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## Changes in cadmium mobility during composting and after soil application

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## ABSTRACT

The effect of twelve weeks of composting on the mobility and bioavailability of cadmium in six composts containing sewage sludge, wood chips and grass was studied, along with the cadmium immobilization capacity of compost. Two different soils were used and Cd accumulation measured in above-ground oat biomass (*Avena sativa* L.). Increasing pH appears to be an important cause of the observed decreases in available cadmium through the composting process. A pot experiment was performed with two different amounts of compost (9.6 and 28.8 g per kg of soil) added into Fluvisol with total Cd 0.255 mg kg<sup>-1</sup>, and contaminated Cambisol with total Cd 6.16 mg kg<sup>-1</sup>. Decrease of extractable Cd (0.01 mol l<sup>-1</sup> CaCl<sub>2</sub>) was found in both soils after compost application. The higher amount of compost immobilized an exchangeable portion of Cd (0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH extractable) in contaminated Cambisol unlike in light Fluvisol. The addition of a low amount of compost decreased the content of Cd in associated above-ground oat biomass grown in both soils, while a high amount of compost decreased the Cd content in oats only in the Cambisol.

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## 1. Introduction

A major limitation of soil application of compost can be the heavy metal contents and their bioavailability to the soil-plant system (Amir et al., 2005). Sewage sludge can serve as important source of heavy metals in many composts. Ciba et al. (2003) reported that increased total heavy metal contents in compost do not necessarily mean that its application as fertilizers contributes a direct hazard to the soil. The determination of total heavy metal content does not provide sufficient information about the risks of bioavailability, the capacity for remobilization and the behavior of the metals in the environment (Hsu and Lo, 2001). Metals can be present in compost and soil in various fractions, from soluble in water to the fractions practically inaccessible to plants.

Cadmium is one of the most toxic elements in the food chain (McLaughlin et al., 1999), and it is one of the most mobile heavy metals in soil. Compost can serve as strong immobilization agent as well. Compost can reduce cadmium availability in soil and can facilitate remediation of Cd contaminated soils because of high sorption capacity of organic matter (Coker, 2006). Similarly, Misra and Pandey (2005) observed in laboratory batch experiments the effective immobilization of Cd in non-humus soil amended with humus soil. As summarized by Bolan and Duraisamy (2003) the addition of organic amendments can increase the complexation of Cd in soil resulting in a decrease of the phytoavailability of metals. Especially in manure-amended soils, a large portion of Cd in soil solution is complexed with dissolved organic carbon. Moreover

the application of sewage sludge to the contaminated soil can decrease the toxic effect of Cd to soil microbial activity (Moreno et al., 2002). The knowledge of the mobility of Cd in compost and soil and its subsequent transfer to plants is very important for a decision making about the application of compost into soils of various physico-chemical properties. Puschenreiter et al. (2005) reviewed that organic amendments like farmyard manure reduce the transfer of metals into crops. Materials containing organic matter are available in large amounts and incorporation into soil is easy, if the contamination is restricted to topsoil. However, repeated application may be necessary and the effectiveness is largely dependent on soil conditions and has to be proved periodically.

In our previous studies, we tested the effect of lime, limestone, bentonite and zeolite as ameliorative materials (Hanc et al., 2006), and the effect on Cd mobility of poultry manure and composts as organic materials (Hanc et al., 2008). One of the most effective stabilizers found was compost. Therefore the current study was implemented to investigate: (i) extractability of cadmium from composts of different composition containing sewage sludge, wood chips and grass during twelve weeks of intensive composting; (ii) cadmium immobilization capacity of compost and bioavailability of Cd in two different soils after compost application and Cd accumulation in associated above-ground oat biomass (*Avena sativa* L.).

## 2. Materials and methods

## 2.1. Composting experiment

Anaerobically stabilized sewage sludges (I and II) from two different waste water treatment plants were tested. Sewage sludge II

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**Table 1**  
Content of cadmium in components (mg kg<sup>-1</sup> of dry matter).

Component	Cd extracted with 0.01 mol l <sup>-1</sup> CaCl <sub>2</sub>	Cd extracted with 0.11 mol l <sup>-1</sup> CH <sub>3</sub> COOH	Total Cd content after HF + HNO <sub>3</sub> digestion
Sewage sludge I (S I)	0.013	0.041	4.0
Sewage sludge II (S II)	0.019	0.018	7.0
Wood chips I <sup>a</sup> (W I)	0.003	0.011	0.1
Wood chips II <sup>b</sup> (W II)	0.003	0.028	0.5
Grass (G)	0.007	0.016	0.2

Detection limits represented 0.001 mg kg<sup>-1</sup> Cd.

<sup>a</sup> From deciduous trees and were finely cut (<10 mm).

<sup>b</sup> From coniferous trees and were cut in larger pieces (<50 mm).

**Table 2**  
Design of experiment and chosen characteristics of individual treatments.

Treatment	Weight portion of components in raw compost (f. m.)	Peak temperature (°C)	Initial C/N (d. m.)	Final C/N (d. m.)	Initial total Cd (mg kg <sup>-1</sup> f. m.)	Initial total Cd (mg kg <sup>-1</sup> d. m.)	Final total Cd (mg kg <sup>-1</sup> d. m.)
1	S I (1/3) + W I (1/3) + G (1/3)	64.5	21.3	12.3	0.45	1.00	1.51
2	S I (1/3) + W II (1/3) + G (1/3)	57.5	17.7	13.6	0.31	0.78	1.61
3	S II (1/2) + W I (1/4) + G (1/4)	53.5	18.1	15.1	0.62	1.81	2.62
4	S II (1/2) + W II (1/4) + G (1/4)	53	13.7	13.3	0.48	1.59	2.65
5	S I (1/2) + W I (1/2)	54	28.7	14.4	0.71	1.24	1.56
6	G (6/7) + W I (1/7)	64	17.3	13.2	0.24	0.85	0.22

d. m. = Dry matter.

f. m. = Fresh matter.

Initial = at the beginning of experiment.

Final = after 12 weeks of composting.

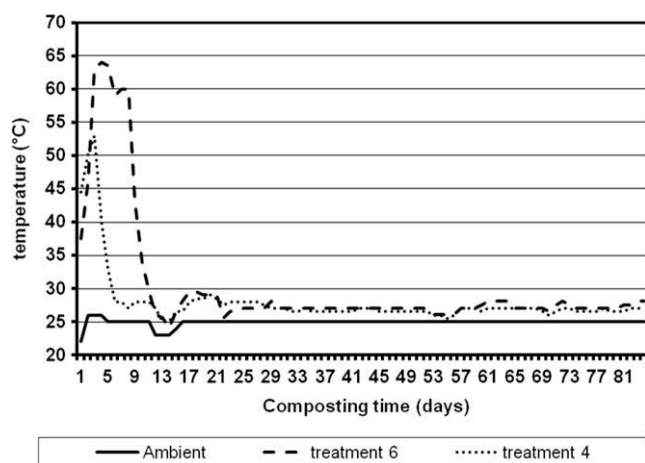
**Table 3**  
Physico-chemical parameters of soils.

Soil	pH/CaCl <sub>2</sub>	C <sub>org.</sub> %	P <sub>MIII</sub> <sup>*</sup> mg kg <sup>-1</sup>	K <sub>MIII</sub> <sup>*</sup> mg kg <sup>-1</sup>	Cd <sub>tot</sub> mg kg <sup>-1</sup>	Cu <sub>tot</sub> mg kg <sup>-1</sup>	Pb <sub>tot</sub> mg kg <sup>-1</sup>	Zn <sub>tot</sub> mg kg <sup>-1</sup>
Fluvisol	5.5	0.57	384	158	0.255	5.62	10.8	50.0
Cambisol	6.2	1.7	51.3	188	6.16	35.7	1022	228

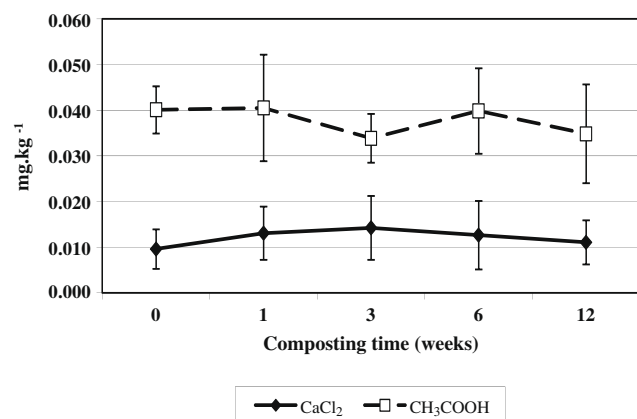
\* MIII = Mehlich III extraction.

originated from a town with majority of metal industry and therefore it contained higher amount of risk elements. Sewage sludge I (S I) passed through thermophilic stabilization unlike psychrophilic one in the case of sewage sludge II (S II). Wood chips I (W I) were obtained from deciduous trees and were finely cut (<10 mm). Wood chips II (W II) were from coniferous trees and were cut in larger pieces (<50 mm). The grass (G) originated from an intensively cultivated lawn. The individual components differed

in Cd content (Table 1). Thoroughly mixed materials were composted in aerated fermenters with air supply at the rate of 240 liters per hour. The composition of individual composts was selected to provide C:N ratios from 13 to 30. No water was added during composting. Incidental leachate was put back into compost before sampling. The composition and chosen characteristics of individual treatments are shown in Table 2. The samples were collected at the beginning, after 1, 3, 6 and 12 weeks (at the end) of composting



**Fig. 1.** Temperature throughout the composting process for treatment 6 (maximum for all treatments) and treatment 4 (minimum for all treatments).



**Fig. 2.** Fluctuation of Cd content extractable with 0.01 mol l<sup>-1</sup> CaCl<sub>2</sub> and with 0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH during composting (average of treatments).

process. They were dried at constant temperature (22 °C) and ground.

2.2. Pot experiment

The composts for the pot experiment were sampled from the fermenters at the end of the incubation experiment. Soil was passed through a 5 mm sieve and air-dried. Physico-chemical parameters of the soils are described in Table 3. Five kilogram of each soil (based on dry weight) was thoroughly mixed with N, P, K applied as ammonium nitrate (200 mg kg<sup>-1</sup> N) and potassium hydrogen phosphate (32 mg kg<sup>-1</sup> P and 80 mg kg<sup>-1</sup> K) in control treatments and with the same amount of nutrients plus composts from the experiment described above at the amount of 48 g and triple amount of 144 g per pot and placed into plastic pots. All

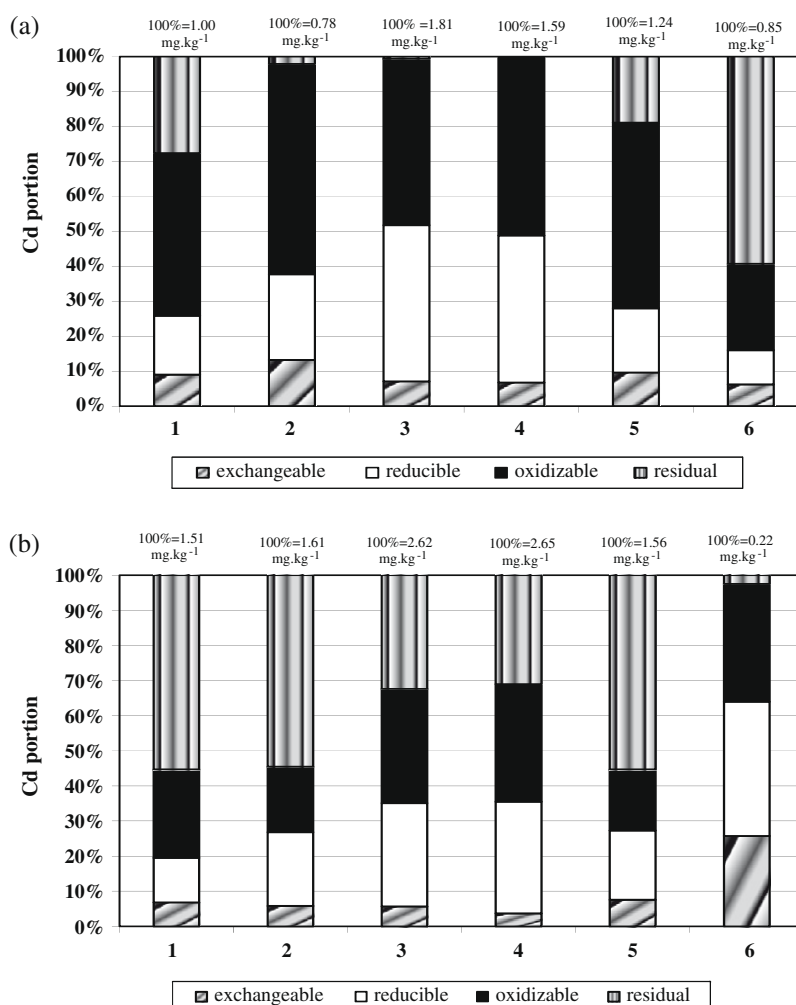
treatments were set up in three replications. Oat (*Avena sativa* L., cv. Atego) was sown in the soil. Twenty plants were left in each pot after germination and grown to wax maturity. Soil moisture was regularly controlled and kept at 60% of its maximum water holding capacity. Demineralized water was used for irrigation. After harvest, soil samples were taken up, above-ground biomass was checked for fresh and dry biomass, ground and analyzed.

2.3. Analytical methods

Values of pH were measured in a 1:20 (w/v) 0.01 mol l<sup>-1</sup> CaCl<sub>2</sub> soluble extract at 20 ± 1 °C by WTW pH 340 i set. The dry matter content was assessed by drying at 105 °C for 24 h. Organic carbon was determined by dichromate oxidation in sulfuric acid solution (Sims and Haby, 1971) and organic nitrogen by the Kjeldahl meth-

**Table 4**  
pH and Cd content extractable with 0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH (mg kg<sup>-1</sup> of dry matter) in 6 treatments of composts during 12 weeks of composting.

Treatments	Beginning		1st week		3rd week		6th week		12th week	
	pH	Cd	pH	Cd	pH	Cd	pH	Cd	pH	Cd
1	6.15	0.038	6.36	0.035	6.63	0.035	6.98	0.035	7.06	0.035
2	6.25	0.056	6.57	0.036	6.65	0.040	6.91	0.040	7.07	0.042
3	6.18	0.021	6.27	0.058	6.35	0.030	6.59	0.078	7.02	0.058
4	6.24	0.032	6.43	0.035	6.51	0.026	6.55	0.031	6.82	0.012
5	6.53	0.058	6.59	0.058	6.45	0.055	6.76	0.040	6.96	0.048
6	6.12	0.035	6.77	0.021	7.21	0.017	7.60	0.015	8.47	0.014



**Fig. 3.** The distribution of Cd into four fractions in six composts at the beginning (a) and at the end (b) of composting process.

od (Bremner, 1960). The available portion of P and K in soil after harvest was determined in the extract of Mehlich III (Mehlich, 1984). Contents of phosphorus in soil extracts were determined colorimetrically using the SKALAR SAN<sup>PLUS</sup> SYSTEM<sup>®</sup> and potassium contents were determined by flame atomic absorption spectrometry (F-AAS, VARIAN SpectrAA-300). Available portions of Cd in compost and soil were determined in 1:10 (w/v) 0.01 mol l<sup>-1</sup> CaCl<sub>2</sub> (Novozamsky et al., 1993) and in 1:20 (w/v) 0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH (Ure et al., 1993). A sequential extraction procedure was applied for assessment of cadmium bound to individual soil fractions and exchangeable (0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH extractable), reducible (0.1 mol l<sup>-1</sup> NH<sub>2</sub>OH.HCl extractable), oxidizable (8.8 mol l<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> followed by 1 mol l<sup>-1</sup> CH<sub>3</sub>COONH<sub>4</sub> extractable), and residual fraction (Ure et al., 1993) where the nomenclature of the fractions was adopted according to Bacon and Davidson (2008). Plant material was combusted in an APION dry mode mineralizer (Miholova et al., 1993). Concentrations of cadmium were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN VistaPro, Varian, Australia). Blank samples represented 15% of the total number of digests, detection limit was calculated as mean + triple standard deviation of blanks.

Detection limits represented 0.001 mg kg<sup>-1</sup> Cd. For quality assurance of the analytical data certified reference material “NCS DC 73350 Poplar leaves” was used.

2.4. Statistical analyses

Data were evaluated by a one-way analysis of variance ANOVA. Tukey's test was used for means comparison, and the statistical significance of hypotheses was assessed at  $\alpha = 0.05$ . All statistical analyses were performed using Statgraphics programme, version 5.1 (Manugistics, 1997).

3. Results and discussion

3.1. Composting process

The maximum and minimum temperature profiles measured during the composting are presented in Fig. 1. Larger differences among treatments were found at the beginning of the experiment. There was a very fast transfer from mesophilic to thermophilic stage. The maximum average temperature was reached after one

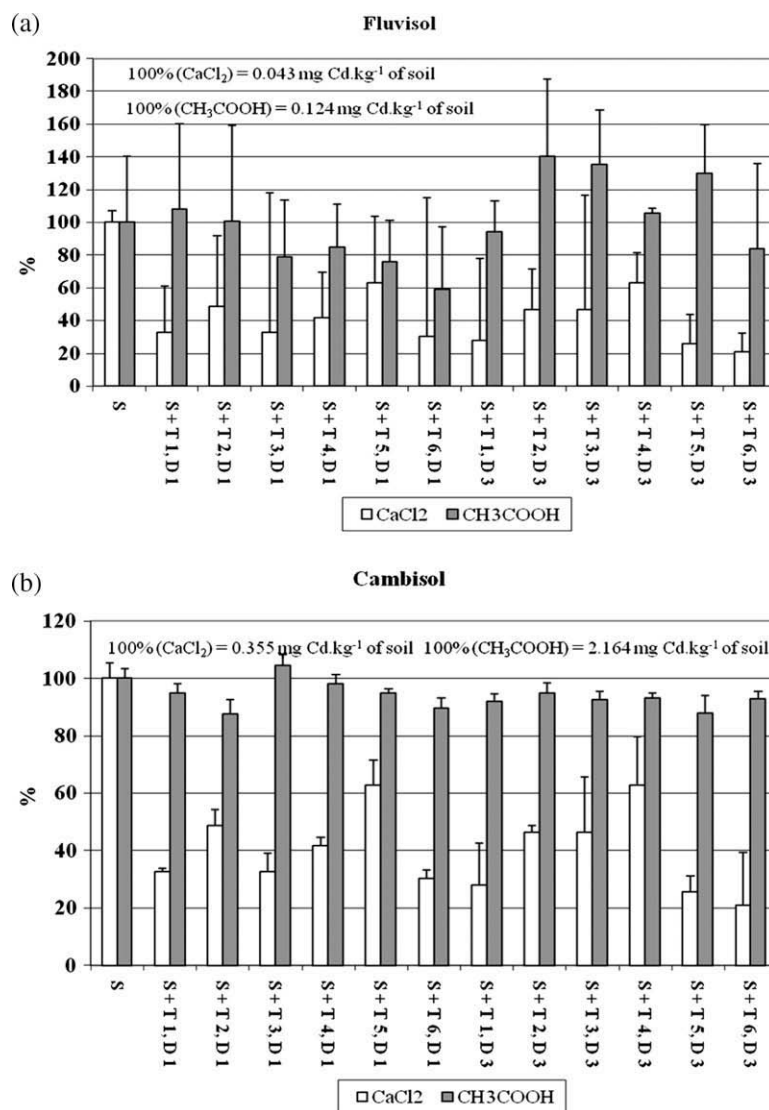


Fig. 4. Relative Cd content extractable with 0.01 mol l<sup>-1</sup> CaCl<sub>2</sub> and 0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH in Fluvisol (a) and Cambisol (b) amended with composts (whisker represents standard deviation of 3 replications within treatment) (S = soil, T = treatment of compost, D = dose).

week because of intensive aeration (an average of 57 °C), and a rapid decline of temperature followed. The most readily biodegradable matter was bioconverted, the microbial activity became less intense, causing the decrease of the temperature. After one month the average temperature tended towards ambient one. The addition of grass caused the highest increase and subsequent decrease of the temperature because of easily biodegradable material. The occasional drops in temperature were caused by opening of biofermenters for mixing and sampling.

One of the most important factors affecting the composting process and availability of cadmium is pH as already discussed in previous investigation (Hanc et al., 2006). In this experiment, uniformly increased pH were found between the initial and final values given in Table 2. The average pH value was 6.2 and 7.2 at the beginning and at the end of composting process, respectively. The lowest pH value was found in compost derived from sewage sludge II and the highest value in compost with a predominant portion of grass. Sewage sludge was anaerobically incubated before composting in contrast to grass and it would be speculated that they contain humic substances with buffering capacity for pH as observed by Amir et al. (2005).

A decreasing trend of organic carbon content during the composting process was found (Table 2). The biggest decrease of organic carbon was found in treatment 2 (70% of initial value). Total nitrogen portion increased in most cases during the composting process because of degradation of organic material and CO<sub>2</sub> escape. Aerobic conditions led to oxidation of mineralized N compounds to nitrate, causing accumulation in compost.

The initial ratio of C/N ranged between 14 and 29 and gradually decreased to 12–15. This decrease was mainly caused by sewage sludge with low C/N ratios.

Total contents of cadmium increased by 58% at the end of the composting process compared to the beginning (Table 2). This was caused by a decrease of organic matter and total mass of compost. The average content of cadmium extracted with 0.01 mol l<sup>-1</sup>

CaCl<sub>2</sub> ranged from 0.010 to 0.014 mg kg<sup>-1</sup> (Fig. 2) confirming low portion of the most mobile Cd in the composts.

The concentration of cadmium extracted by 0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH was found to be approximately 3 times higher than by CaCl<sub>2</sub> (Fig. 2). Diluted acetic acid is characterized as an extractant releasing exchangeable, water and acid soluble element fractions (Miller et al., 1986). Therefore, one would expect that it extracts more than the plant-available portion of elements in soil. The highest initial Cd content (1.81 mg kg<sup>-1</sup> of dry matter) was in compost derived from sewage sludge II (treatment 3). The exchangeable portion of Cd tended to decrease in concentration during the composting process in response to the increase of pH as documented in Table 4.

Fig. 3 illustrates that most of the Cd was found in the oxidizable fraction at the beginning of composting (52% in an average of five treatments of total amount). The portion decreased by half at the end of the process. The greatest decrease was found in compost with sewage sludge I, wood chips II and grass. The cadmium portion in exchangeable and reducible fractions decreased during incubation of composts with sewage sludge portion as well (by 35% and 22%, respectively). The decrease of Cd in the exchangeable fraction can be due to increasing pH during the composting process (from 6.2 at the beginning to 7.2 at the end). The behavior of cadmium in treatment six where only grass and wood chips were applied was unique, most likely caused by heterogeneity of the mixture and too low a content of Cd. Grass is easy degradable material and Cd could have been released into solution which occurred in this treatment. Although the C:N ratio varied among treatments, there was no clear indication that these differences influenced Cd mobility.

### 3.2. Soils

The Cd availability in soil fertilized by composts differed depending on soil parameters and extracting agents used.

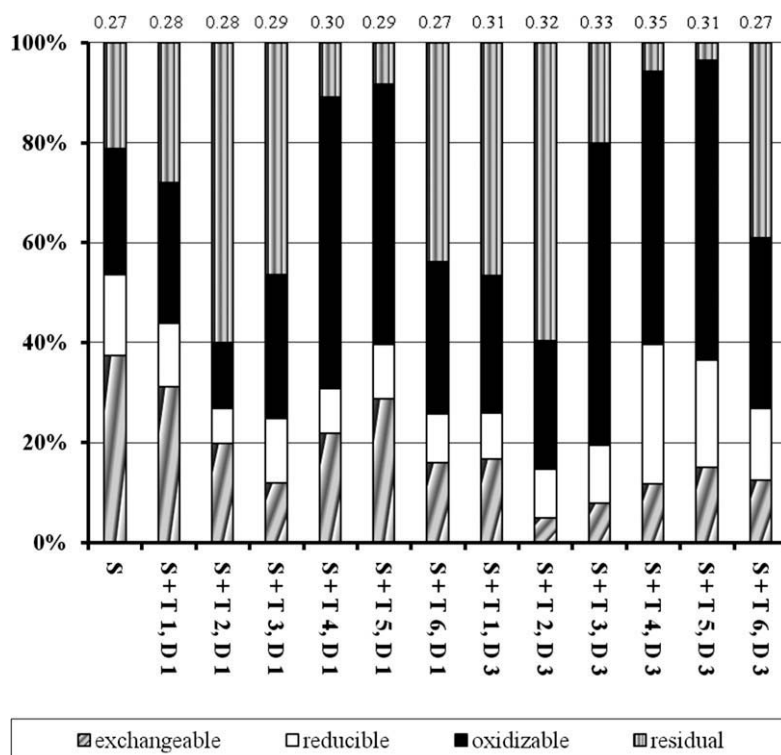


Fig. 5. Distribution of Cd in Fluvisol after composts application (total Cd content in mg kg<sup>-1</sup> is above bars) (S = soil, T = treatment of compost, D = dose).

Cadmium extractable with 0.01 mol l<sup>-1</sup> CaCl<sub>2</sub> significantly decreased after application of all treatments of composts in Fluvisol (Fig. 4a) and Cambisol (Fig. 4b). The strongest decrease of Cd content was found in Fluvisol amended with triple amount of treatment 6 (0.009 mg Cd.kg<sup>-1</sup>). Decrease of Cd extracted in 0.01 mol l<sup>-1</sup> CaCl<sub>2</sub> was generally found in Cambisol (Fig. 4b) after the triple amount of compost compared to control soil (by 40–50%) and the simple compost rate (by 20–30%). This is consistent with Perez-de-Mora et al. (2006) who found a decline of Cd released with the same extracting agent in their experiment with heavy metals contaminated soil, especially in the first two years after compost application. In our experiment, the application of a triple amount of compost with sewage sludge I and wood chips I (treatment 5) significantly decreased the available Cd (0.01 mol l<sup>-1</sup> CaCl<sub>2</sub>) content in Cambisol (0.193 mg Cd kg<sup>-1</sup>) compared to a single rate of application of the same compost (0.262 mg Cd kg<sup>-1</sup>). The other differences among single and triple treatments were generally not statistically significant because of high standard deviations among the samples.

Different behavior of cadmium extracted with 0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH was found. Cadmium was apparently released from

the oxidizable fraction after the triple amount of compost application into Fluvisol. The effect was caused by higher mineralization of composts in the sandy Fluvisol. Due to the organic matter oxidation, Cd can be released into more available portions. No statistical differences were found in Cd extracted with 0.11 mol l<sup>-1</sup> CH<sub>3</sub>COOH among treatments in Cambisol containing higher amount of organic matter and higher pH value compared to Fluvisol. A 6% lower content of exchangeable Cd was found in Cambisol amended with composts (average of all treatments) compared to the control. Standard deviations among replications within the treatment were markedly less in Cambisol than in Fluvisol due to the higher Cd content in Cambisol.

Because of the visible effect of individual treatments on cadmium mobility in sandy Fluvisol, a sequential extraction procedure was applied in this case to assess in more detail the changes in cadmium among individual soil fractions. Distribution of individual cadmium fractions in Fluvisol fertilized with composts is presented in Fig. 5. The highest exchangeable Cd portion (38%) was found in Fluvisol without compost fertilization. Addition of all six types of composts decreased the portion of this fraction in soil. The highest decrease was found in soil after application of treatments 2 and 3.

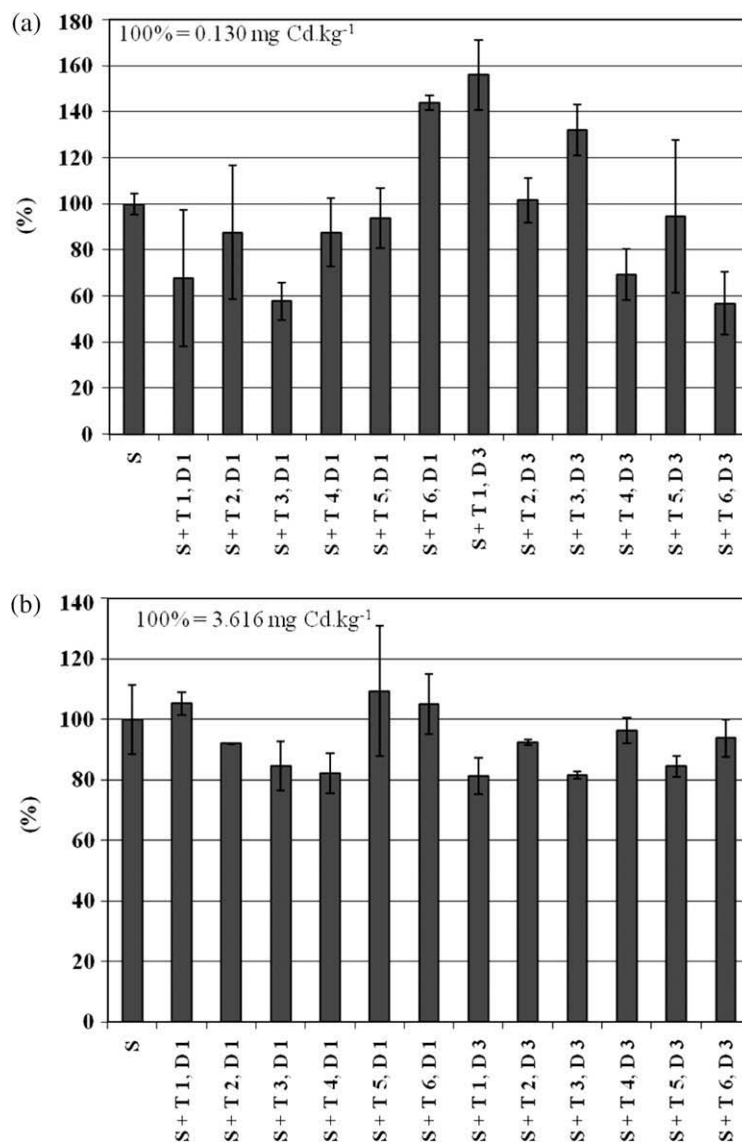


Fig. 6. Relative content of Cd in above-ground biomass grown on Fluvisol (a) and Cambisol (b) after composts application (whisker represents standard deviation of 3 replications within treatment) (S = soil, T = treatment of compost, D = dose).

The triple amount of compost decreased the exchangeable Cd portion by 47% and 69% compared to the lower amount and control group, respectively. Kim and McBride (2006) showed that the addition of sewage sludge to the soils with high organic matter content (between 3.6% and 4.9%) resulted in increased labile Cd fraction suggesting that Cd can persist in labile forms in spite of the previous stabilization of the sludge. Similar findings were published by Sloan et al. (1997) in a long-term experiment 15 years after the application of biosolids. The increasing mobile portions of Cd ( $0.005 \text{ mol l}^{-1}$  extractable) with increasing sludge application rate was described, as well (Wong et al., 2001).

Reducible fractions made up the smallest portion of all fractions (12% in an average soil fertilized with composts), although 25% of the total content was found in the compost (Fig. 5). The highest Cd portion in the oxidizable fraction was found after application of composts containing mostly sewage sludge (treatments 4 and 5). The high portion of organically bound Cd in soil fertilized with compost was caused by the addition of stabilized organic matter into the soil and by cadmium sorption by soil organic matter as seen by Shuman et al. (2001). Cadmium in the residual fraction is generally considered permanently bound in the crystal lattice and so not capable of entering the food cycle under normal conditions (Ciba et al., 2003). The highest Cd portion in the residual fraction (60%) was found in soil after the application of compost made of sewage sludge I, wood chips II and grass (treatment 2) in both triple and single rates. Application of all composts into Fluvisol decreased the fraction of exchangeable cadmium.

### 3.3. Plants

The content of Cd in oat grown on Fluvisol (Fig. 6a) varied more than in oat grown on Cambisol (Fig. 6b). This could have been caused by lower pH, lower content of clay and organic matter, and also by higher relative heterogeneity of the composts with relatively high content of Cd in uncontaminated Fluvisol. The differences among Cd content in oat grown on Cambisol were not significant and that was consistent with low Cd mobility through higher sorption capacity. We can only speculate that cadmium derived from compost was immobilized in organic matter after compost addition and it was not transferred to plants, similar to work published by Li et al. (2000), Shuman et al. (2001) and Businelli et al. (1996). Addition of a triple rate of compost into Cambisol decreased Cd content in the above-ground biomass by 12% in an average.

## 4. Conclusion

It can be concluded that availability of cadmium was decreased at the end of the composting process. This trend was supported by increases of pH and probably development of stable high molecular organic matter. The cadmium availability in soil amended with compost differed depending on soil properties and extracting agents. Immobilization of the easily extractable Cd was evident in both soil types after compost application. The higher amount of compost increased the content of available Cd in light Fluvisol and it correlated with high amount of Cd in oat biomass caused with easy degradability of compost at aerated Fluvisol. Both amounts of compost application decreased Cd content in oat biomass grown on Cambisol in consequence of Cd availability decrease in this soil type. Detailed study of compost effect on cadmium mobility in soils of various properties and uptake of other plants will be necessary in further research.

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