



Effect of composting on the mobility of arsenic, chromium and nickel contained in kitchen and garden waste

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ABSTRACT

The study was focused on evaluation of possible changes in As, Cr, and Ni mobility and fractionation during composting of kitchen and garden waste. Fresh bio-waste taken up seasonally was thoroughly mixed with woodchips in the wet weight portion of 3:1 and the mixture was put into batch-wise aerated fermenters under 3 air flow rates. An increased drop in exchangeable Cr and Ni was found in kitchen and garden waste after 12 weeks of composting, respectively. The exchangeable content of As decreased only during kitchen waste composting. The order of fractions in the final compost was as follows: residual > oxidizable > exchangeable > reducible. The proportion of Cr and Ni in exchangeable fraction decreased after composting more than 3- and 4-fold, respectively. Results proved that an intensive composting process is a suitable method for immobilization of Cr and Ni, and for decreasing total As contained in household bio-waste.

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1. Introduction

A Council Directive from 1999 on the landfill of waste, asked European countries to reduce biodegradable municipal solid waste in landfill to 35% of their 1995 levels by 2016 (CEC, 1999).

In most European countries, municipal solid waste contains about 50% of organic material basically consisting of a combination of kitchen and garden waste. Composting is one of the more efficient methods of handling bio-waste and enables recycling of organic matter to make use of the nutrients present in the waste (Epstein, 1997). Many countries introduced compost standards regulating product quality, including maximum total trace elements or potentially toxic elements concentrations (Madrid, 2010). For instance, Czech Decree No. 341/2008 Coll., on details of bio-waste handling regulates these elements in compost: As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, and Zn. Two groups of composts were established, based on qualitative parameters. The first group is intended for agricultural land, the second for non-agricultural purposes. The maximum total content of As, Cr and Ni for the first group is 10 mg/kg, 100 mg/kg and 50 mg/kg, respectively. Arsenic is a major concern, because its maximum concentration in compost intended for agricultural purpose is difficult to meet. The maximum levels in compost of the second group are mostly less strict and depend on type of use.

Compost standards throughout the world refer to the total concentration of these potentially toxic elements. However, the

elements associated with different fractions have dissimilar impacts on the environment and their phytotoxicity connects to some forms rather than the total content. The sequential chemical extraction of elements can provide an understanding of chemical fractions and a predicting mobility, bioavailability and leaching rate (Tessier et al., 1979). For a better understanding of the potentially toxic element mobility in composts, the observation of potential changes in total and mobile element contents during composting were provided. Leita and DeNobili (1991) determined the water-extractable fractions of Cd, Zn, Cu, and Pb and investigated changes in water-soluble organic C during the complete composting of a pile of ground municipal solid waste. A progressive increase in total heavy metals concentrations during the composting period was not accompanied by a corresponding increase in the water-extractable amounts of metals. The influence of municipal solid waste composting on the concentration, water solubility, and phase association of Pb, Cd, Zn, and Cu at high concentrations in the starting materials, was studied more recently by Castaldi et al. (2006). They demonstrated that during composting, the heavy metals in the starting materials were redistributed from more labile and soluble forms to more stabilized ones.

The potential for excessive amounts of potentially toxic elements to contaminate food chains through municipal solid waste compost additions is thought to depend on the source material used in the compost and the final concentrations of potentially toxic elements in the compost (Veeken and Hamelers, 2002). Manual sorting of bio-waste by producers is more effective than downline sorting of mixed waste (Richard and Woodbury, 1992). Amlinger et al. (2004) concluded that the potentially toxic element contents in manually source-segregated compost were

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typically reduced by a factor of 2–10, compared with mechanically treated material. Generally, separately sorted bio-waste in households should not be contaminated by other sources. However, the natural background content of bio-waste constituents may result in potentially toxic element content for bio-waste compost that exceeds legal standards (Veeken and Hamelers, 2002). Moreover, the contents of potentially toxic elements in composts are known to be much higher than those of most agricultural soils and as a result, the repeated application of composts to soil over time tends to promote element accumulation. Bioavailability issues are increasingly considered as a potential factor. Among potentially toxic elements, contents and bioavailability of Cd, Cu, and Zn are primarily discussed because of their higher mobility and potential environmental risk (Paradelo et al., 2011; Dimambro et al., 2007; Leita and DeNobili, 1991). In the opposite, Cr and Ni are considered as the elements characterized by low availability, especially in composted sewage sludge (Paradelo et al., 2011; Zheng et al., 2007; Jakubus and Czekala, 2010). Even so, opposing findings were presented concerning Ni mobility in municipal solid waste compost by Smith (2009). Therefore, we resolved to evaluate Cr and Ni mobility and fractionation changes during composting of household bio-waste. Moreover, information concerning the changes and mobility of arsenic during composting are relatively limited (Zhang et al., 2008; Diaz-Bone et al., 2011) and so we decided to include arsenic to the set of investigated potentially toxic elements.

Change of aeration is one of the factors easily controlled in practical composting by active aeration or turnover frequency. The assumption is to change the mobility of potentially toxic elements by various aeration levels.

The aim of this study was to determine the changes in As, Cr and Ni mobility and fractionation during composting under various aeration levels of household bio-waste and to find out if composting reduces or enhances the phytotoxicity of elements.

The novelty in this work consists of the use of household bio-waste separately collected from two styles of residential density, over four climate seasons.

2. Methods

2.1. Composting experiment

The raw material was obtained from urban settlement (kitchen waste) with a predominant portion of fruit and vegetable bio-waste and family houses (garden waste) with grass, leaves and wood from gardens as the main components in every season during a single year. A detailed description of the composition and properties of used bio-waste over all four seasons is shown in our previous study (Hanc et al., 2011).

The 12-week composting experiments were carried out in laboratory reactors of 70 L capacity, with perforated stokers enhanced by 40 mm thick polyethylene foam insulation to reduce heat loss. The reactors were kept in a room at 25 °C. Fresh bio-waste was chopped with sharp knife on a wood floor and then thoroughly mixed with woodchips (<3 cm) as a bulking agent in the wet weight portion of 3:1 to improve structure, enhance aeration and absorb excess liquids (Eklind and Kirchmann, 2000a). An 18 kg of the mixture was put into each of 6 aerated fermenters during every season. Three fermenters contained mixtures of kitchen waste and another three with garden waste. The moisture of all materials was regularly controlled during composting and maintained from 50% to 80% depending on the type of bio-waste. An active aeration device was used, to push air through the composted materials from the bottom. The mixtures were batch-wise aerated for 5 min out of each half hour during the first 2 weeks

and 2.5 min in every half hour during the following 10 weeks, due to the decreasing demand of oxygen for microorganisms in later stages of composting. There were 3 air flow rates (low – L, medium – M, high – H) corresponding to 1.1, 2.2 and 3.3 L air h⁻¹ kg⁻¹ of initial fresh bio-waste mixture in the first 2 weeks. On the basis of our previous experiences, we found that medium aeration was usually sufficient to achieve the optimal parameters of composting as well as the quality of final compost. The further two levels were included as a deviation above and below this medium level. Very low aeration levels are insufficient for effective composting, yet on the other hand, increased aeration merely increases cooling of composted material.

Before sampling, the eventual leachate was returned to the composted material to achieve a closed loop. Four samples of 250 g from every reactor were collected at the beginning of the experiment; then after 2, 6 and 12 weeks. The resulting samples were dried at laboratory temperature and ground.

2.2. Analytical methods

Dry matter (DM) content was assessed by drying at 105 °C for 24 h. Moisture content was calculated at 100 – DM. Measurements of pH were made on samples mixed with deionized water (1:10 (w/v dry basis) by WTW pH 340 i (WTW, Germany). Volatile solids (VS) concentration was established from ignition loss in samples kept at 550 °C for 12 h. Organic carbon was determined by dichromate oxidation in sulfuric acid solution (Sims and Haby, 1971) and total nitrogen by the Kjeldahl method (Bremner, 1960). Humic substances were analyzed according to the modified methodology of Lechner and Smidt (2003). Briefly, 10 g of each sample was extracted with 50 mL of 0.1 mol L⁻¹ sodium pyrophosphate and shaken overnight. Centrifugation followed and an initial extract (IE) was obtained. The humic acids were precipitated by adding 37% HCl (pH 2). After centrifugations, the treated supernatant with fulvic acid (FA) content was used for a photometric determination. The humic acid fraction (HA) was determined by subtraction of optical density of IE – FA. Conversion from optical density into % of volatile solids was accomplished by gravimetric calibration. Total element contents were determined in the digests obtained by pressurized wet-ashing (HNO₃ + HCl + HF) with microwave heating Ethos 1 (MLS GmbH, Germany). The exchangeable content of elements in compost was ascertained in 1:20 (w/v) 0.11 mol L⁻¹ CH₃COOH. A sequential extraction procedure was applied for the assessment of elements associated with individual fractions as exchangeable (0.11 mol L⁻¹ CH₃COOH extractable), reducible (0.1 mol L⁻¹ NH₂OH·HCl extractable), oxidizable (8.8 mol L⁻¹ H₂O₂ followed by 1 mol L⁻¹ CH₃COONH₄ extractable), and residual fraction (Ure et al., 1993) where the nomenclature of the fractions was adopted according to Bacon and Davidson (2008). Concentrations of elements were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN VistaPro, Varian, Australia) with axial plasma configuration. Certified reference material 7004 Loam (Analytika s.r.o., Czech Republic) was used for quality assurance of the analytical data.

2.3. Statistical analyses

All statistical analyses were performed using the STATISTICA 9.0 software (StatSoft, 1995 Tulsa). One-way analysis of variance (AN-OVA) at a 95% confidence level, followed by Tukey's test, determined variances among the three aeration rates and seasons during composting. Spearman's correlations were explored between the main parameters of composting and exchangeable content of elements at probability levels of 0.05 and 0.01.

3. Results and discussion

3.1. Course of chosen properties during composting

A considerable increase in pH was recorded during the first two weeks in both types of bio-waste (Fig. 1a and b). The pH increased by more than two pH units during that brief time, then slowed after two weeks. This may be attributed to the drop in aeration intensity, the volatilization of ammoniacal nitrogen and H⁺ release as a result of microbial nitrification process by nitrifying bacteria (Eklind and Kirchmann, 2000b). Unlike composting of household bio-waste, the pH of vermicomposted sewage sludge mixed with sugarcane trash was lower after 90 days than its initial values (Suthar, 2010). In our experiment, variations increased during the process among seasons. The highest variance in pH occurred between summer and winter in the case of final kitchen compost. Values of pH differed significantly during composting of garden bio-waste from spring and other seasons.

Volatile solids content gradually decreased during composting over all seasons, which characterizes a properly operating process (Fig. 2a and b). As in the feedstock, volatile solid content in final garden compost followed the seasonal sequence of spring and summer < autumn and winter, coinciding with an increase in lignin components (Hanc et al., 2011). Humic acids as a proportion of organic matter can play an important role in controlling the extractability of potentially toxic elements in composts. The highest contents of humic acids were found in composts from spring and autumn (Table 1). However, humic acids are especially formed in the later curing stages of composting. The differences in humic acids content among seasons could be decreased by longer composting period. In majority of cases, intensive air supply led to a higher development of humic acids in composts.

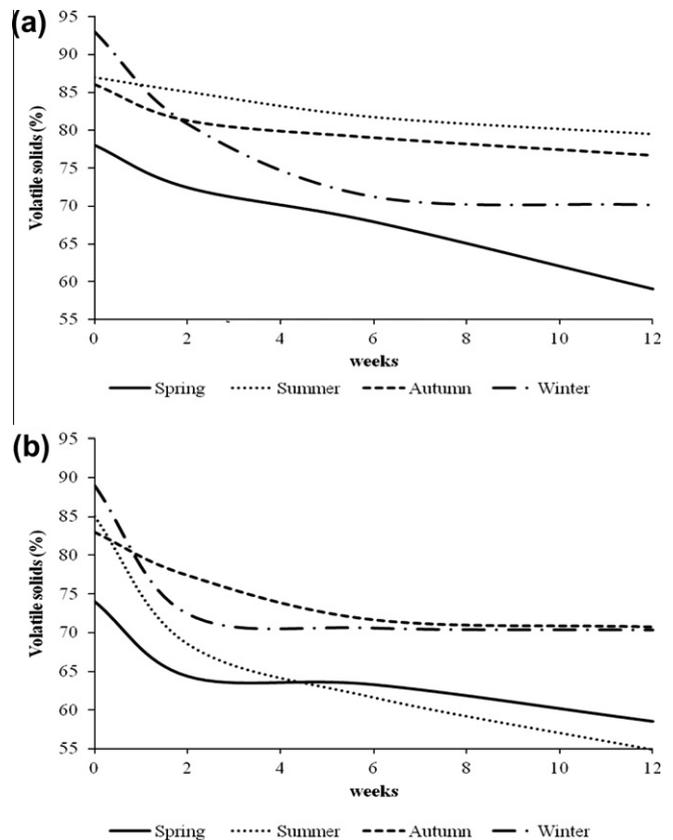


Fig. 2. Course of volatile solids during composting of kitchen waste (a) and garden waste (b) in seasons (average of 3 aeration levels).

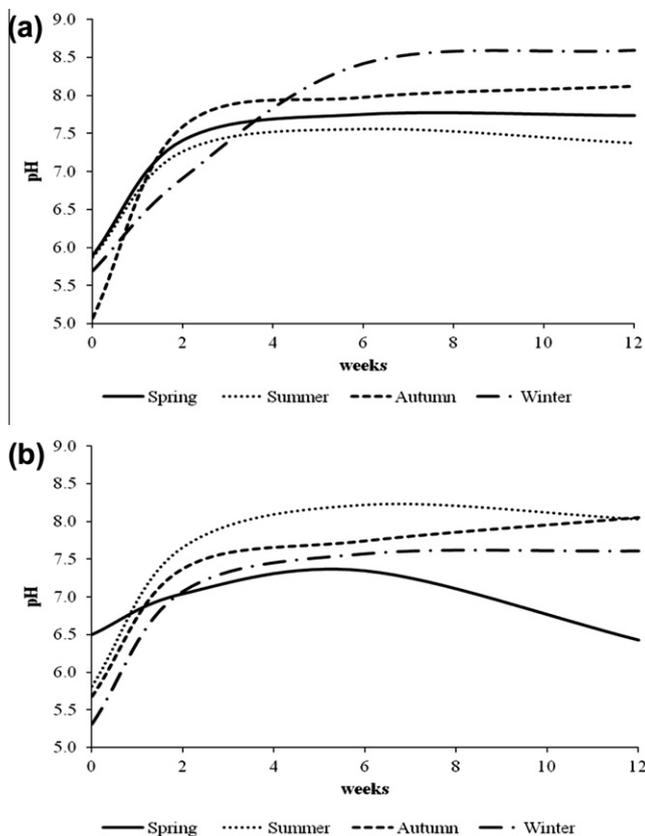


Fig. 1. Course of pH during composting of kitchen waste (a) and garden waste (b) in seasons (average of 3 aeration levels).

Table 1

Content of humic acids (% of volatile solids) in final compost originated in kitchen and garden waste, collected seasonally, after 12 weeks of composting under low (L), medium (M) and high (H) aeration (mean value and standard deviation were obtained from 4 samples).

Content of humic acids (% of volatile solids) in final compost					
Compost	Aeration	Spring	Summer	Autumn	Winter
Kitchen	L	8.2 ± 1.3	2.0 ± 0.2	11.1 ± 0.3	4.0 ± 1.5
	M	8.3 ± 0.3	3.8 ± 0.7	12.4 ± 1.2	3.3 ± 0.4
	H	5.0 ± 0.6	4.2 ± 0.2	13.6 ± 0.9	4.6 ± 0.6
Garden	L	8.4 ± 0.7	6.7 ± 0.9	8.1 ± 1.2	4.2 ± 0.5
	M	8.6 ± 0.3	9.0 ± 0.1	8.2 ± 1.4	4.0 ± 0.3
	H	9.6 ± 0.8	11.4 ± 2.3	7.9 ± 0.1	4.1 ± 0.1

An increasing trend of total nitrogen during the composting process (Fig. 3a and b) was probably caused by a decrease in the carbon substrate, resulting from CO₂ loss (Rasapoor et al., 2009). On average, there was almost no difference in N content between kitchen and garden compost, although some statistical variation was found among seasons.

3.2. Changes in the exchangeable content of elements during composting

Mean exchangeable contents of As, Cr and Ni during composting are shown in Tables 2 and 3.

The exchangeable content of arsenic in mixtures of kitchen waste was 2.8 times higher compared to garden waste mixtures at the beginning of composting. Over an average of seasons, exchangeable As decreased to 60% and 64% after 2 weeks of composting of kitchen and garden waste, respectively. During the next

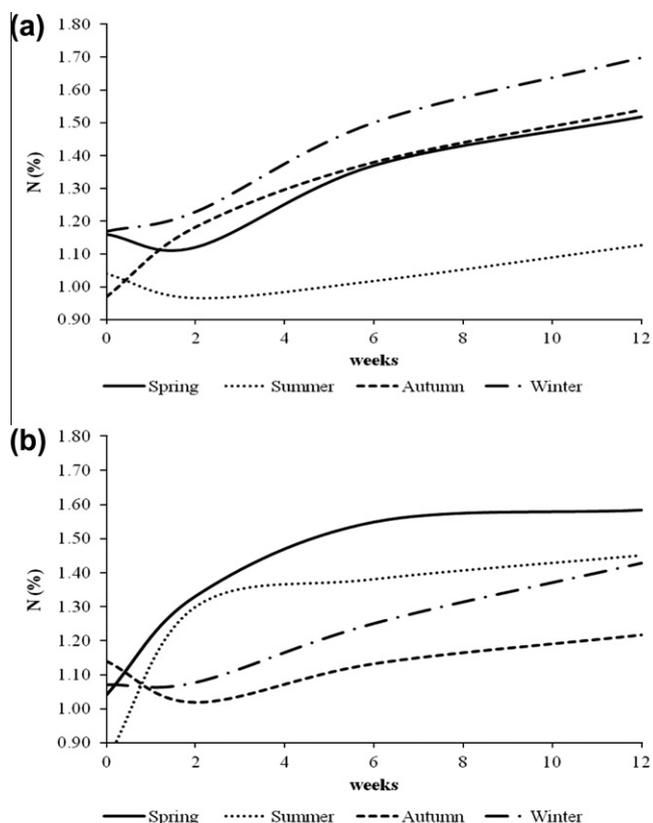


Fig. 3. Course of nitrogen during composting of kitchen waste (a) and garden waste (b) in seasons (average of 3 aeration levels).

Table 2

Mean exchangeable content of elements extractable with $0.11 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ (mg kg^{-1} of dry matter) in composting mix and during composting under low (L), medium (M) and high (H) aeration of kitchen waste, collected seasonally (mean value was obtained from 4 samples).

Element	Weeks	Aeration	Spring	Summer	Autumn	Winter	
As (mg kg^{-1})	0	Mix	1.196b	8.072a	1.348b	0.442c	
		L	0.461a;b	1.856b;a	1.634a;a	0.454a;b	
	2	M	0.434a;c	2.379ab;a	1.214ab;b	0.356ab;c	
		H	0.437a;c	2.597a;a	1.154b;b	0.222b;c	
	6	L	0.186a;c	2.987b;a	0.324a;b	0.631a;b	
		M	0.220a;c	3.503ab;a	0.295a;b	0.638a;b	
	12	H	0.213a;c	3.859a;a	0.192a;c	0.609a;b	
		L	0.976ab;a	0.983b;a	0.745a;b	0.681a;b	
		M	1.065a;a	0.908b;a	0.832a;b	0.622a;b	
		H	0.829b;b	2.168a;a	0.755a;b	0.637a;b	
	Cr (mg kg^{-1})	0	Mix	0.304b	0.109c	0.526a	0.149c
			L	0.090a;b	0.109a;b	0.412a;a	0.121ab;b
2		M	0.083a;b	0.113a;b	0.315a;a	0.126a;b	
		H	0.075a;c	0.115a;b	0.259a;a	0.074b;c	
6		L	0.052a;b	0.110b;a	0.154a;a	0.111a;a	
		M	0.085a;c	0.121ab;b	0.149a;a	0.067b;c	
12		H	0.076a;b	0.148a;a	0.145a;a	0.032b;c	
		L	0.130a;b	0.057a;c	0.247a;a	0.067a;c	
		M	0.149a;b	0.041a;d	0.208ab;a	0.077a;c	
		H	0.152a;a	0.054a;b	0.199b;a	0.044a;b	
Ni (mg kg^{-1})		0	Mix	0.721b	1.161a	0.774b	0.552c
			L	0.259a;b	1.088a;b	1.088a;a	0.716a;a
	2	M	0.217a;c	0.208b;c	0.925a;a	0.586ab;b	
		H	0.183a;d	0.324a;c	0.870a;a	0.528b;b	
	6	L	0.173a;b	0.163a;b	0.525a;a	0.428a;a	
		M	0.173a;c	0.115a;c	0.497a;a	0.251b;b	
	12	H	0.181a;b	0.172a;b	0.449a;a	0.186b;b	
		L	0.229a;c	1.210b;a	0.529a;b	0.221a;c	
		M	0.230a;c	1.513b;a	0.406b;b	0.097a;d	
		H	0.257a;b	1.623a;a	0.348b;b	0.144a;c	

Data are the means of four replications. Means with the same first letter in a column and second letter in a row within element and time in weeks are not significantly different at $\alpha = 0.05$.

10 weeks, the trends varied. At the end of composting, 75% and 122% of initial exchangeable As was contained in kitchen and garden waste composts, respectively. Sawhney et al. (1996) reported that leaching of arsenic (more than 20% of the initial arsenic content of compost) was much higher than leaching of cadmium, chromium, nickel and lead amounting to about 3% of the total initial content. Leaching of arsenic declined rapidly with time before reaching a baseline, indicating that initial leaching was of water soluble salts or exchangeable ions. In our experiment, regarding samples from summer uptake, the initial and final exchangeable As contents were the highest among seasons caused by the high total content of As in used feedstock. Low aeration rates were sufficient to reduce As exchangeable content.

The exchangeable content of chromium gradually decreased during composting. A more significant drop in Cr was recorded in the case of kitchen waste by 34%, 47% and 56% after 2, 6 and 12 weeks, respectively. This compared to garden waste by 18%, 29% and 35% after the same period. Substantial decreases in exchangeable Cr were found during composting of garden bio-waste from winter although the initial composting mix contained the highest amount of exchangeable Cr among seasons. It is interesting that bio-waste from winter contained the lowest content of total Cr among the seasons. In many cases, increased aeration intensity failed to decrease exchangeable Cr content significantly, but a decreased trend of Cr is visible. The trend could be explained by the higher formation of stable metal-humus complexes under intensive aeration rates.

A decrease of exchangeable nickel showed an opposite trend from chromium between composting of kitchen and garden waste. Significant differences in exchangeable Ni were often found during composting of garden bio-waste from summer and autumn, and then from spring and winter. High aeration intensity was required

Table 3
Mean exchangeable content of elements extractable with 0.11 mol L⁻¹ CH₃COOH (mg kg⁻¹ of dry matter) in composting mix during composting under low (L), medium (M) and high (H) aeration of garden waste, collected seasonally (mean value was obtained from 4 samples).

Element	Weeks	Aeration	Spring	Summer	Autumn	Winter	
As (mg kg ⁻¹)	0	Mix	0.738b	1.115a	1.437a	0.595b	
		L	0.497a;b	1.122a;a	1.121a;a	0.243a;c	
		M	0.466a;b	1.003a;a	0.567b;b	0.289a;c	
	2	H	0.482a;b	1.230a;a	0.263b;c	0.330a;c	
		L	0.247a;c	1.727a;a	0.164a;d	0.826a;b	
		M	0.144a;c	1.409b;a	0.140a;c	0.885a;b	
	6	H	0.240a;c	1.799a;a	0.242a;c	0.693a;b	
		L	0.798a;b	1.926b;a	0.618b;b	0.727a;b	
		M	0.822a;b	1.972b;a	0.841ab;b	0.932a;b	
	12	H	0.554b;d	2.517a;a	1.130a;b	0.864a;c	
		Mix	0.284ab	0.118c	0.249b	0.326a	
		L	0.110a;c	0.200a;b	0.313a;a	0.103a;c	
Cr (mg kg ⁻¹)	0	M	0.088a;c	0.171a;b	0.250ab;a	0.144a;b	
		H	0.094a;b	0.172a;a	0.207b;a	0.134a;b	
		L	0.082a;b	0.188a;a	0.144a;a	0.091a;b	
	6	M	0.069a;c	0.220a;a	0.117a;b	0.104a;b	
		H	0.074a;c	0.215a;a	0.137a;b	0.106a;bc	
		L	0.165a;a	0.121a;b	0.163a;a	0.106a;b	
	12	M	0.144a;ab	0.133a;b	0.186a;a	0.083a;c	
		H	0.153a;b	0.114a;c	0.198a;a	0.101a;c	
		Mix	0.502c	0.989a	0.988ab	0.761b	
	Ni (mg kg ⁻¹)	0	L	0.130a;b	0.649a;a	0.772a;a	0.653a;a
			M	0.160a;c	0.728a;a	0.574b;b	0.580a;b
			H	0.144a;c	0.726a;a	0.561b;b	0.593a;b
6		L	0.139a;c	0.603a;a	0.455a;b	0.399a;b	
		M	0.122a;c	0.714a;a	0.548a;b	0.417a;b	
		H	0.101a;c	0.646a;a	0.489a;b	0.367a;b	
12		L	0.209a;b	0.347a;a	0.397a;a	0.193a;b	
		M	0.180a;b	0.345a;a	0.398a;a	0.256a;b	
		H	0.242a;b	0.410a;a	0.510a;a	0.282a;b	

Data are the means of four replications. Means with the same first letter in a column and second letter in a row within element and time in weeks are not significantly different at $\alpha = 0.05$.

Table 4
Spearman linear correlation coefficients *R* between main parameters and exchangeable form of elements, during 12 weeks composting of kitchen waste.

Kitchen waste composting	As	Cr	Ni
<i>Low aeration</i>			
Weight of total fresh mass	-0.03	0.29*	0.19
Weight of total dry mass	-0.16	-0.18	-0.19
pH	-0.14	0.10	-0.23
Volatile solids	0.25	0.12	0.39**
N	-0.46**	0.02	-0.21
C:N	0.39**	0.02	0.31*
Humic acids	-0.22	0.90**	-0.28
<i>Medium aeration</i>			
Weight of total fresh mass	-0.18	0.17	0.26
Weight of total dry mass	-0.15	0.02	-0.12
pH	-0.31*	-0.18	-0.35*
Volatile solids	0.47**	0.23	0.15
N	-0.34*	0.00	-0.16
C:N	0.38**	0.10	0.22
Humic acids	0.51*	0.80**	0.39
<i>High aeration</i>			
Weight of total fresh mass	-0.07	0.23	0.27
Weight of total dry mass	-0.26	-0.04	-0.15
pH	-0.21	-0.02	-0.29*
Volatile solids	0.39**	0.36*	0.42**
N	-0.35*	-0.02	-0.08
C:N	0.38**	0.09	0.16
Humic acids	-0.47	0.82**	-0.19

* Different at the significance level $\alpha = 0.05$.

** Different at the significance level $\alpha = 0.01$.

Table 5
Spearman linear correlation coefficients *R* between main parameters and exchangeable form of elements, during 12 weeks composting of garden waste.

Garden waste composting	As	Cr	Ni
<i>Low aeration</i>			
Weight of total fresh mass	-0.18	0.26	0.49**
Weight of total dry mass	-0.29*	-0.24	-0.18
pH	0.41**	0.21	0.18
Volatile solids	-0.32	0.31	0.41*
N	0.04	-0.27	-0.73**
C:N	-0.19	0.32*	0.68**
Humic acids	-0.17	0.82**	0.14
<i>Medium aeration</i>			
Weight of total fresh mass	-0.41**	0.17	0.47**
Weight of total dry mass	-0.52**	-0.29*	-0.27
pH	0.55**	0.33**	0.37**
Volatile solids	-0.37**	0.19	0.27
N	0.27	-0.23	-0.51**
C:N	-0.39**	0.21	0.46**
Humic acids	0.36	0.32	0.12
<i>High aeration</i>			
Weight of total fresh mass	-0.34*	0.19	0.41**
Weight of total dry mass	-0.51**	-0.24	-0.27
pH	0.56**	0.37**	0.53**
Volatile solids	-0.31*	0.11	0.25
N	0.26	-0.42**	-0.48**
C:N	-0.40**	0.33*	0.45**
Humic acids	0.39	0.01	0.27

* Different at the significance level $\alpha = 0.05$.

** Different at the significance level $\alpha = 0.01$.

3.3. Relationships between available elements and other parameters

for a marked decline of Ni, only in kitchen waste mixtures. Low aeration proved sufficient for the composting of garden waste.

Prediction of risk element availability during composting is affected by many factors (Tables 4 and 5). Arsenic showed a good

Table 6

Total concentration of As, Cr and Ni (in mg kg⁻¹) in the mixture at the beginning and end of composting under low (L), medium (M) and high (H) aeration intensity in every season.

Type of waste	Element	Time	Spring	Summer	Autumn	Winter
Kitchen	As (mg kg ⁻¹)	Beginning	11.0 ± 1.4	17.2 ± 1.6	13.9 ± 1.0	7.7 ± 0.9
		End – L	15.6 ± 2.2	4.9 ± 0.6	13.1 ± 1.9	3.0 ± 0.5
		End – M	12.6 ± 6.8	7.4 ± 2.3	13.0 ± 2.3	5.0 ± 0.7
		End – H	6.2 ± 0.7	7.7 ± 4.9	11.5 ± 0.6	3.0 ± 0.3
Garden	As (mg kg ⁻¹)	Beginning	11.0 ± 0.5	21.1 ± 2.7	9.3 ± 0.5	15.8 ± 1.6
		End – L	8.5 ± 0.5	1.9 ± 0.5	5.5 ± 1.6	3.4 ± 0.5
		End – M	8.5 ± 0.8	2.6 ± 0.5	3.4 ± 0.6	3.3 ± 0.3
		End – H	16.4 ± 1.6	3.5 ± 0.8	17.7 ± 1.4	3.2 ± 0.4
Kitchen	Cr (mg kg ⁻¹)	Beginning	12.0 ± 0.1	9.8 ± 0.2	8.0 ± 0.1	3.9 ± 0.0
		End – L	21.5 ± 2.1	8.1 ± 0.3	12.4 ± 0.7	10.1 ± 1.1
		End – M	26.6 ± 2.2	10.2 ± 1.8	13.6 ± 1.0	9.6 ± 1.7
		End – H	27.3 ± 1.5	10.9 ± 1.8	12.9 ± 0.6	8.1 ± 0.7
Garden	Cr (mg kg ⁻¹)	Beginning	11.6 ± 0.5	18.0 ± 0.2	9.4 ± 0.1	6.3 ± 0.0
		End – L	17.4 ± 1.2	12.7 ± 2.0	14.4 ± 1.8	11.2 ± 2.4
		End – M	18.8 ± 1.9	15.1 ± 1.3	13.7 ± 2.9	9.8 ± 0.1
		End – H	20.3 ± 2.9	17.9 ± 1.8	15.5 ± 0.8	10.0 ± 0.8
Kitchen	Ni (mg kg ⁻¹)	Beginning	4.8 ± 0.1	5.1 ± 0.0	3.9 ± 0.2	2.4 ± 0.0
		End – L	10.3 ± 0.9	4.2 ± 0.1	7.5 ± 1.5	5.7 ± 0.3
		End – M	12.0 ± 1.2	5.4 ± 1.2	7.7 ± 1.2	5.1 ± 0.5
		End – H	12.5 ± 0.1	5.7 ± 2.0	7.7 ± 1.2	4.9 ± 1.0
Garden	Ni (mg kg ⁻¹)	Beginning	4.8 ± 0.2	7.8 ± 0.1	4.7 ± 0.1	3.4 ± 0.0
		End – L	8.9 ± 0.4	4.5 ± 0.7	6.5 ± 0.4	5.9 ± 0.8
		End – M	9.3 ± 1.4	5.7 ± 0.6	6.4 ± 0.8	6.1 ± 0.7
		End – H	9.0 ± 1.0	7.7 ± 0.5	6.4 ± 0.1	6.2 ± 0.5

± Standard deviation among 4 up-taken samples.

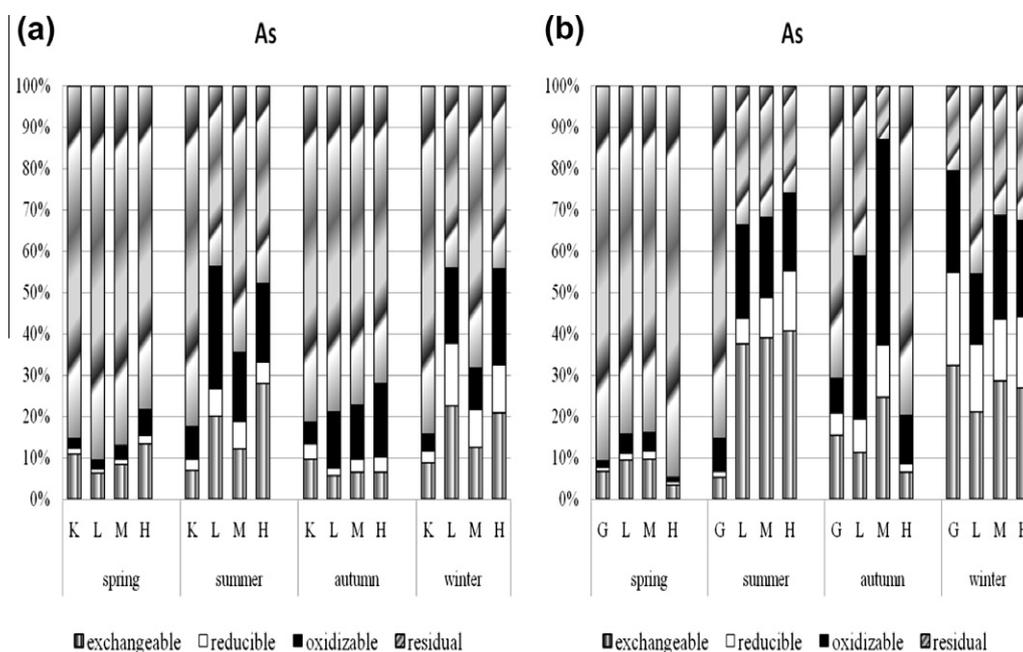


Fig. 4. Fluctuation of As in % of total content among fractions in kitchen waste (a) and garden waste (b) mixtures at the beginning (K or G) and after 12 weeks of composting under low (L), medium (M) and high (H) aeration intensity in every season.

correlation between the increase of total nitrogen and the decrease of As during composting of kitchen waste under all aerations. On the other hand, the C:N rate increased the availability of As. A decrease in the total weight of dry mass during composting indirectly correlated with available As, but only garden waste mixtures. Gradually increased pH positively affected availability during composting of that material, dependent on the aeration rate. In the case of kitchen waste with stable composition, a negative but non-significant relationship was found. Opposing trend in pH and exchangeable As content between composting of kitchen and gar-

den waste may be explained by their different pH values. Taking into consideration the composition of kitchen waste, the pH of kitchen waste was lower (5.6) than garden waste (5.9). Yet in spite of that fact, final kitchen waste compost achieved higher pH values. It might be speculated that extremely low and high pH could increase the mobility of As by a reduction of As^{V+} on As^{III+}.

Exchangeable chromium in kitchen waste mixtures presented a very close positive correlation with humic acids. This fraction of Cr seems to have a high affinity for newly formed humic acids during the composting of that material.

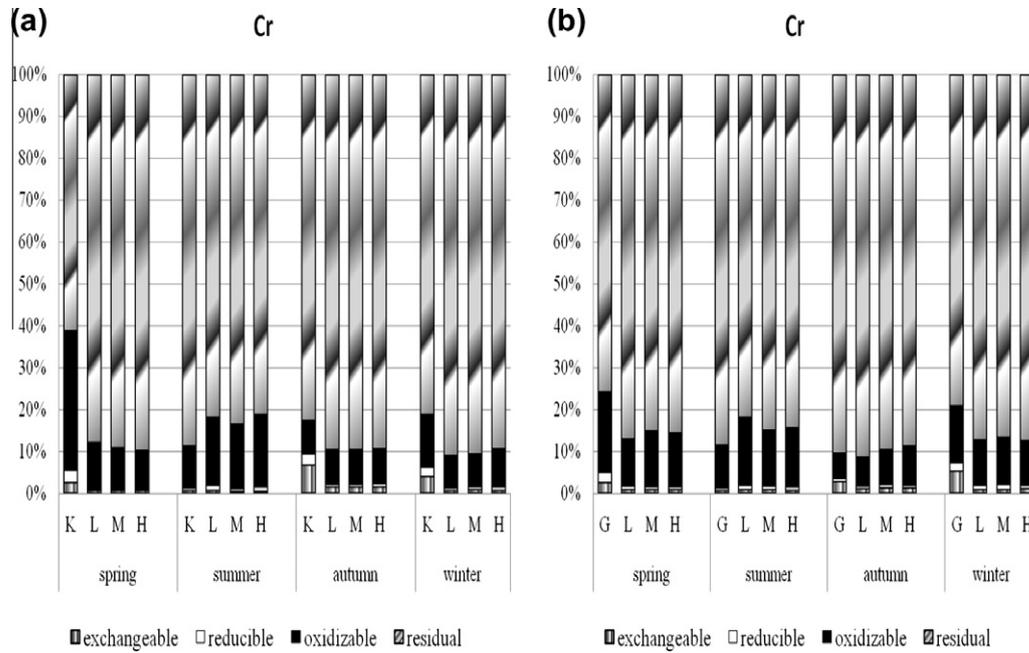


Fig. 5. Fluctuation of Cr in% of total content among fractions in kitchen (a) and garden waste (b) mixtures at the beginning (K or G) and after 12 weeks of composting under low (L), medium (M) and high (H) aerated intensity in every season.

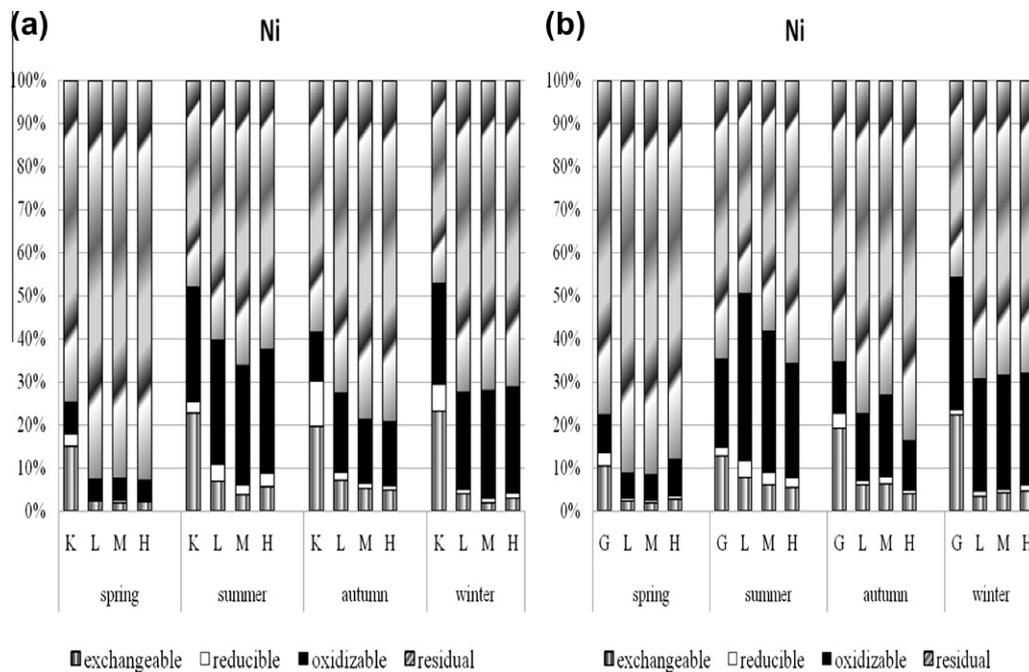


Fig. 6. Fluctuation of Ni in% of total content among fractions in kitchen (a) and garden waste (b) mixtures at the beginning (K or G) and after 12 weeks of composting under low (L), medium (M) and high (H) aerated intensity in every season.

Different compositions and characteristics of the original bio-waste affected the relationship between available nickel and pH. Kitchen waste showed a negative correlation during the composting and garden waste proved positive. This apparent contradiction may be explained by the course of pH and exchangeable Ni content. A remarkable increase in pH was achieved in the first 2 weeks of composting. Over the next 10 weeks, pH almost leveled off. Values of pH decreased after six weeks in the case of garden waste collected in spring. Further, the exchangeable content of Ni increased after only 2 weeks during the composting of kitchen

waste from autumn and winter. Amir et al. (2005) reported that mobile Ni increased with declining pH and organic matter content during sewage sludge composting. Negative correlations were found between nitrogen and exchangeable Ni contents during garden waste composting. These correlations were significant, unlike the correlations related to the composting of kitchen waste. This was caused by an increase in nitrogen content during composting of both bio-wastes and a decrease in exchangeable Ni content. The decrease was more obvious in the case of garden waste compared to kitchen waste composting. As it is evident from Table 5, negative

correlations between N and exchangeable Ni content were closely related to positive correlation between C:N and Ni content.

3.4. Total contents of elements

The total content of Cr and Ni increased at the end of composting as shown in Table 6. This would be expected from a loss of organic matter during the composting process, due to the release of carbon dioxide and other volatile molecules such that the metals become more concentrated (Hanc et al., 2009). The weight of total dry mass decreased during the composting of kitchen and garden waste by 48% and 37%, respectively. The highest total contents of Cr and Ni were found in initial mixtures and final composts from spring and summer. That corresponded with the content of elements in the original bio-waste from these seasons. Higher aeration rates increased the total content of Cr and Ni.

In the case of As, there were no significant differences between the composting of kitchen and garden waste. The issue of sample heterogeneity must be considered because the standard deviations were very high, almost 50%. The highest values among seasons were found in summer months, probably caused by high As content in soil as an important component of used bio-waste. In a majority of cases, all aeration levels used were able to decrease the total content of As. Losses of volatile arsine, methylarsine, dimethylarsine and trimethylarsine were observed during anaerobic incubation of sewage sludge (Michalke et al., 2000). Although the experimental conditions and/or analyzed material did not fully correspond to our experiment, losses of volatile compounds during composting must be taken into account. Recently, Diaz-Bone et al. (2011) studied the biotransformation of arsenic during composting. Time resolved investigation revealed a highly dynamic process during self-heated composting of plant material where extraordinary high concentrations of up to 150 mg kg⁻¹ methylated arsenic species as well as conversion rates up to 50% for arsenic were observed. They concluded that because of the high mobility of methylated species this process needs to be considered in organic waste treatment of arsenic contaminated waste materials.

3.5. Portion of individual fractions of elements

Unlike the absolute exchangeable As content, a lower percentage of exchangeable As (Fig. 4a and b) was found in kitchen waste (9.1%) than garden waste (14.9%) mixtures. These percentage increased by the end of 12 weeks composting to 13.5–21.5%, respectively. The reducible and oxidizable fractions in the initial mixture were about 3% to 10% and increased to a doubled range of 6–20%. However, the majority portion was made up of residual fractions; an initial 83.4% and 66.8% in the kitchen and garden waste mixture, respectively, which dropped to 66.4% and 49.8%. This was mainly evident during the spring season.

For Cr (Fig. 5a and b), a relatively low 3% was found for exchangeable fractions of bio-waste mixture at the start of composting, and this number dropped to about 0.9% by the completion of the process. A residual fraction of Cr, some 87% persisted in the final compost, which is in agreement with the composting of sewage sludge (Liu et al., 2007; Jakubus and Czekala, 2010). The reducible fraction decreased from 1.9% to 0.8%. This may be caused by reduction of Cr(VI) to Cr(III) by microorganisms, followed by the combination of Cr(III) with decomposed organic materials (Wang, 2000). There were no substantial differences found in the behavior of Cr during composting of kitchen and garden waste at three aeration levels.

Some authors recognized Ni (Fig. 6a and b) as a potentially mobile and water-soluble element and that the labile pool in compost could be relatively easily solubilized by mild extractants (Tisdell and Breslin, 1995). In our experiment, exchangeable fractions

constituted 20% and 16% in initial kitchen and garden waste mixtures, respectively. Composting decreased these portions 5 times in the case of kitchen waste and 3.5 times in the case of garden waste. Greater percentages of Ni in composts were associated with the oxidizable fraction, which may have been due to nickel's affinity for organics. The majority of Ni was found in the residual fraction and was slightly increased by composting, from 57% to 76% and from 63% to 74% in samples from kitchen and garden waste, respectively. Similarly, Alvarenga et al. (2007) found a majority of Ni in the residual fraction of garden waste compost. Zheng et al. (2007) applied sequential extraction to investigate the changes in Ni and Cr fractions in sewage sludge treated by forced-aeration composting. Ni and Cr concentrations increased by 30.4% and 36.0%, respectively, during the composting process, with H₂O and CO₂ volatilization being a major contributor to the change. It was found that the exchangeable, carbonate-bound, Fe–Mn oxide-bound, and organic matter-bound Ni and Cr were transformed to residual fractions. Composting appeared to reduce Ni and Cr mobility by stabilizing the two metals and thereby making them less mobile, comparable to our findings.

4. Conclusions

It was proven that composting is a suitable method for reducing available chromium, nickel and total arsenic contained in household bio-waste originating from both urban densities and separately collected over four seasons. The order of fractions in the final compost was as follows: residual > oxidizable > exchangeable > reducible. The portion of Cr and Ni in exchangeable fractions decreased after composting more than 3- and 4-fold, respectively. For low exchangeable content of risk elements in compost originated in household bio-waste, the final product could be suitable for remediation of contaminated soil.

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