



## Cadmium and Zn availability as affected by pH manipulation and its assessment by soil extraction, DGT and indicator plants

Iqbal Muhammad, Markus Puschenreiter\*, Walter W. Wenzel

BOKU, University of Natural Resources and Life Sciences, Vienna, Department of Forest and Soil Sciences, Konrad Lorenz Straße 24, A-3430 Tulln, Austria

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### ABSTRACT

Manipulation of soil pH by soil additives and / or rhizosphere processes may enhance the efficiency of metal phytoextraction. Here we report on the effect of nitric acid additions to four polluted soils on Cd and Zn concentrations in soil solution ( $C_{\text{soln}}$ ) and 0.005 M  $\text{Ca}(\text{NO}_3)_2$  extracts, and related changes in the diffusive fluxes and resupply of the metals as assessed by diffusive gradients in thin films (DGT). The responses of these chemical indicators of bioavailability were compared to metal uptake in two indicator plant species, common dandelion (*Taraxacum officinale* F.H. Wigg) and narrow leaf plantain (*Plantago lanceolata* L.) grown for 75 days in a pot experiment.

Lowering soil pH increased  $C_{\text{soln}}$ , the 0.005 M  $\text{Ca}(\text{NO}_3)_2$ -soluble fractions and the DGT-measured Cd and Zn concentrations ( $C_{\text{DGT}}$ ) in the experimental soils. This was associated with enhanced uptake of Cd and Zn on soils acidified to pH 4.5 whereas plants did not survive at pH 3.5. Toxicity along with decreased kinetics of metal resupply (calculated by the 2D DIFS model) in the strong acidification treatment suggests that moderate acidification is more appropriate to enhance the phytoextraction process.

Each of the chemical indicators of bioavailability predicted well ( $R^2 > 0.70$ ) the Cd and Zn concentrations in plantain shoots but due to metal toxicity not for dandelion. Concentration factors, i.e. the ratio between metal concentrations in shoots and in soil solution (CF) indicate that Cd and Zn uptake in plantain was not limited by diffusion which may explain that DGT did not perform better than  $C_{\text{soln}}$ . However, DGT is expected to predict plant uptake better in diffusion-limited conditions such as in the rhizosphere of metal-accumulating phytoextraction crops.

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### 1. Introduction

Cadmium and Zn share a similar geochemical behavior and often occur together as environmental pollutants in soils, sediments, plants and other endpoints (Adriano, 2001). Main pollution sources of both elements in soil include mining and smelter activities, urban and industrial wastes, and for Cd long-term fertilization of rock phosphate to agricultural soils (Adriano, 2001; McLaughlin et al., 1999).

Normal (background) concentrations in world soils are reported to range between 0.02 and 6.2 mg kg<sup>-1</sup> for Cd, and 1 and 900 mg kg<sup>-1</sup> for Zn (Adriano, 2001). Soils containing 5–20 mg Cd kg<sup>-1</sup> or 600–3000 mg Zn kg<sup>-1</sup> typically require remedial action as they are likely to pose a risk for the environment (Eikmann and Kloke, 1991).

Currently a number of technologies are available to remediate Cd/Zn-polluted soils. Engineering-based technologies are typically invasive, expensive, and may generate secondary wastes and additional risks to the environment (Wenzel et al., 1999). Phytoremediation has been considered as less expensive, virtually non-invasive and

environmentally-friendly alternative with high public acceptance. Among the various phytoremediation technologies, phytoextraction, i.e. the removal of soil pollutants by cropping and harvesting metal-accumulating plants is the method of choice for relatively mobile metals such as Cd and Zn.

Phytoextraction largely depends on (i) the plant's ability to accumulate the pollutants in the shoots, and (ii) the bioavailability of soil pollutants. The bioavailability of metals in soil is controlled by soil factors such as pH, cation exchange capacity, drainage status of soil, organic matter and soil clay types. Soil pH is a master variable of metal solubility, speciation in soils and plant uptake. The solubility of cationic metals such as Cd and Zn is known to increase with decreasing pH (Adriano, 2001).

Lowering soil pH by rhizosphere processes, e.g. by co-cropping of root zone acidifiers such as red alder and metal accumulators such as willows, or soil amendments such as elemental sulfur has been proposed as effective means to increase metal cation uptake by phytoextraction crops (e.g. Wenzel et al., 1999; Wenzel, 2009) and has been demonstrated in pot and field experiments (Kayser et al., 2000; Kukier et al., 2004; Wang et al., 2006).

Regarding their uptake behavior, plants may be categorized into three types, i.e. indicators, accumulators and excluders (Adriano,

\* Corresponding author. Tel.: +43 1 47654 3126.

E-mail address: [markus.puschenreiter@boku.ac.at](mailto:markus.puschenreiter@boku.ac.at) (M. Puschenreiter).

2001). Indicator plants are widely used for biological monitoring of several environmental indicators, e.g., pollutant level in soil, water logging, nitrogen deficiency and fertility. Many authors have previously discussed the advantages of biological monitoring (e.g., Wittig, 1993; Bargagli, 1998). *Taraxacum officinale* is characterized by wide-spread ecological distribution, which makes this plant particularly interesting for biological monitoring of pollutants (Djingova and Kuleff, 1993; Simon et al., 2006). *Plantago lanceolata* is also a common perennial plant species in native and agricultural ecosystems of temperate climatic zones and has been suggested as an indicator plant for bioavailable forms of Cd and Zn in soil (Leštan et al., 2003; Zupan et al., 1997).

The potential metal bioavailability in soil is traditionally assessed by chemical extraction (e.g. by 1 M  $\text{NH}_4\text{NO}_3$ , 0.005 M  $\text{Ca}(\text{NO}_3)_2$  or 0.05 M  $\text{Na}_2\text{-EDTA}$ ) or by measuring soil solution concentrations in water extracts (Prüeß, 1997; Gray et al., 1999). However, these equilibrium-based approaches do not account for the depletion at the root–soil interface and depletion-induced resupply from the solid phase. A promising tool to study the dynamics of trace elements in soil solution and to mimic the processes in the rhizosphere is the diffusive gradients in thin films technique, DGT (Davison and Zhang, 1994). Deployment of DGT lowers the concentration of metals locally in the soil solution at the DGT–soil interface. The mass of the metal accumulated in the DGT device mainly depends on the soil solution concentration and the fluxes, i.e. the diffusional transport and the kinetics of metal resupply from labile pools in the solid phase (Zhang et al., 2001; Harper et al., 1998). The ratio of  $C_{\text{DGT}}$  (interfacial metal concentration) to the concentration in the soil solution is termed R and describes the metal resupply characteristics in a given soil as it is related to the solid phase labile pool size ( $K_{\text{dl}}$ , partition coefficient for the labile species) and the response time ( $T_c$ ) of the soil to depletion. The latter is directly related to the rate constant of the resupply process (Zhang et al., 2001; Harper et al., 1998).

DGT has been used for more than a decade to study the bioavailability and resupply of essential and toxic elements in soil (Zhang et al., 2001; Nolan et al., 2005). Several studies have confirmed good correlation between metal concentration in plants and their measurement by DGT (Zhang et al., 2001, 2004; Song et al., 2004; Fischerova et al., 2005; Koster et al., 2005).

Efficient phytoextraction within acceptable time is often hindered by limited availability of the target pollutants (Wenzel, 2009). Selection of appropriate soil amendments or the design of rhizosphere manipulation to adjust soil pH requires detailed information on the related changes in metal solubility, extractability, metal resupply from the solid phase and the resulting phytoavailability to plants. As soils are highly diverse in their properties, it is difficult to predict the response of metal bioavailability to soil pH manipulation.

We selected four polluted soils representing a range of soil solution concentrations of Cd and Zn and related  $K_{\text{dl}}$  values to determine the effects of lowering the pH on (1) Cd and Zn extractability and solubility; (2) metal fluxes and resupply determined by the DGT technique; (3) metal accumulation in indicator plants, including the assessment of potential toxicity effects. Using this dataset we evaluated the predictive power of the chemical and biological indicators of bioavailability and their application to design proton-aided phytoextraction technologies.

## 2. Materials and methods

### 2.1. Experimental soils and acidification treatments

Four soils, ARNB (Arnoldstein, Austria), PR2 (Příbram, Czech Republic), GÖ (Gyöngyösoroszi, Hungary) and SK (Banská Štiavnica, Slovakia) were used in this experiment (Table 1). These soils are classified as A horizons of Cambisols (IUSS Working Group WRB, 2006) and had been polluted with Zn and Cd over several hundred years

**Table 1**  
Selected properties of the experimental soils.

| Selected properties of the soils                      | Units                          | Soils |      |      |      |
|---|--------------------------------|-------|------|------|------|
|   |                                | ARNB  | PR2  | GÖ   | SK   |
| Sand  | $\text{g kg}^{-1}$             | 486   | 572  | 627  | 742  |
| Silt  | $\text{g kg}^{-1}$             | 359   | 325  | 9.1  | 184  |
| Clay  | $\text{g kg}^{-1}$             | 155   | 103  | 182  | 74   |
| WHC <sup>a</sup>                                      | $\text{g kg}^{-1}$             | 470   | 720  | 440  | 430  |
| Total carbon  | $\text{g kg}^{-1}$             | 26    | 66   | 24   | 104  |
| Organic carbon  | $\text{g kg}^{-1}$             | 25.5  | 66   | 23.1 | 10.4 |
| CEC <sup>b</sup>                                      | $\text{cmol}_c \text{kg}^{-1}$ | 1.6   | 2.8  | 22.9 | 18.6 |
| Total Cd  | $\text{mg kg}^{-1}$            | 4.68  | 2.67 | 8.35 | 7.34 |
| EDTA–extractable Cd                                   | $\text{mg kg}^{-1}$            | 2.75  | 0.49 | 4.09 | 5.11 |
| $\text{NH}_4\text{NO}_3$ –extractable Cd              | $\text{mg kg}^{-1}$            | 0.7   | 0.05 | 0.07 | 3.05 |
| $C_{\text{dsoil}}$                                    | $\mu\text{g cm}^{-3}$          | 0.03  | 0.01 | 0.02 | 0.05 |
| $K_{\text{dl}}^c$ of Cd ( $\text{Na}_2\text{-EDTA}$ ) | $\text{L kg}^{-1}$             | 103   | 62.4 | 203  | 108  |
| $K_{\text{dl}}^c$ of Cd ( $\text{NH}_4\text{NO}_3$ )  | $\text{L kg}^{-1}$             | 26.2  | 6.4  | 3.5  | 64.4 |
| Total Zn  | $\text{mg kg}^{-1}$            | 464   | 242  | 1840 | 1060 |
| EDTA–extractable Zn                                   | $\text{mg kg}^{-1}$            | 118   | 83   | 744  | 363  |
| $\text{NH}_4\text{NO}_3$ –extractable Zn              | $\text{mg kg}^{-1}$            | 44    | 4.5  | 7    | 308  |
| $Zn_{\text{soil}}$                                    | $\mu\text{g cm}^{-3}$          | 1.54  | 1.16 | 1.79 | 9.56 |
| $K_{\text{dl}}^c$ of Zn ( $\text{Na}_2\text{-EDTA}$ ) | $\text{L kg}^{-1}$             | 76.7  | 71.6 | 416  | 38   |
| $K_{\text{dl}}^c$ of Zn ( $\text{NH}_4\text{NO}_3$ )  | $\text{L kg}^{-1}$             | 28.6  | 3.9  | 3.9  | 32.2 |
| pH ( $\text{H}_2\text{O}$ )                           | –                              | 5.64  | 5.35 | 6.95 | 5.91 |
| $\text{CaCO}_3$                                       | $\text{g kg}^{-1}$             | 0     | 0.1  | 5.1  | 0    |

<sup>a</sup> Water holding capacity.

<sup>b</sup> Cation exchange capacity.

<sup>c</sup> Labile  $K_{\text{dl}}$  [distribution coefficient between labile pool (extracted by 0.05 M  $\text{Na}_2\text{-EDTA}$  or  $\text{NH}_4\text{NO}_3$ ) and soil solution ( $C_{\text{soil}}$ )].

due to atmospheric deposition derived from metal smelters and processing. Initial soil pH values and other characteristics are shown in Table 1.

Prior to use in the pot experiment, all four soils were air dried, passed through a 2-mm sieve to remove pieces of stones and homogenized. Water holding capacity (WHC) was determined by placing the soils on filter paper on a shallow pan of water until the soil was saturated. Then the soils were allowed to drain in water-saturated atmosphere until the drainage was complete and the water content was determined.

The soils were acidified with  $\text{HNO}_3$  to obtain the targeted pH levels, further referred as A1 (pH 4.5) and A2 (pH 3.5); the original pH level is termed A0. For calculation of the amounts of  $\text{H}^+$  needed to obtain the targeted pH levels in each soil, a preliminary incubation experiment was conducted in which a known amount of  $\text{H}^+$  was added in the form of  $\text{HNO}_3$  to the soils prior to 5 days incubation at 25 °C and 65% of the WHC. The amounts of the  $\text{H}^+$  and the corresponding volumes of 14.44 M nitric acid required to obtain the targeted pH values in the main experiment are shown in Table 2. Three batches for each soil (A0, A1 and A2 level) were adjusted to

**Table 2**  
Amounts of  $\text{H}^+$  ions in the form of nitric acid ( $\text{HNO}_3$ ) added to prepare final soil treatments.

| Soil | Target pH             | $\text{H}^+$ ions          |  |
|------|-----------------------|----------------------------|--|
|      |                       | $\text{mmol kg}^{-1}$ soil | 14.44 M $\text{HNO}_3$<br>$\text{mL kg}^{-1}$ soil |
| ARNB | A0 (original soil pH) | 0                          | 0  |
|      | A1 (4.5 pH level)     | 24.3                       | 1.7  |
|      | A2 (3.5 pH level)     | 63.5                       | 4.4  |
| PR2  | A0 (original soil pH) | 0                          | 0  |
|      | A1 (4.5 pH level)     | 51                         | 3.5  |
|      | A2 (3.5 pH level)     | 113                        | 7.8  |
| GÖ   | A0 (original soil pH) | 0                          | 0  |
|      | A1 (4.5 pH level)     | 75                         | 5.2  |
|      | A2 (3.5 pH level)     | 116                        | 8  |
| SK   | A0 (original soil pH) | 0                          | 0  |
|      | A1 (4.5 pH level)     | 30                         | 2  |
|      | A2 (3.5 pH level)     | 71                         | 5  |

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