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Changes in metal availability, desorption kinetics and speciation in contaminated soils during repeated phytoextraction with the Zn/Cd hyperaccumulator *Sedum plumbizincicola*

Zhu Li [a], Mingyun Jia [b], Longhua Wu [a, *], Peter Christie [a], Yongming Luo [a, c]

[a] Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[b] State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[c] Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

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ABSTRACT

Phytoextraction is one of the most promising technologies for the remediation of metal contaminated soils. Changes in soil metal availability during phytoremediation have direct effects on removal efficiency and can also illustrate the interactive mechanisms between hyperaccumulators and metal contaminated soils. In the present study the changes in metal availability, desorption kinetics and speciation in four metal-contaminated soils during repeated phytoextraction by the zinc/cadmium hyperaccumulator *Sedum plumbizincicola* (*S. plumbizincicola*) over three years were investigated by chemical extraction and the DGT-induced fluxes in soils (DIFS) model. The available metal fractions (i.e. metal in the soil solution extracted by $CaCl_2$ and by EDTA) decreased greatly by >84% after phytoextraction in acid soils and the deceases were dramatic at the initial stages of phytoextraction. However, the decreases in metal extractable by $CaCl_2$ and EDTA in calcareous soils were not significant or quite low. Large decreases in metal desorption rate constants evaluated by DIFS were found in calcareous soils. Sequential extraction indicated that the acid-soluble metal fraction was easily removed by *S. plumbizincicola* from acid soils but not from calcareous soils. Reducible and oxidisable metal fractions showed discernible decreases in acid and calcareous soils, indicating that *S. plumbizincicola* can mobilize non-labile metal for uptake but the residual metal cannot be removed. The results indicate that phytoextraction significantly decreases metal availability by reducing metal pool sizes and/or desorption rates and that *S. plumbizincicola* plays an important role in the mobilization of less active metal fractions during repeated phytoextraction.

1. Introduction

Metal pollution of some soils has become a serious environmental concern and a potential threat to human health. The technique of phytoextraction using hyperaccumulators has been shown to be successful in remediating soils polluted with metals (McGrath et al., 2006; Japenga et al., 2007; Li et al., 2012). However, the technique requires long periods of remediation effort and successive or numerous crops are needed to remove adequate metal from contaminated soils to achieve safe levels (Koopmans et al., 2008; Li et al., 2014). During the process of phytoextraction soil metal availability will change as prolonging the remediation time increases interactions between soil and plant. Both short-term phytoextraction and rhizosphere experiments on hyperaccumulators show clear decreases in soil metal availability in contaminated soils after phytoextraction and in rhizosphere soils as compared to bulk soils (Keller and Hammer, 2004; Liu et al., 2011). However, after short-term phytoextraction the decreased available metal may be replenished through soil metal re-equilibration (Keller and Hammer, 2004). Investigation of metal availability changes over relatively long time periods may help to elucidate metal changes and to alleviate the environmental risk of metals due to phytoextraction. In addition, compared to short-term phytoextraction, the enhanced plant–soil interactions and more marked decrease in soil metals during long periods of phytoextraction can give more information on the mechanisms of phytoextraction. Moreover, the efficiency of remediation can decrease during repeated phytoextraction as shown by Li et al. (2014), and the further discrimination of changes in soil metals during phytoextraction might help to elucidate the factors involved.

* Corresponding author.
  E-mail address: lhwu@issas.ac.cn (L. Wu).

Numerous methods have been used to investigate the behavior of metals in soils. Chemical extraction tests are among the most commonly and widely used methods for predicating or estimating the bioavailability of various forms of metals (D'Amore et al., 2005). Choice of chemical agent depends on the specific points of interest of the study. Concentrated acids are usually used as to determine total amounts of metals present and estimate the total potentially harmful metals. Soil solution metal or weaker agents extractable metal fractions are relatively soluble and bioavailable. The water-extractable or soil solution metals are commonly considered to be the most readily available fraction to biota (Seguin et al., 2004). Weak chemical agents, e.g. $CaCl_2$, $Ca(NO_3)_2$ and $BaCl_2$, extract fractions that have been used to denote metal availability to plants as shown in some studies (Peijnenburg et al., 2007; Meers et al., 2007a). Extraction with 0.01 M $CaCl_2$ has been suggested for estimating metal availability (Novozamsky et al., 1993; Houba et al., 2000) and gives a good indication of metal availability to plants (Meers et al., 2007b). The metal fraction extracted by EDTA is used to denote potentially available and mobile metal due to the strong metal complexing ability of EDTA (Anju and Banerjee, 2011). Sequential extraction tests have been used widely to investigate metal physico-chemical forms and to study the effects of soil processes and changes in environmental conditions on soil metal availability and mobility. The three-step procedure proposed and modified by the Community Bureau of Reference (BCR) (Ure et al., 1993; Sahuquillo et al., 1999) has been widely accepted as the 'standard method' and its application has increased recently (Pueyo et al., 2008; Anju and Banerjee, 2011). In the present study, single extracts with different extraction abilities (i.e. soil solution, $CaCl_2$ and EDTA) and the BCR test were used to investigate changes in metal availability and combined forms during long-term phytoextraction.

Soil metal mobility and availability depend largely on metal desorption from the soil solid phase and on metal concentration in the soil solution. If metal desorption from the solid phase is kinetically limited then this may be a factor limiting plant metal uptake (Zhang et al., 2006). The technique of diffusive gradients in thin films (DGT) is based on kinetic principles and can reflect the soil metal desorption process when metals in the soil solution are depleted at the interface between the roots and the soil (Davison et al., 2000). The kinetic information can be obtained by the model of DGT induced fluxes in soils (DIFS). The DIFS model has been used to study the metal desorption kinetics of contaminated soils (Ernstberger et al., 2005; Zhang et al., 2006) and changes in metal desorption kinetics induced by hyperaccumulators (Fitz et al., 2003). In the present study the changes in soil metal desorption kinetics during the repeated phytoextraction of four metal-contaminated soils with contrasting soil properties were investigated using the DIFS model.

The plant metal uptake and remediation efficiency of four metal-contaminated soils in long-term phytoextraction has been investigated in a previous study (Li et al., 2014). In the present study soil metal changes during the long-term phytoextraction were further investigated by single and sequential extractions and using the DIFS model. The aim was to elucidate changes in metal availability, associated forms and desorption kinetics in the different soils and to understand the possible soil metal processes induced by interactions between soil and plant during long-term phytoextraction.

2. Methods and materials

2.1. Soil characterization

Four types of metal contaminated soil were collected from the arable layer (top 15 cm) of agricultural fields in different parts of China. Two acid soils were collected from Dabaoshan in Guangdong Province, south China, and Huludao in Liaoning Province, north China, and are referred to as DBS and HLD, respectively. The soil from DBS is a Ferralic Anthrosols that has been polluted by metal mining activities and the soil from HLD is a Haplic Lixixols whose main pollution source is a zinc factory that has operated for several decades. The other two soils are calcareous soils which were collected from Zhujiawu and Shuanglingdong in Zhejiang Province, east China, and are labeled ZJW and SLD, respectively. They are from an area polluted by a copper smelter and the soil type is Hydragric Anthrosols. Each of the four contaminated soils was first air-dried and then passed through a 2-mm nylon sieve and mixed thoroughly. The metal contaminated soils were continuously phytoextracted using *Sedum plumbizincicola* for three years over seven successive crops in a glasshouse located in Nanjing. Soil samples were collected after the third harvest (P3) and the seventh harvest (P7) during long-term phytoextraction. Together with the soils without remediation (NP) there were a total of three types of soil samples with different cropping phytoextraction collected from the pot experiment during the experiment. After phytoextraction by seven crops the total Zn concentrations in the DBS, HLD, SLD and ZJW soils (P7) decreased by 37, 52, 12, and 19%, respectively, and Cd concentrations decreased by 64, 89, 37, and 38% compared to the NP soil (Table 1). All these soil samples were firstly air-dried, then passed through a 2-mm nylon sieve and were used to evaluate the soil metal changes induced by phytoextraction.

Portions of the sieved soils were used for determination of selected soil chemical properties. Soil pH, soil total organic carbon (TOC), soil cation exchange capacity (CEC), and soil total metal were analyzed by previously published methods (Li et al., 2014). Free iron/aluminum oxides (Fe_d/Al_d) were extracted with $Na_2S_2O_4$—$Na_3C_6H_5O_7$—$NaHCO_3$ and determined by atomic absorption spectrophotometry (Varian SpectrAA 220FS, Varian, Palo Alto, CA). The particle size distribution was determined with a Beckman LS230 laser diffraction apparatus. Selected chemical properties of the contaminated soils with or without phytoextraction are shown in Table 1.

2.2. Calculation of DGT concentration and DIFS

Information on the standard piston DGT devices and the method of calculation of DGT concentration were described in a previous study (Li et al., 2014). In brief, the concentration of metal at the interface of the DGT device and the soil (C_{DGT}) was calculated as follows,

$$C_{DGT} = C_E(V_{HNO_3} + V_{gel})\Delta g / tADf_e \qquad (1)$$

Where C_E is the concentration of metal in the 1 M HNO_3 elution solution ($\mu g\ l^{-1}$), V_{HNO3} is the volume of HNO_3 added to the resin gel (1 ml), V_{gel} is the volume of the resin gel, typically 0.15 ml,f_e is the elution factor for each metal, typically 0.8, t is the deployment time (in sec), A is the exposure area, typically 2.54 cm^2, Δg is the thickness of the diffusive gel (0.08 cm) plus the thickness of the filter membrane (0.014 cm), and D is the diffusion coefficient of the metal in the gel.

Comparing the concentration of C_{DGT} to the measured soil solution (gained by centrifugation as described in Li et al. (2014) concentration (C_{soln}) provides a ratio, R, which is dimensionless and gives an indication of the extent of the depletion of the soil solution concentration at the interface with the DGT:

$$R = C_{DGT}/C_{soln} \qquad (2)$$