Direct and subsequent effect of compost and poultry manure on the bioavailability of cadmium and copper and their uptake by oat biomass

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ABSTRACT

Direct and subsequent influence of added organic materials on changes of cadmium and copper bioavailability in soil and their accumulation in aboveground oat (*Avena sativa* L.) biomass was studied in a three-year experiment. Mineral NPK, poultry manure and two types of composts were used as fertilizers. The average portion of available cadmium and copper from their total content in soil in all treatments was 0.94% and 0.25%, respectively. After application of poultry manure the concentration of available Cd increased during experimental years, contrary to Cu. The Cd uptake increased proportionally with available Cd content in soil almost in all treatments during experimental years (correlation coefficient $R = 0.54$; $P < 0.05$). The Cu uptake was however different than Cd uptake, mainly in the second and third year. The lowest uptake of Cu was found in the first experimental year and was in close positive correlation with yields of dry biomass.

Keywords: compost; soil; cadmium; copper; availability; oat

Sewage sludge, sewage sludge compost and green waste compost are alternative amendments to traditional manures. Poultry manures are mostly uniform in physical appearance and rich in fibre, ammonia nitrogen and moisture (Georgakakis and Krintas 2000). Composting and the application of compost and sewage sludge to the soil follow the principles of recycling and sustainability and present a potential way to avoid disposal to landfill (Petersen et al. 2003). Compost has a positive effect on physical, chemical, and biological soil parameters. However, besides favourable substances (e.g. macronutrients) composts may be a potential source of contaminants of different origin.

Previous research has shown that the chemical form of a heavy metal is important in determining compost quality, because it determines the metal availability for plant uptake or leachability into the groundwater (Chwastowska and Skalmowski 1997). Sorption of heavy metals depends on pH value, clay content, organic matter, Al, Fe, Mn oxides and complexation with ligands (Chuan et al. 1996, Hanč et al. 2006).

Among toxic heavy metals, cadmium is one of the most dangerous for human health. Cadmium is an irritant to the respiratory tract and exposure to this pollutant can lead to anaemia, renal damage, or osseous disease with effects similar to osteoporosis. Cd is a very toxic element for plants and animals and no essential biological functions were found until now (Alloway 1990, Corami et al. 2008). Cadmium may enter agricultural soils through atmospheric deposition and through the use of phosphate fertilizers and sewage sludge (Nicholson et al. 2003). Copper belongs to the least mobile heavy metal. Complexation reactions involving soil organic matter, and especially its more active humified components, i.e., humic acids and

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Table 1. Weight portion of feedstock in raw compost (in % dm)

Compost I	(%)	Compost II	(%)
Sewage sludge	52	wood chips	25–30
Poultry manure	21	grass	25–30
Straw	27	leaves	10–27
		vegetable waste	10–20
		tobacco	4–8

fulvic acids, play a key role in the speciation of Cu in soil controlling its physico-chemical behavior, biological availability, accumulation and mobility (Plaza et al. 2005).

The objective of this study was to evaluate direct as well as subsequent influences of composts and poultry manure addition on the changes of bioavailability of cadmium and copper in soil and to investigate the uptake and translocation of these elements into the aboveground oat biomass during three years.

MATERIAL AND METHODS

Bioavailability and uptake of cadmium and copper were investigated in a pot experiment with Luvisol [pH_{KCl} = 6.4, C_{org} = 1.71%, 139 mg available P/kg, 225 mg available K/kg, (P and K was determined in the extract of Mehlich 3; Mehlich 1984), 0.26 mg total Cd/kg and 20.7 mg total Cu/kg] amended by organic materials (poultry manure, compost I and compost II). The composition of individual composts was mainly optimized according to the rate of C:N ratio. Compost I contained sewage sludge, wheat straw and poultry manure. Compost II was produced from green waste biomass; their composition is shown in Table 1. The contents of some elements in composts and in their components are shown in Table 2.

Soil was air-dried, passed through a 5 mm sieve, and 5 kg of soil (based on dry weight) was thoroughly mixed with organic materials and fertilized with major nutrients in the form of NH_4NO_3, K_2HPO_4, KCl and H_3PO_4 in the first year of experiment. Treatments were set up in four replications. The rates of the organic materials were calculated to apply 1.5 g N/pot. This amount corresponds to approximately 70 tons of fresh material per hectare. In the treatment with mineral fertilizer (control) the following amounts were applied: 1.5 g N, 0.921 g P and 1.817 g K/pot. The input of nutrients in organic and mineral forms at the beginning of experiment is presented in Table 3.

The rate of 0.75 g of N as NH_4NO_3 was added into each pot in the second and the third year. After the incorporation of different organic materials

Table 2. The total contents of chosen metals (mg/kg) and major nutrients (%) in composts and in their components (in dry matter)

Sample	Cd (mg/kg)	Cu (mg/kg)	N (%)	P (%)	K (%)
Poultry manure	0.232	47.70	5.48	1.18	1.81
Straw	0.102	5.61	1.29	1.48	1.20
Sewage sludge	3.760	326.00	3.50	2.39	0.53
Compost I	3.120	193.00	3.00	1.84	1.29
Compost II	1.950	48.50	2.33	0.55	2.83

Table 3. The input of nutrients in organic and mineral forms into soil of the pot experiment (g/pot)

Treatment	N		P		K	
	organic	mineral	organic	mineral	organic	mineral
NPK	0.0	1.5	0.00	0.92	0.00	1.82
Poultry manure	1.5	0.0	0.33	0.60	0.50	1.32
Compost I	1.5	0.0	0.92	0.00	0.65	1.17
Compost II	1.5	0.0	0.36	0.56	1.82	0.00

the soil was placed into plastic pots and sown with oat (*Avena sativa* L., cv. Zlatak). After emergence oat plants were thinned to 20 plants per pot and grown up to harvest. Soil moisture was regularly controlled and kept at 60% of its maximal water holding capacity. After the harvest of oats, soil samples were taken and the soil was stored in the pots after slow air-drying and used again in the second and third years of experiment.

The total concentrations of trace elements in the soils were determined in the digests obtained by the following two-step decomposition procedure. Exactly 0.5 g of a sample was decomposed by dry ashing in Apion Dry Mode Mineralizer. The ash was then decomposed in a mixture of HNO_3 and HF, evaporated to dryness at 160°C and dissolved in diluted *Aqua regia* (Száková et al. 1999b). A certified reference material RM 7001 Light Sandy Soil was applied for the quality assurance of analytical data.

The available share of Cd and Cu in soil after harvest was extracted with 1 mol/l NH_4NO_3 in the ratio 1:2.5 (w/v), which is able to release weakly bound elements in the soil correlating significantly with element uptake by plants (Száková et al. 1999a).

Plant material was decomposed by modified dry ashing procedure in the mixture of oxidizing gases by APION equipment (Miholová et al. 1993). Contents of elements in soil and plant digests and soil extracts were determined by inductively coupled plasma optical emission spectrometry with axial plasma configuration (ICP-OES, VARIAN VistaPro, Varian, Australia). The quality of plant analyses was assessed by certified reference materials. For statistical evaluation of the analytical data the analysis of variance (Tukey $\alpha < 0.05$) by the Statgraphics programme, version 5.1 (Manugistics 1997) was applied.

RESULTS AND DISCUSSION

Application of individual fertilizers resulted in changes of soil pH (Figure 1). Compost and poultry manure application resulted in an increase of soil pH compared to control in the first vegetation period. Similar results were found by Ouédraogo et al. (2001). The increased pH in the soil fertilized with organic fertilizers can be explained by relatively high concentrations of ammonium nitrogen in these fertilizers. Subsequent decrease of pH in the following vegetation periods of our experiment was confirmed by Moreno et al. (1996) as well. The effect could be most likely determined by initial pH value of the soil and organic matter and soil buffering capacity. The highest pH value was found after addition of compost I (mainly sewage sludge with pH 8.0), whereas soil fertilized with mineral forms of nutrients had the lowest pH (Courtney and Mullen 2007). The use of alkaline fertilizers could be an advantage mainly in acidic soils, although high pH could also cause a reduction in the availability of some nutrients in other soils. Decreasing trend of pH level during three years of our experiment was apparently caused by

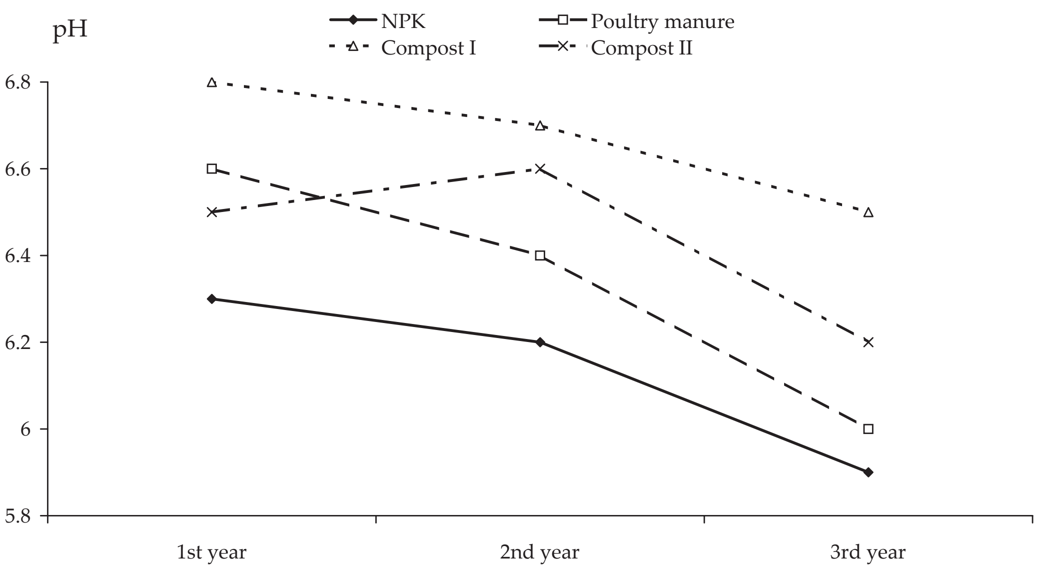

Figure 1. The changes of soil pH (0.01 mol/l $CaCl_2$) values in vegetation periods

mineralization of organic matter from compost as well as from root biomass.

Cadmium

The contents of available cadmium determined in 1 mol/l NH_4NO_3 are shown in Figure 2. The lowest available Cd content was found in soil treated with compost I although this material contained the highest level of total cadmium suggesting low mobility of Cd in the sewage sludge. Similarly, Chaudri et al. (2007) observed greater NH_4NO_3 extractable Cd in the liquid sludge and metal salt experiments than in the sludge cake ones. Compost II increased available Cd content in soil by 24% compared to the control treatment in the first year and this trend of increasing Cd availability continued in the following years. Application of poultry manure and compost I decreased available Cd content by 16% compared to control but total Cd content increased by 76% compared to control. It can be explained by Cd sorption on stabilized organic matter. In the second year the highest content of available element in soil with NPK was determined. Available Cd content decreased relatively by 60% at compost I treatment compared to NPK. By 136% more available Cd was found in soil treated with compost II compared to compost I; differences between these treatments were however not statistically significant. The weak Cd bounds in soil after compost II application caused an increase of available Cd fraction. The stability of organic matter of individual fertilizers plays an important role in Cd release into soil solution. The highest content of available Cd was measured in the case of NPK treatment in the third year (3.6 µg Cd/kg). Individual treatments did not statistically differ except for NPK and compost I. The average portion of available cadmium from the total content in soil was 0.94%. The highest value was found after NPK addition (1.23%) and the lowest after compost I application (0.56%). The available Cd portion in soil increased during three years after treatment of NPK and poultry manure, whereas it decreased after the application of both composts. It demonstrates that composts are suitable to reduce available Cd content in soil even if they contain higher amount of total cadmium compared to soil.

The cadmium uptake by aboveground plant biomass varied among treatments especially in the first year (Figure 3). The highest value was found at NPK treatment (6.2 µg Cd/pot). Poultry manure and compost I application decreased Cd uptake 3.5 times (1.7 µg per pot compared to the control), which was the lowest uptake obtained during three years. It was caused by low Cd content in plants. It can be claimed that an application of high-quality organic matter into soil decreases cadmium uptake by aboveground plant biomass. It is possible that Cd remained in the roots and was not translocated into the shoots. Roots possess a significant cation exchange capacity and this may form part of the mechanism of moving ions through the outer part of the root to the plasmalemma where active

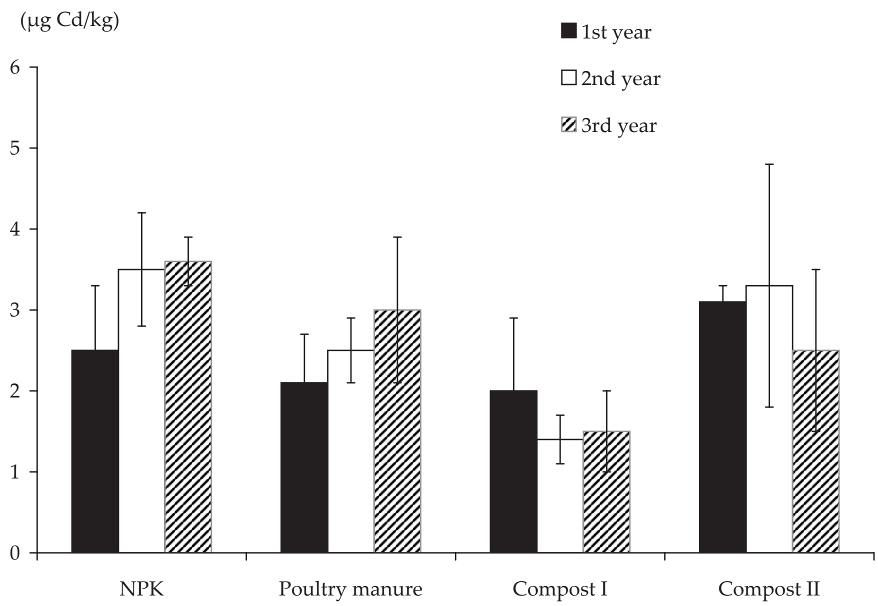

Figure 2. Content of soil available cadmium extracted by 1 mol/l NH_4NO_3

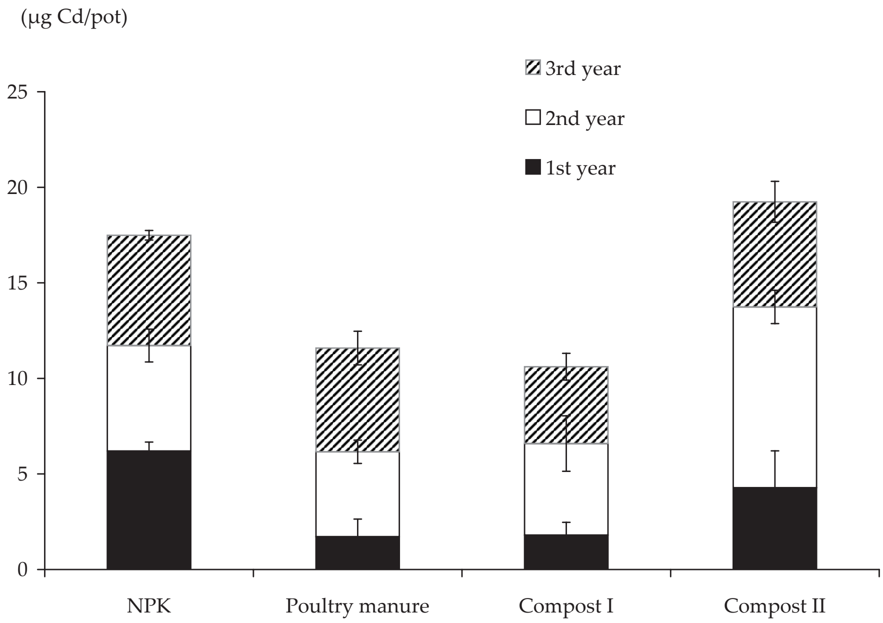

Figure 3. Uptake of cadmium by aboveground oat biomass within a three-year period

absorption occurs. Our results correspond with Tlustoš et al. (1997) who found a decrease of the cadmium content in oat biomass after manure application into the experimental soil. Similarly, Mench et al. (1998) described greater Cd concentrations in wheat grain from the NPK-fertilized plot than from the manure treated soil. The addition of organic materials into soil can build up Cd stable complexes which are not able to enter plant cells. These changes were not consistent with the changes in the amount of total Cd in soil; these changes were higher in manure-treated soil compared to soils with NPK fertilizers. Bartl et al. (2002) found that mineral fertilization increased Cd content in potato tubers unlike application of composted biowaste. The results of Shuman et al. (2002) showed that a decrease in phytotoxicity was attributed to redistribution of Cd from the water soluble and exchangeable fractions to the organic fraction, which decreased the plant availability and Cd uptake. The importance of soil physicochemical properties were documented by Chaudhuri et al. (2003) where the application of sewage sludge to acidic (pH 5.2) sandy soil with low cation exchange capacity resulted in a substantial increase of available cadmium portion. The Cd uptake at NPK treatment was decreased by 11% in the second year although the yield of biomass was higher than in the previous year. The uptake of Cd very closely (94%) correlated with Cd content in plant biomass. Application of compost II increased Cd uptake twice compared to NPK, which may be the result of high yield of biomass. It seems that relatively labile organic matter increases Cd uptake by plants (Moreno et al. 1996). No statistically significant differences were found among treatments in the third year. The lowest value was obtained in the treatment with compost I. Various contents of Cd in the used materials did not affect the uptake of Cd by aboveground biomass. Total Cd uptake by oat biomass at control NPK treatment was 1.3%, at poultry manure 0.8%, at compost I 0.7% and at compost II 1.3% from total Cd content in soil. Cadmium added with organic fertilizers was only little used by plants. There was a weak correlation ($R = 0.317$; $P < 0.05$) between Cd content in dry oat biomass and available Cd content in soil treated with organic fertilizers.

Copper

Poultry manure decreased the concentration of soil available copper during three vegetation periods contrasting thus with available cadmium. It was apparently caused by copper uptake by oat biomass, proceeding humification of supplied organic matter and creation of stabile Cu complexes with humus substances (McLaren and Clucas 2001). The same trend in Cu and Cd available contents was found in soil amended with compost I as well as compost II in every year. The highest available Cu content was found in the treatment with com-

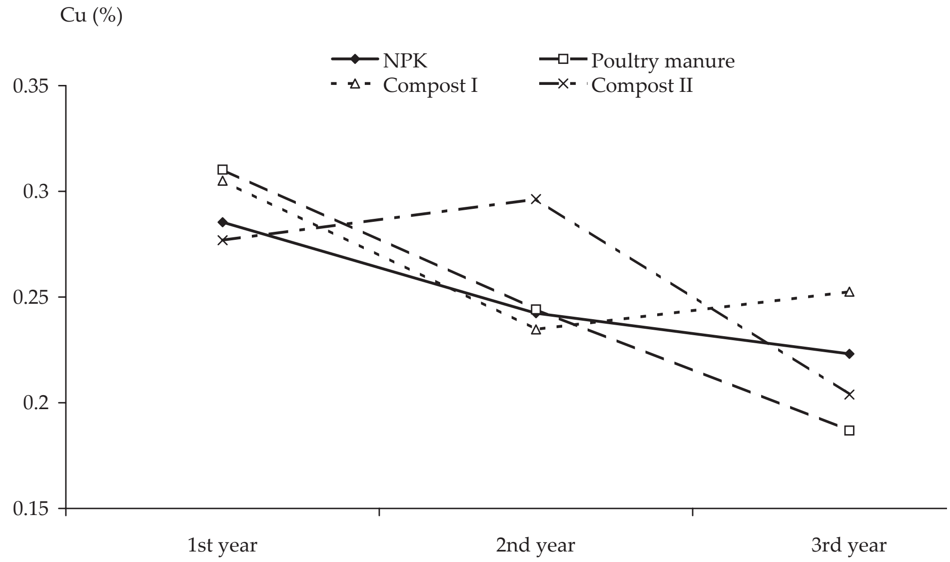

Figure 4. The changes of available copper portion from total copper content in soil during vegetation periods

post I in the first year (average value was 68 μg/kg). On the contrary, the lowest content of available Cu correlated with total Cu content in this material was found in soil with compost II. Vaca-Paulín et al. (2006) found an increased Cu sorption capacity and lower content of available copper in soil amended with composts compared to unfertilized soil. Evidently, composition and application rate of composts play an important role in the increase of Cu sorption. Lower contents of Cu were found in the second year of the treatments except in soil with compost II. Application of this material increased available Cu content in soil by 26.6% compared to the control NPK. In the last year the highest value (by 23.2% compared to the control) in soil with compost I was measured and it was higher than in the previous year. Compost I treatment statistically differed from poultry manure and compost II. The portion of available copper (0.25%) of the total content was lower (Figure 4) than in the case of cadmium. The predominant portion of copper is bound to relatively stable fraction represented by iron and manganese oxides and stable organic complexes (Zheljazkov and Warman 2004). There was a decreasing trend during the three years in all treatments. The most remarkable decrease was found after poultry manure addition (from 0.31 to 0.24%).

Figure 5 illustrates the average uptake of copper by the aboveground oat biomass. The uptake of Cu was different from uptake of Cd, mainly in the second and third years. The lowest uptake was found in the first experimental year. That was in close correlation with yields of dry biomass. The uptake of Cu did not increase with rising Cu concentration in soil in the first year of experiment. The highest uptake was reached at treatment with NPK (136.6 μg/pot). Poultry manure and compost II decreased Cu uptake by 54% and compost I by 73%. Although compost I contained four times more total Cu than compost II, Cu uptake by biomass was lower compared to compost II. It could be caused by Cu localization in roots at high level. In the second year Cu uptake increased and was in close correlation with yield of biomass again. Application of compost and poultry manure showed the opposite effect compared to Cd in the same year. The highest Cu uptake was found at poultry manure treatment (286.9 μg/pot). It was by 40% more compared to NPK. Compost I decreased the uptake of Cu by 7.8% compared to NPK but compost II increased it by 19.3%. The uptake of Cu decreased by more than half in the third year compared to the previous one. The uptake decreased at compost I treatment by 22% compared to NPK and it was the lowest among three studied years (66.9 μg/pot). The highest Cu uptake was found in soil treated with poultry manure (88.2 μg/pot). No significant differences were found among treatments of this year. The total uptake was the same (0.4%) at treatments with NPK and poultry manure. This parameter did not exceed 0.25% and 0.3% from total content of copper in soil at compost I and compost II treatments, respectively. It is obvious from the obtained results that plants took up only a small part of the total content of copper. It was substantially less than in the case of cadmium. It appeared that there

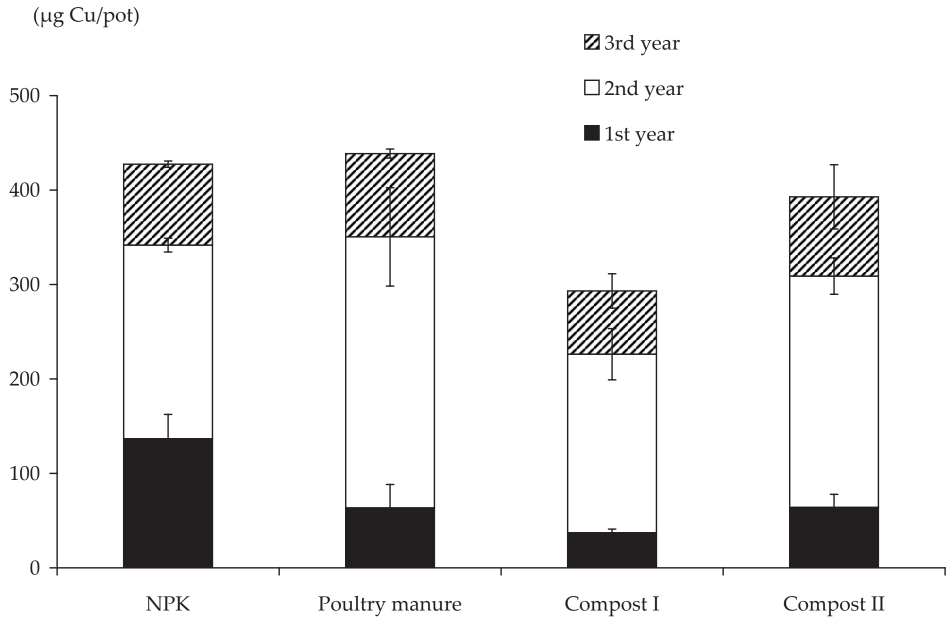

Figure 5. Uptake of copper by aboveground oat biomass within a three-year period

was no correlation (R = 0.08; P < 0.05) between the content of Cu in dry oat biomass and available Cu content in soil treated with organic fertilizers. Results suggest that organic fertilizers with high content of copper can be used safely into soil.

We can conclude that the application of various biosolids to the soil resulted in the decrease of both plant-available portion of Cd in soil and uptake of this element by oat biomass and this effect persisted during three subsequent vegetation periods. High affinity of copper to compost and sewage sludge matrices resulted in a low available copper fraction decreasing during composting process (McLaren and Clucas 2001). It is evident that a detailed study of long-term effect of biosolids on soil element mobility and plant availability will be necessary in further research.

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