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Bioavailability of Lead and Cadmium in Soils Artificially Contaminated with Smelter Fly Ash

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Abstract This study evaluated lead and cadmium uptake by maize grown on soils artificially spiked with smelter fly ash and possible changes in chemical fractionation of these metals in the soil. Maize grown on the less contaminated soil (1,466 mg Pb kg^{-1}; 19 mg Cd kg^{-1}) did not exhibit any chlorosis/necrosis symptoms or lower biomass yields compared to the control. The addition of the chelating agent ethylenediaminetetraacetic acid increased lead uptake by maize, as expected. Neither maize cultivation nor the addition of the chelant influenced significantly the chemical fractionation of lead and cadmium in the soil during the experiment.

Keywords Contamination · Smelter fly ash · Bioavailability · Metal

Air pollution control technologies in several metallurgical plants have not always been fully efficient. In such cases, a portion of the fly ash, substantially enriched in metallic contaminants, could escape from the smelter stacks and deposited in the nearby environments. Soils in the vicinity of the smelters can thus contain high concentrations of metallic elements (up to 10 g kg^{-1}; Ettler et al. 2005a; Sterckeman et al. 2002). Investigations of metal speciation and mobility in the fly ash and in soils affected by smelter emissions [including (bio)availability studies] are important for a better understanding of their biogeochemical cycling in such extreme environments (Ettler et al. 2005a, b, c; Sterckeman et al. 2002; Komárek et al. 2007a). It is generally accepted that lead (Pb) is one of the least mobile and bioavailable metals in soils. On the other hand, the high mobility of cadmium (Cd) in contaminated soils is well known. Nevertheless, there has also been evidence of a significant Pb pool present in the exchangeable fraction of some soils heavily contaminated by Pb-smelting industry (Ettler et al. 2005a). Therefore, Pb originating from fly ash, which can be present as highly soluble Pb chlorides (Ettler et al. 2005b), can pose a great risk to the environment (e.g., high mobility and bioavailability leading to toxicological risks). The aim of this study was to evaluate (1) maize (*Zea mays* L.) uptake of Pb and Cd from a soil spiked with fly ash originating from a flue gas treatment plant of a secondary Pb smelter and (2) the changes in chemical fractionation of Pb and Cd in the soil during maize cultivation.

Materials and Methods

Fly ash was sampled from the bottom of bag-type filters in a secondary Pb smelter located in Příbram, Czech Republic. The dissolution/decomposition of fly ash (0.1 g) was performed in teflon beakers (Savillex®, Minnetonka, USA) in a mixture of 1 ml HNO_3 and 5 ml HF on a hot plate at 150°C overnight. The concentrations of metallic elements were determined by atomic absorption spectrometry (AAS;

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Varian SpectrAA 280 FS, Australia) under standard analytical conditions. The contents of total inorganic carbon (TIC) and total sulphur (S) in solid residues were determined using Eltra CS500 and Eltra CS530 C/S analyzers (Neuss, Germany). The content of Cl in residue digests was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Spectro, Germany). The mineralogical composition of the fly ash was determined by X-ray diffraction analysis (XRD) using a PANanalytical X'Pert Pro diffractometer (conditions: Cu Ka radiation, 40 kV and 30 mA, 2theta range 5–80°, step 0.02, counting time of 300 s using a X'Celerator detector). The qualitative analysis of XRD patterns was performed using PANanalytical X'Pert HighScore software, version 1.0d (PANalytical, Netherlands) and ICDD PDF-2 database. The chemical and mineralogical compositions of the fly ash are given in Table 1.

The soil used for the experiment was an agriculturally used Gleyic Cambisol from the field experimental station of the Research Institute of Crop Production in Prague. The sampling site was located in Humpolec, Czech Republic. No important contamination source was present in the vicinity of the studied site. The following basic physicochemical soil characteristics were determined: pH (1:2.5 w/v ratio of soil and deionised water), organic C (C_{org}, catalytic oxidation), cation exchange capacity (CEC, sum of basic cations and Al extracted with 0.1 M $BaCl_2$), clay content (hydrometer method). The air-dried soil was sieved (10-mm) and homogenised with the fly ash: 4.98 kg of soil with 20 g and 4.90 kg of soil with 100 g of the fly ash (total of 5 kg) in order to obtain metal concentrations commonly found in smelter-affected soils. The soil was moisturised with deionised water to obtain a water holding capacity of approximately 60%. Maize (*Zea mays* L., cv. Rivaldo) was chosen for the pot experiment as the tested plant species because of its tolerance to toxic metals (uses in phytoextraction studies) and it represents a commonly cultivated crop in Central Europe (Komárek et al. 2007a). Ten seeds of maize were sown in each pot containing 5 kg of soil. After 2 weeks of growth, these were reduced to four plants per pot. The plants were fertilised with 1 g of N (NH_4NO_3); 0.16 g of P and 0.4 g of K (K_2HPO_4) per pot. The experiment was carried in an outdoor vegetation hall and plants were watered once a day using only deionised water in order to maintain approximately 60% of the water holding capacity. The chelant EDTA (ethylenediaminetetraacetic acid) at 2.5 mmol kg^{-1} was applied to maize plants after 70 days from sowing. Despite being criticised, chelating agents have been intensively investigated as mobilising agents used in phytoextraction studies (Schmidt 2003). EDTA was chosen for being highly efficient at enhancing Pb uptake into plants (Nowack et al. 2006; Komárek et al. 2007a). All treatments (control included) were conducted in triplicates.

Table 1 Selected chemical and mineralogical parameters of the fly ash

Chemical composition	Mean ± SD[a]
Pb (mg kg^{-1})	248 300 ± 18 200
Cd (mg kg^{-1})	4 460 ± 240
Na (mg kg^{-1})	204 810 ± 2 630
K (mg kg^{-1})	32 770 ± 770
S (%)	6.45 ± 0.01
TIC (%)	0.10 ± 0.01
Cl (%)	19.9 ± 0.4

Mineralogical composition

Phase	Formula	Relative abundance[b]
Caracolite	$Na_3Pb_2(SO_4)_3Cl$	Dominant
K-Pb chloride	$KCl \cdot 2PbCl_2$	Trace
Lead sulphite	$PbSO_3$	Trace
Galena	PbS	Trace
Phosgenite	$PbCl_2 \cdot PbCO_3$	Trace
Salts	$NaCl/Na_2SO_4$	Dominant

[a] n = 6 for Pb and Cd, n = 3 for other elements

[b] Estimated from XRD patterns

The above-ground biomass was harvested after 100 days (at full ripeness) from the beginning of the experiment, washed carefully using deionised water, dried at 60°C until constant weight and finely ground prior to decomposition. Plant samples were decomposed using the dry ashing procedure described by Miholová et al. (1993): An aliquot part of the plant samples was decomposed in a mixture of oxidising gases ($O_2 + O_3 + NO_x$) at 400°C for 10 h in Dry Mode Mineraliser Apion (Tessek, Czech Republic). The ash was then dissolved in 1.5% HNO_3. Metal concentrations in digests were determined using ICP-OES (Vista Pro, Varian, Australia). In order to evaluate the measurement precision and accuracy, the standard reference material DC73350 Leaves of Poplar (China National Analysis Centre for Iron and Steel, China) was used.

Pseudo total metal concentrations in soils were determined using the *aqua regia* dissolution (USEPA method 3051a) under microwave conditions (Ethos 1, Milestone, Italy). In order to obtain information about the chemical fractionation of Pb in the soil before and after the plant experiment, the modified BCR (Community Bureau of Reference, European Commission) sequential extraction procedure proposed by Rauret et al. (2000) was used and the following fractions were obtained: (1) exchangeable, (2) reducible, (3) oxidisable, (4) residual. Metal concentrations in digests were determined using ICP-OES. Results obtained from the sequential extraction procedure were controlled by the sum of all fractions compared to pseudo total concentrations (Rauret et al. 2000). The digestion procedure was evaluated by the certified reference material Light Sandy Soil 7002 (Analytica, Prague, Czech Republic). All the chemicals used were of analytical grade (Lachema, Czech Republic and Merck, Germany). All statistical analyses were performed using software Statistica 8.0 (StatSoft).

Results and Discussion

The basic physico-chemical characteristics of the studied soil together with Pb and Cd pseudo total concentrations before and after soil spiking with the fly ash are given in Table 2. The concentrations of approximately 1,500 mg Pb kg^{-1} in agricultural soils contaminated by the smelting industry are more realistic (Šichorová et al. 2004; Ettler et al. 2005a) than the much higher modelled concentration of 7,300 mg Pb kg^{-1}. Therefore, the results obtained from the lower fly ash treatment are more applicable to field conditions. *T*-test statistical analyses showed that the addition of the lower concentration (20 g fly ash per 5 kg soil) did not significantly influence biomass yields of maize ($t = 0.28$, $p = 0.79$); however, a consequent addition of 2.5 mmol EDTA kg^{-1} to this spiked soil negatively influenced the production of biomass ($t = 2.32$, $p = 0.04$; Table 3), which can be attributed to a higher concentration of mobilised toxic metals (especially Pb) and/or EDTA toxicity to plants (Vassil et al. 1998; Komárek et al. 2007a). A significant reduction of the biomass yields was observed for maize grown on the soil spiked with the higher concentration of the fly ash (100 g fly ash per 5 kg soil). The plants showed symptoms of chlorosis and necrosis and withered, producing only a negligible amount of biomass (Table 3). For this reason, EDTA was not added to this variant.

Table 2 Basic physico-chemical soil characteristics and pseudo total (*aqua regia*-extractable) Pb and Cd concentrations in the studied soil

pH_{H_2O}	5.7
CEC (mmol kg^{-1})	133
C_{org} (%)	2.9
Clay (%)	10.9
Pseudo total metal concentrations (mg kg^{-1}; n = 3)	Mean ± SD
Original soil	
Pb	39.7 ± 4.8
Cd	0.48 ± 0.03
20 g fly ash per 5 kg soil	
Pb	1 466 ± 38
Cd	18.6 ± 0.1
100 g fly ash per 5 kg soil	
Pb	7 331 ± 15
Cd	98.0 ± 10.6

The highest Cd and Pb concentration was observed in maize plants grown on soil treated with 100 g fly ash per 5 kg^{-1}. These extreme metal concentrations were associated with very low biomass yields and toxicity symptoms, as mentioned earlier (Table 3). In the case of the soil treated with 20 g fly ash 5 kg^{-1}, the application of EDTA increased significantly Pb concentrations in maize shoots (according to *t*-test analysis, $t = 2.47$, $p = 0.03$). This is in accordance with other works dealing with EDTA-assisted phytoextraction of Pb from soils as EDTA is a strong chelating agent with a high affinity to form complexes with Pb (Schmidt 2003). These complexes are not readily available for plants but are taken up via passive uptake mechanisms through the apoplasm (Nowack et al. 2006). On the other hand the statistically significant decrease of Cd concentrations in maize shoots after the EDTA application ($t = 2.25$, $p = 0.048$; Table 3) can be attributed to the ability of EDTA to complex free ions in the soil solution, including Cd^{2+}, making them less available. The fact that lower EDTA concentrations can decrease the bioavailability of free metals, according to the Free Ion Activity Model has already been demonstrated for Cu^{2+} and Zn^{2+} (which has a similar biogeochemical behaviour to Cd^{2+}; Nowack et al. 2006). Higher Cd contents in maize shoots without the application of EDTA is also consistent with the fact that dissolution of the fly ash induces the release of Cd ions which are readily forming

Table 3 Biomass yields, Pb and Cd concentrations in maize plants grown on fly ash-spiked soil (Mean ± SD; n = 3)

Treatment[a]	Biomass yield (g pot^{-1})	mg Cd kg^{-1}	mg Pb kg^{-1}
Control	79.1 ± 7.3	0.20 ± 0.04	1.37 ± 0.21
20 g fly ash	77.5 ± 11.4	45.6 ± 10.3	20.5 ± 4.0
20 g fly ash + EDTA	70.2 ± 4.6	31.4 ± 9.7	39.4 ± 16.6
100 g fly ash	4.9 ± 0.1	371 ± 47	655 ± 53
100 g fly ash + EDTA	NA	NA	NA

[a] Spikes and EDTA additions reported per 5 kg in each pot

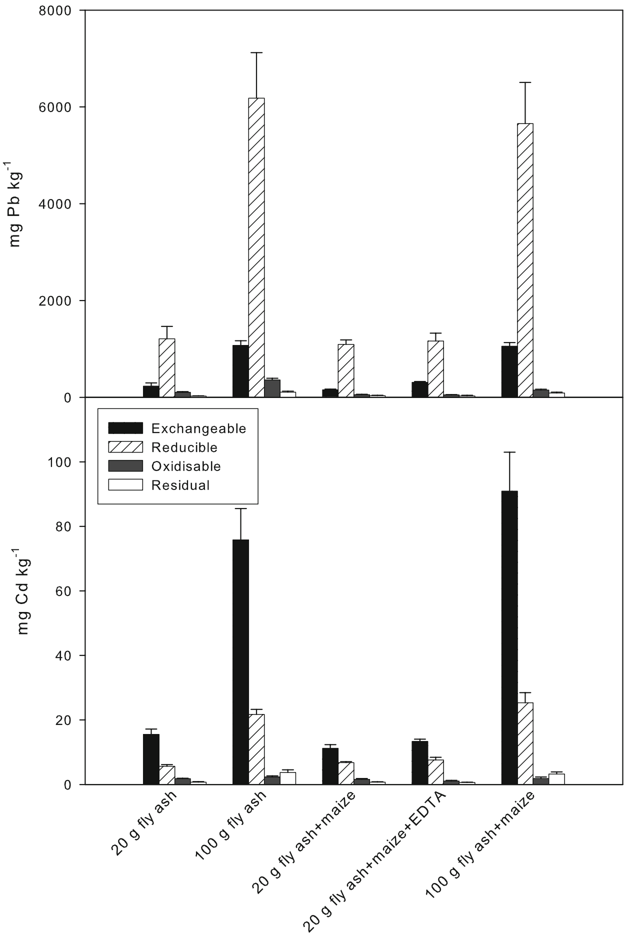

Fig. 1 Pb and Cd fractionation in the studied soil after the spiking with fly ash (spikes and EDTA additions reported per 5 kg in each pot; Mean ± SD; n = 3)

chlorocomplexes (Ettler et al. 2005c) that can be easily transported into the plant as shown by previous phytoextraction studies using chloride salts (Komárek et al. 2007b).

Results of the fractionation analysis are shown in Fig. 1. As fly ash phases are readily soluble (Ettler et al. 2005b, c), the metallic elements are probably quickly redistributed within the soil compartments showing the final chemical fractionation as observed in smelter-affected agricultural soils (e.g., Ettler et al. 2005a, Komárek et al. 2007a). While Cd was mainly present in the exchangeable fraction, which is in accordance with its high mobility in soils, a majority of Pb was associated mostly with the reducible soil fraction. The results suggest that neither the maize cropping nor the addition of EDTA influenced to a great extent the fractionation of Pb and Cd in the soil. However, the treatment 20 g fly ash + maize reflected the significantly lowest exchangeable concentrations of both metals (according to the Duncan test at $p < 0.05$). This can be explained by the fact that maize grown on the treated soil depleted the pool of readily available Cd and Pb via root uptake (Fig. 1; Table 3). Both Cd and Pb are released from easily soluble caracolite (Cd substitutes for Pb in its 6-fold coordination apatite-like structure of caracolite due to similar ionic radius, Ettler et al. 2005b) as observed during experimental leaching of the fly ash (Ettler et al. 2005b, c). The speciation in solution is dominated by chlorocomplexes (Ettler et al. 2005c) that are removed from the soil by maize as described by Komárek et al. (2007b). Slightly higher Pb concentrations in the exchangeable fraction obtained after the addition of EDTA are a result of Pb mobilisation by the chelating agent. The results obtained from the 100 g fly ash + maize treatment cannot be precisely interpreted due to the very poor growth of the maize plants. This study proved that high plant uptake of Cd and Pb originating from fly ash dissolution can be of high environmental and agricultural significance (Pichtel and Bradway 2008) and precautions (e.g., stabilisation methods) should be made to avoid contamination of agricultural crops grown in smelting areas.

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