

ASSESSMENT OF WATER-SOLUBLE HEAVY METAL FORM CONTENTS IN COMPOSTED BIODEGRADABLE MUNICIPAL WASTES

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ABSTRACT

Some kinds of municipal wastes reveal considerable contents of organic matter and nutrients, which after returning to element cycling may be used by plants. It causes that municipal wastes are very good initial material for composting. The use of composts for improving soil properties and soil fertilization may raise controversy, particularly when they are produced of waste substances. Heavy metals concentrations may be one of the factors limiting environmental application of this type of materials. Total contents of these elements in composts allows to assess their potential applications but does not include their bioavailability. Presented research results aimed at determining the effect of municipal waste composting with various additions (starch, edible oil and urea) on the contents of water-soluble forms of cadmium, chromium, lead and nickel in the obtained composts. Total contents of the analyzed heavy metals were assessed after sample mineralization at 450°C for 5 hours and dissolving the remains in diluted HNO₃ (1:2). Water-soluble form of heavy metals was separated using sequential chemical extraction acc. to McLaren and Crawford's method. Heavy metals content was determined in the obtained extracts using ICP-AS method in JY 238Ultrac trace apparatus (Jobin Yvon). From among the studied metals the smallest amount of total cadmium forms was assessed. The contents of water-soluble forms of the analyzed heavy metals in composts were conditioned by the extraction time and increased after 30 days. Cadmium was an exception in compost with starch and compost with urea, whereas nickel in compost with urea.

Key words: municipal wastes, composts water-soluble forms of heavy metals

INTRODUCTION

Because of their properties some municipal wastes are used as an initial material for composting process. Waste composting allows to improve their biological properties and chemical composition. Specific conditions emerge during composting, connected with heightened microbial activity and relatively high temperature, which contributes to liquidation of sanitary hazards of the composted materials. Supplements of various materials may be used during the process to optimize chemical composition, simultaneously intensifying the rate of occurring changes [Baran et al 2002]. Waste composting allows to obtain the product which can find environmental applications once it meets the respective quality requirements [Rosik-Dulewska 2001]. Waste heavy metals concentrations may prove a factor limiting environmental use of these materials. Total contents of these elements in composts make possible estimation of their use but it does not comprise their bioavailability assessment. Presented research aimed at determining the effect of composting municipal wastes with various supplements (starch, edible oil and urea) on the contents of water-soluble forms of cadmium, chromium, lead and nickel in the obtained composts subjected to extraction.

MATERIALS AND METHODS

Researched was raw (heating) compost of plant wastes leaving bioreactor chamber of composting plant operating in MUT-Kyberferm system. Organic material remained in the chamber for 14 days. The following wastes were used proportionately for preparing the initial material for analyses: fresh cuttings 10.2 %; fine cuttings 33.7 %; pomace 21.9 %; grass 23.1 % and tobacco waste 11.0 %. The composting process of initial material (heating compost) was conducted for 210 days in insulated containers with 20 dm³ capacity. The experiments comprised the following variants in two replications:

Object I – heating compost (control),

Object II – heating compost + starch,

Object III – heating compost + edible oil,

Object IV – heating compost + urea.

Starch, edible oil or urea supplements constituted 5 % in relation to heating compost fresh mass. After the components were thoroughly mixed, the material was placed in containers equipped with aerating system. The temperature and moisture inside the containers were checked during composting. Mass losses of the composted material were checked at two-week intervals, the materials inside the containers were stirred and water losses were supplemented. When the composting process was completed the materials were thoroughly mixed and sifted through a sieve to isolate a fraction with >1cm diameter (mesh fraction) and <1cm (minus mesh); subsequently samples for chemical assessments were collected. Edible starch and edible oil were used and chemically pure urea. The following assessments were made in the initial material and in the materials obtained after composting process using methods described in the papers by Baran and Turski [1996]:

- dry weight content at the temperature of 105 °C for 12 hours,
- pH measured by potentiometer in organic materials and water suspension, maintaining 1:10 dry weight to water ratio,
- electrical conductivity by conductometer,
- organic carbon content by Tiurin's method,
- total contents of analysed heavy metals (Cd, Cr, Pb and Ni) were assessed after sample mineralization in a muffle furnace (450 °C for 5 hours) and dissolving the remains in diluted (1:2) nitric acid,
- bi-distilled water was used for separating water-soluble forms of the studied heavy metals [Bogacz 1996].

Heavy metals concentrations in the obtained extracts were assessed by means of ICP-AES method in JY 238 Ultrace apparatus (Jobin Yvon). Presented results of analyses constitute arithmetic means of two replications differing by a maximum of 5 %. Standard error (SE) was computed for mean values presented in tables. Mean pH values of the tested composts and standard error values were computed after converting pH into hydrogen ion concentration.

RESULTS AND DISCUSSION

Dry matter content in the investigated organic materials after composting was diversified not only in relation to added component but also due to the analyzed compost fraction (mesh fraction or minus mesh) (Tab. 1). In comparison with "heating compost" collected after leaving bioreactor chamber, dry matter content increased in the mesh fraction of all composts. Increase in compost minus mesh fraction dry matter was registered only on the object where starch was added to "heating" compost. pH is one of the most important chemical characteristics of waste substances. Conducted experiments demonstrated an apparent increase in the value of discussed parameter in the discussed composts in comparison with the initial material - "heating" compost. (Tab. 1 and 2).

Recommended measure of compost salinification is their electrolytic conductivity [Baran and Turski 1996]. Excess of soluble salts in composts, at their environmental application may lead to total plant wilting or development of many diseases. Electrolytic conductivity of water solutions depends on the kind of soluble substances, their concentrations and the temperature. Value of electrolytic conductivity was the highest in both fractions of compost without admixtures (Tab. 2).

Organic carbon content diminished in minus mesh fraction of all composts in comparison with the content assessed in "heating" compost collected after its leaving the bioreactor (Tab. 1 and 2). On the other hand the highest content of this component was found in the mesh fraction.

Tab. 1 Selected proprieties of raw "heating " compost after leaving the bioreactor

Parameter	Value
Dry weight $\text{g}\cdot\text{kg}^{-1}$	549.8 ± 2.20
pH H_2O	$6.52 \pm < 0.01$
Organic C $\text{g}\cdot\text{kg}^{-1}$ s.m.	320.1 ± 7.16
Electrolytic conductivity $\text{mS}\cdot\text{cm}^{-1}$	5.58 ± 0.07
Cd $\text{mg}\cdot\text{kg}^{-1}$ s.m.	0.67 ± 0.01
Pb $\text{mg}\cdot\text{kg}^{-1}$ s.m.	11.52 ± 0.22
Ni $\text{mg}\cdot\text{kg}^{-1}$ s.m.	10.01 ± 0.49
Cr $\text{mg}\cdot\text{kg}^{-1}$ s.m.	29.58 ± 2.80

\pm SE (standard error). n = 2

Tab. 2 Selected properties of organic materials after composting

Objects		Dry weight $\text{g}\cdot\text{kg}^{-1}$	pH H_2O	Organic C $\text{g}\cdot\text{kg}^{-1}$ d.m.	Electrolytic conductivity $\text{mS}\cdot\text{cm}^{-1}$
Heating compost (control)	Mesh fraction	515.0 ± 20.2	$7.85 \pm < 0.01$	309.9 ± 4.1	6.31 ± 0.07
	Minus mesh	571.2 ± 15.6	7.82 ± 0.03	342.2 ± 22.4	6.74 ± 1.08
Heating compost + starch	Mesh fraction	645.9 ± 28.6	7.84 ± 0.03	312.1 ± 3.7	5.98 ± 0.06
	Minus mesh	705.7 ± 18.5	7.97 ± 0.01	397.0 ± 12.6	5.43 ± 0.30
Heating compost + edible oil	Mesh fraction	512.7 ± 21.7	7.74 ± 0.02	302.8 ± 7.7	5.90 ± 0.07
	Minus mesh	560.1 ± 16.4	8.40 ± 0.01	331.6 ± 22.3	5.06 ± 0.01
Heating compost + urea	Mesh fraction	544.3 ± 24.7	7.58 ± 0.01	318.5 ± 6.0	5.76 ± 0.27
	Minus mesh	590.7 ± 15.8	7.57 ± 0.01	337.4 ± 12.2	5.87 ± 0.06

\pm SE (standard error). n = 2

Total content of cadmium (Tab. 3) remained on a similar level ($0.81\text{-}0.86 \text{ mg}\cdot\text{kg}^{-1}$), however it was slightly higher – $0.91 \text{ mg}\cdot\text{kg}^{-1}$ in the compost with urea supplement. Considering total cadmium content, the studied composts (irrespective of compost fraction) may be classified to the first class on the basis of limits stated in the EU regulations [Hogg et al. 2002]. Cadmium content extracted with water was the highest in compost with urea supplement. The share of this form in total cadmium content after 18 hours in mesh fraction constituted 38 % of the total content. A decline in the content was observed after 30 days. Cd- H_2O constituted 28 % of the total mass. A decrease in water-soluble

cadmium was observed also in compost with an admixture of starch (over 6 % after 30 days from composting completion). In the other variants a slight increase in water-soluble cadmium was noted after 30 days, e.g. in control compost by $0.002 \text{ mg} \cdot \text{kg}^{-1}$ and in the compost with oil by $0.014 \text{ mg} \cdot \text{kg}^{-1}$.

Tab. 3 Cadmium content in organic materials after composting process

Objects		Total Cd $\text{mg} \cdot \text{kg}^{-1}$	Cd – H ₂ O $\text{mg} \cdot \text{kg}^{-1}$ (after 18 hrs.)	Cd – H ₂ O $\text{mg} \cdot \text{kg}^{-1}$ (after 30 days)
Heating compost (control)	Mesh fraction	0.86 ± 0.02	$0.060 \pm < 0.01$	0.062 ± 0.02
Heating compost + starch	Mesh fraction	0.81 ± 0.05	$0.051 \pm < 0.01$	$0.046 \pm < 0.01$
Heating compost + edible oil	Mesh fraction	0.81 ± 0.01	$0.032 \pm < 0.01$	$0.046 \pm < 0.01$
Heating compost + urea	Mesh fraction	0.91 ± 0.09	$0.350 \pm < 0.01$	0.254 ± 0.01

\pm SE (standard error), n = 2

Total content of nickel (Tab. 4) was the highest in compost with urea supplement, by almost 50 % in comparison with the other combinations. Considering their total nickel contents and independently of the fraction, on the basis of EU regulations, the studied composts may be classified in the first class [Hogg et al. 2002]. Diversification of the total nickel content in the tested materials was reflected in differentiated amounts of this element extracted with water. The greatest amount of water-soluble nickel forms was assessed in compost with urea supplement. After 18 hours the amount in extracts was almost 4 times higher. After 30 days the contents of Ni-H₂O increased in each variant, except compost with urea admixture. In this case, the content diminished by $0.008 \text{ mg} \cdot \text{kg}^{-1}$. Releasing the content of water-soluble nickel was observed after 30 days in the control object. Total nickel content in the studied materials was small, similar as water-soluble fraction content. These are stable and biologically inactive nickel forms. Rosik-Dulewska [2001] stated that, irrespectively of the season in which the compost was manufactured, the greatest amounts of nickel became accumulated in the residue fraction.

Tab. 4 Content of nickel in organic materials after composting

Objects		Total Ni $\text{mg} \cdot \text{kg}^{-1}$	Ni – H ₂ O $\text{mg} \cdot \text{kg}^{-1}$ (after 18 hrs.)	Ni – H ₂ O $\text{mg} \cdot \text{kg}^{-1}$ (after 30 days)
Heating compost (control)	Mesh fraction	15.97 ± 0.39	0.68 ± 0.01	1.00 ± 0.02
Heating compost + starch	Mesh fraction	15.30 ± 1.14	0.64 ± 0.02	0.84 ± 0.012
Heating compost + edible oil	Mesh fraction	16.82 ± 1.26	0.56 ± 0.01	0.70 ± 0.08
Heating compost + urea	Mesh fraction	27.16 ± 4.04	2.59 ± 0.02	2.51 ± 0.04

\pm SE (standard error), n = 2

Total content of lead (Tab. 5) in the analyzed composts was on a similar level: $13.78 - 15.62 \text{ mg} \cdot \text{kg}^{-1}$. Assessed total Pb content allows to count the investigated composts to the first class [Hogg et al. 2002]. After 18 hours the content of lead extracted with water was the greatest in the compost with urea

supplement. The amount was between 5 and 9 times bigger in comparison with the other composts. After 30 days a clear increase in Pb – H₂O was observed in each variant. Water-soluble lead concentration increased most (over twice) in the compost with urea admixture and slightly less in the control compost. In the other two variants the increase in the content was respectively: 1.11 mg ·kg⁻¹ in the compost with starch admixture and 1.30 mg ·kg⁻¹ in the compost with added edible oil.

Tab. 5 Content of lead in organic materials after composting

Objects		Total Pb mg·kg ⁻¹	Pb – H ₂ O mg·kg ⁻¹ (after 18 hrs.)	Pb – H ₂ O mg·kg ⁻¹ (after 30 days)
Heating compost (control)	Mesh fraction	14.87 ± 0.16	0.49 ± 0.07	2.42 ± 0.32
Heating compost + starch	Mesh fraction	15.36 ± 1.09	0.41 ± 0.07	1.52 ± 0.08
Heating compost + edible oil	Mesh fraction	15.62 ± 0.40	0.33 ± 0.03	1.63 ± 0.07
Heating compost + urea	Mesh fraction	15.49 ± 2.36	2.30 ± 0.10	4.95 ± 0.08

± SE (standard error), n = 2

Difference in total chromium content between objects was 10 mg ·kg⁻¹. It was the difference between the control and the object where urea was added (Tab. 6). Chromium concentration after water extraction was the highest in compost with urea addition. This content differed considerably from the values assessed in the other materials. After 30 days Cr-H₂O concentrations increased in each experimental variant. Water-soluble chromium content increased most, by 0.81 mg ·kg⁻¹ in the control compost. In compost with urea supplement, extracted chromium content bound to organic matter was smaller than determined after extraction with water. Assessed small concentrations of most mobile chromium fraction were corroborated by previous investigations conducted by Gondek [2006]. Also studies conducted by Czekala et al [1996] revealed that both in sewage sludge and in composts with this sludge share the content of water-soluble chromium was small, constituting from 0.05 % to 0.14 % of total chromium.

Tab. 6 Content of chromium in organic materials after composting

Objects		Total Cr mg·kg ⁻¹	Cr – H ₂ O mg·kg ⁻¹ (after 18 hrs.)	Cr – H ₂ O mg·kg ⁻¹ (after 30 days)
Heating compost (control)	Mesh fraction	39.17 ± 1.22	0.84 ± 0.01	1.65 ± 0.06
Heating compost + starch	Mesh fraction	40.03 ± 3.37	0.79 ± 0.01	1.45 ± 0.04
Heating compost + edible oil	Mesh fraction	44.92 ± 2.46	0.72 ± 0.02	1.19 ± < 0.01
Heating compost + urea	Mesh fraction	48.26 ± 4.15	6.47 ± 0.11	6.90 ± 0.10

± SE (standard error), n = 2

CONCLUSIONS

1. Total contents of heavy metals in the analyzed municipal waste composts do not exclude their agricultural use.
2. Contents of individual water-soluble heavy metal forms differed in the investigated composts depending on the analyzed material and supplement to the composted mass (starch, edible oil or urea).
3. The contents of heavy metals extracted with water were small, which evidences low mobility of these elements in the analyzed composts.
4. The contents of water-soluble heavy metals forms were increasing with extraction time in almost each experimental variant.

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