between organic carbon content in soil and the contents of Zn, Pb and Cd forms in combinations with humus compounds. All statistical calculations were made using Statistica 7.1 pl package.

Results

Fertilization with manure and composts (Table 3) caused a significant increase in the soil pH in comparison with the value assessed in the mineral salts treatment, particularly after the first year of the experiment. The best deacidifying effect was registered after the application of mixed municipal wastes compost (CII).

After two years of the experiment, significantly higher contents of organic carbon were noted in the soil, to which manure or composts were added in comparison with the values assessed in the soil from the treatment where no fertilization was applied or in the soil fertilized only with mineral materials (Table 3).

Table 3

Soil pH and contents of organic carbon in soil assessed after the first and second year of the experiment

Fertilization	pH KCl		Organic C [g · kg^{-1} soil d.m.]	
	1st year	2nd year	1st year	2nd year
0	5.51^{c*}	5.38^{b}	15.21^{a}	14.93^{a}
M	5.40^{b}	5.24^{a}	15.55^{ab}	15.20^{a}
SM	5.59^{e}	5.57^{de}	16.44^{bc}	16.33^{bc}
CI	5.68^{f}	5.53^{cd}	16.26^{bc}	16.22^{bc}
CII	6.29^{g}	6.28^{g}	16.60^{bc}	16.23^{bc}

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

In both years of the investigations markedly highest total zinc concentrations were found in the soil with a supplement of compost prepared from municipal wastes (Table 4).

Table 4

Zinc content in soil after the first and second year of the experiment

Fertilization	Total Zn		Zn-NH_4EDTA		Share of Zn-NH_4EDTA in total Zn content [%]	
	[mg · kg^{-1} soil d.m.]					
	1st year	2nd year	1st year	2nd year	1st year	2nd year
0	103.8^{a*}	102.8^{a}	14.90^{a}	14.61^{a}	14.3	14.2
M	106.6^{ab}	104.5^{a}	15.60^{ab}	14.47^{a}	14.6	13.9
SM	108.6^{ab}	107.2^{ab}	16.61^{bc}	16.28^{bc}	15.3	15.2
CI	111.0^{b}	111.1^{b}	17.27^{c}	17.24^{c}	15.6	15.5
CII	126.8^{c}	129.7^{c}	23.34^{d}	22.76^{d}	18.4	17.6

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

In the soil of the other treatments the total form of zinc contents did not reveal any significant diversification. The analysis of zinc contents extracted from the soil by means of NH_4EDTA solution after both years of the research revealed the biggest amounts of this Zn form in the soil fertilized with mixed municipal wastes compost (CII), however the share of this zinc form in the total contents did not exceed 18.5 % and on average was by 2.5 % higher than in the soil fertilized with compost based on plant wastes (CI) or manure (SM). Organic carbon content in soil significantly influenced zinc concentrations in combinations with humus compounds ($r = +0.724$; $p < 0.05$).

Significantly highest total lead content after both years of the experiment was assessed in the soil of the treatment where compost prepared from mixed municipal

wastes (CII) was used (Table 5). Also the content of lead in combinations with humus compounds was the highest in the soil from compost produced from mixed municipal wastes (CII) treatment. Mean content (for both years) of Pb-NH_4EDTA in this treatment soil was 18.55 mg · kg^{-1} soil d.m., which constituted 55.5 % of this element total soil content. The content of Pb-NH_4EDTA revealed a positive relationship with the soil organic carbon content ($r = +0.538$; $p < 0.05$).

Table 5

Lead content in soil after the first and second year of the experiment

Fertilization	Total Pb		Pb-NH_4EDTA		Share of Pb-NH_4EDTA in total Pb content [%]	
	[mg · kg^{-1} soil d.m.]					
	1st year	2nd year	1st year	2nd year	1st year	2nd year
0	29.30^{b*}	27.92^{ab}	14.17^{ab}	14.20^{ab}	48.4	50.9
M	28.55^{ab}	27.60^{a}	14.12^{ab}	13.95^{a}	49.5	50.5
SM	28.86^{ab}	27.59^{a}	14.71^{bc}	14.28^{abc}	51.0	51.8
CI	29.32^{b}	28.66^{ab}	14.91^{c}	14.49^{abc}	50.9	50.6
CII	33.61^{c}	33.28^{c}	18.93^{e}	18.16^{d}	56.3	54.6

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

The highest concentrations of total cadmium after the first year of the experiment were assessed in the soils of compost or manure treatments (Table 6).

Table 6

Cadmium content in soil after the first and second year of the experiment

Fertilization	Total Cd		Cd-NH_4EDTA		Share of Cd-NH_4EDTA in total Cd content [%]	
	[mg · kg^{-1} soil d.m.]					
	1st year	2nd year	1st year	2nd year	1st year	2nd year
0	0.863^{cd}	0.700^{a}	0.347^{bc}	0.273^{a}	40.2	39.0
M	0.813^{bc}	0.701^{a}	0.322^{abc}	0.265^{a}	39.6	37.8
SM	0.900^{cde}	0.744^{ab}	0.298^{ab}	0.290^{ab}	33.1	39.0
CI	0.927^{de}	0.881^{cde}	0.323^{abc}	0.385^{c}	34.8	43.7
CII	0.978^{e}	0.749^{ab}	0.263^{a}	0.282^{ab}	26.9	37.7

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

After the second year of the experiment the total cadmium content decreased in the soils of all treatments and generally did not reveal any greater diversification. The content of cadmium bound in organic combinations with the soil humus compounds did not differ significantly either regarding the year of the investigations or applied fertilization. Assessed Cd-NH_4EDTA contents did not reveal any significant relationship with organic carbon concentrations. The highest share of this cadmium fraction in

the total content was registered in the soil where compost made of plant and other biodegradable wastes (CI) was applied.

Discussion

Deacidifying effect of the applied composts and manure should be explained by a relatively big load of mainly calcium supplied to the soil with these materials (Table 2). Increasing the soil pH in result of using as fertilizers composts prepared from municipal wastes was observed also by other authors [2, 7].

The increase in soil total concentrations of zinc, cadmium and lead after the application of composts registered in the presented research were also noted by Labetowicz and Ozarowski [2] and by Gorska et al [7] after the application of composts prepared from mixed municipal wastes. Also Izewska et al [8] observed greater concentrations of zinc, lead and cadmium in the soil fertilized with municipal sewage sludge and compost prepared from sewage sludge.

Application of composts for soil fertilization is connected not only with supplying a considerable load of heavy metals but also enriching it in organic matter, which has been demonstrated by numerous investigations [2, 3, 7] and confirmed by the presented results.

Organic matter in mature composts usually shows a considerable ability to bind heavy metals both in the processes of simple ion exchange between the soil solid phase and soil solution, but also through forming coordination compounds [9]. According to Christensen and Christensen [10] and Stroebel et al [11] humic acids may increase bioavailability of heavy metals resulting from the formation of chelates available to plants. Fresh, non-humified organic matter from the ripe or unripe composts provides a source of non-specific humus substances, eg organic acids or polysaccharides forming sparingly soluble complexes with heavy metal ions [12]. Observed in the presented experiment weaker binding of zinc by the soil organic substance in comparison with lead, was also observed by Brazauskiene et al [13] after sewage sludge compost supplying to the soil. The phenomenon should be explained by a greater affinity of humus acids functional groups to lead ions than to zinc ions [14]. According to Baran and Turski [15] humus compounds, beside clay minerals and hydrated iron and aluminium oxides, participate in lead sorption in soil, which is evidently visible in acid soils, where lead bound to organic matter constitutes the main fraction [14].

No significant differences in cadmium fraction bound to humus compounds extracted from the soil fertilized with organic materials or unfertilized or fertilized with mineral salts were observed in the presented investigations. Results of research conducted by Mohamed et al [16] point that introducing organic matter to the soil decreases content of Cd soluble and exchangeable fractions but increases concentrations of fractions bound to humus compounds and residual. The quoted authors explain the transformation of cadmium soluble forms into insoluble ones by among others increasing soil pH and growing contents of organic matter in soil. According to Udom et al [17] increase in organic matter content in soil stimulates formation of durable complexes of humic compounds with cadmium ions and therefore diminishes the share of this element soluble fraction in the total contents.

Conclusions

1. Significantly lower acidification was assessed in the soil fertilized with swine manure and composts than in the soil with mineral salt supplement or in the unfertilized soil.

2. Fertilization with composts increased organic carbon content in soil in comparison with this component content assessed in the soil from the mineral salts treatment.

3. The highest total zinc and lead contents were assessed in the soil with added compost prepared from mixed municipal wastes. The contents of total cadmium forms generally did not differ significantly considering the applied fertilization.

4. The determined contents of lead and zinc in combinations with humus compounds revealed a positive relationship with organic carbon content. A supplement of manure or composts to the soil did not affect significantly the changes of the contents of cadmium bound to humus compounds.

References

[1] Dziadowiec H. Zesz Probl Post Nauk Rol. 1993;411:269-282.
[2] Łabętowicz J., Ożarowski G. Zesz Probl Post Nauk Rol. 2000;472:489-496.
[3] Convertini G, Ferri D, Montemurro F, Maiorana M. Proc. of the 13th Int Soil Conservation Organization Conference, Brisbane: 2004;628:1-4.
[4] Gondek K, Filipek-Mazur B. Acta Agrophys. 2006;8(3):579-590.
[5] Baran S, Turski R. Ćwiczenia specjalistyczne z utylizacji odpadów i ścieków. Wyd AR. Lublin: 1996.
[6] Zeien H, Brümmer GH. Böden Mitteilnng Dtsch Bodenkundl Gesellsch. 1989;59(1):505-510.
[7] Górska EB, Stępień W, Russel S. Zesz Probl Post Nauk Rol. 2007;520:287-293.
[8] Iżewska A, Krzywy E, Wołoszyk Cz. J Elementol. 2009; 14(3):457-466.
[9] Weber J, Karczewska A, Drozd J, Licznar M, Licznar S, Jamroz E, Kocowicz A. Soil Biol Biochem. 2007;39:1294-1302.
[10] Christensen JB, Christensen TH. Environ Sci Technol. 1999;33:3857-3863.
[11] Strobel BW, Borggaard OK, Hansen HCB, Andersen MK, Raulund-Rasmussen K. Eur J Soil Sci. 2005;56:189-196.
[12] Shuman LM. J Environ Qual. 1999;28:1442-1447.
[13] Brazauskiene DN, Paulauskas V, Sabiene N. J Soils Sedim. 2008;8:184-192.
[14] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Wyd Nauk PWN. Warszawa: 1993.
[15] Baran S, Turski R. Degradacja, ochrona i rekultywacja gleb. Wyd AR. Lublin: 1996.
[16] Mohamed I, Ahamadou B, Li M, Gong M, Cai P, Liang W, Huang Q. J. Soils Sedim. 2010 [online] http://www.springerlink.com/content/j778871238021313/fulltext.pdf
[17] Udom BE, Mbagwu JSC, Adesodun JK, Agbim NN. Environ Int. 2004;30:467-470.

WIĄZANIE CYNKU, KADMU I OŁOWIU PRZEZ PRÓCHNICĘ W GLEBIE NAWOŻONEJ KOMPOSTAMI

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

Abstrakt: Wiązanie metali ciężkich przez związki próchniczne zmniejsza dostępność tych pierwiastków dla roślin, ich wymywanie z gleby oraz powoduje częściową ich detoksykację. Materia organiczna wprowadzona do gleby wraz z kompostami może w znaczący sposób wpływać na dostępność metali ciężkich dla roślin, stąd też celem badań przeprowadzonych w oparciu o dwuletnie doświadczenie wazonowe było określenie wpływu

nawożenia kompostami z odpadów roślinnych i innych biodegradowalnych oraz z niesegregowanych odpadów komunalnych na wiązanie cynku, kadmu i ołowiu przez próchnicę glebową. Dla porównania analizowanych cech do schematu doświadczenia wprowadzono obiekty, w których zastosowano obornik od trzody chlewnej oraz azot, fosfor i potas w formie mineralnej. Zawartość Zn, Cd i Pb w połączeniach ze związkami próchnicznymi wyekstrahowano z gleby roztworem NH_4EDTA o stężeniu 0,025 mol · dm^{-3} według sekwencyjnej ekstrakcji chemicznej opracowanej przez Zeiena i Brümmera. W uzyskanych ekstraktach zawartości Zn, Cd i Pb oznaczono metodą ICP-AES na aparacie JY 238 Ultrace.

W glebie nawożonej obornikiem oraz kompostami stwierdzono istotnie mniejsze zakwaszenie niż w glebie z dodatkiem soli mineralnych oraz w glebie nienawożonej zarówno po pierwszym, jak i po drugim roku badań. Nawożenie kompostami spowodowało zwiększenie zawartości węgla organicznego w glebie w porównaniu do zawartości C organicznego oznaczonej w glebie z dodatkiem soli mineralnych. Największe ogólne zawartości Zn i Pb oznaczono w glebie z dodatkiem kompostu z niesegregowanych odpadów komunalnych. Zawartości ołowiu i cynku związane ze związkami próchnicznymi wykazywały dodatnią zależność z zawartością węgla organicznego i były największe w glebie z dodatkiem materiałów organicznych. Największe ogólne zawartości form po pierwszym roku badań oznaczono w glebach z obiektów, w których zastosowano komposty i obornik, zaś po drugim roku zawartość Cd w glebie nie różniła się istotnie ze względu na zastosowane nawożenie. Dodatek do gleby obornika lub kompostów nie powodował istotnych zmian zawartości kadmu w połączeniach ze związkami próchnicznymi.

Słowa kluczowe: cynk, kadm, ołów, próchnica, gleba, kompost