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Effects of dissolved organic matter from the rhizosphere of the hyperaccumulator *Sedum alfredii* on sorption of zinc and cadmium by different soils

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ABSTRACT

Pot experiments were conducted to investigate the changes of the dissolved organic matter (DOM) in the rhizosphere of hyperaccumulating ecotype (HE) and non-hyperaccumulating ecotype (NHE) of *Sedum alfredii* and its effects on Zn and Cd sorption by soils. After planted with HE, soil pH in the rhizosphere reduced by 0.5–0.6 units which is consistent with the increase of DOM. The hydrophilic fractions (51%) in DOM from the rhizosphere of HE (HE-DOM) was much greater than NHE-DOM (35%). In the presence of HE-DOM, Zn and Cd sorption capacity decreased markedly in the following order: calcareous clay loam > neutral clay loam > acidic silty clay. The sorption isotherms could be well described by the Freundlich equation ($R^2 > 0.95$), and the partition coefficient (K) in the presence of HE-DOM was decreased by 30.7–68.8% for Zn and 20.3–59.2% for Cd, as compared to NHE-DOM. An increase in HE-DOM concentration significantly reduced the sorption and increased the desorption of Zn and Cd by three soils. DOM derived from the rhizosphere of the hyperaccumulating ecotype of *S. alfredii* could significantly reduce metal sorption and increase its mobility through the formation of soluble DOM–metal complexes.

1. Introduction

Phytoextraction, the use of green plants to clean up contaminated soil, has attracted attention as an environmentally friendly low-input remediation technique. This technology makes use of pollutant-accumulating (usually hyperaccumulator) that extract pollutants from the soil and accumulate them in the harvestable above-ground biomass [1,2]. Hundreds of hyperaccumulators have been identified in the past three decades, and many studies have been carried out to investigate the mechanisms of uptake, transport, and detoxification of pollutants [3–5]. However, potential use of hyperaccumulators in phytoremediation is limited by a lack of knowledge of many basic plant processes [6]. Most heavy metals have low mobility in soils, and are not easily absorbed by plant roots. However, hyperaccumulating plants show an extraordinary ability to absorb metals from the soil and accumulate them in the shoots under both low and high metal levels. For example, the decrease in the concentration of Zn in the soil solution during the growth of *Thlaspi caerulescens* accounted for only 1% of the Zn accumulated by the plant [7]. Similarly, decreases in the NH_4NO_3-extractable concentration of Zn in the soil after the growth of *T. caerulescens* has been found to account for only 10% [8] and 25% [9] of the Zn accumulated in the shoots. These results suggest that *T. caerulescens* was effective in mobilizing Zn from less soluble fractions of the soils. Many studies have investigated factors regulating the growth of hyperaccumulator plants for maximum metal removal from contaminated sites [10,11]. Whereas, rhizosphere processes that regulate hyperaccumulation have not yet been fully elucidated, the mechanisms of how hyperaccumulator plants solubilize and take up heavy metals from contaminated soils are still unclear [12].

Dissolved organic matter (DOM) consists of several types of low molecular weight organic compounds, such as polyphenols, simple aliphatic acids, amino acids and sugar acids. It is one of the most important factors affecting metal mobility and phytotoxicity in soils [13]. For example, plants release organic acids to take up Fe from the soil, especially under conditions of Fe deficiency [14]. DOM present in root exudates, such as carboxylic acids, is involved in mobilization of inorganic phosphorus (P) in the rhizosphere by changing soil pH, displacing P from sorption sites, chelating P-immobilizing metal cations and forming soluble metal chelate complexes with P [15]. Fitz et al. [16] found that dissolved organic carbon (DOC) concentrations in the rhizosphere soil solution of *Pteris vittata* were increased by 86% and appeared to enhance total Fe solubility due to complexation reactions. To date, although

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many workers have dealt with the adsorption characteristics of DOM on soil constituents and its effect on metal adsorption and solubility in the soil solution [17–19], there is a lack of information concerning the influence of DOM on the availability of heavy metals in the rhizosphere of hyperaccumulator [20,21].

Sedum alfredii grows in old Pb/Zn mining areas of southeast China, and has been identified as a Zn/Cd-hyperaccumulator [22]. This plant has exceptional abilities to tolerate and accumulate high concentrations of Zn/Cd, and the characteristics of large biomass, rapid growth, asexual propagation, and perennial growth make it an ideal plant for studying mechanisms responsible for hyperaccumulation as well as for enhancing phytoremediation practices. To date, studies on the mechanism of metal tolerance and hyperaccumulation of *S. alfredii* were mainly focused on the uptake [23,24] and subcellular distribution characteristics [25,26], while no information is available about DOM in the rhizosphere of this plant. The aims of this study were (1) to investigate the changes of DOM in the rhizosphere of *S. alfredii* grown in contaminated soils; and (2) to assess the effects of DOM from the rhizosphere of *S. alfredii* on Zn and Cd sorption via batch studies by three different soils with different physicochemical properties.

2. Materials and methods

2.1. Plant propagation and soil characterization

The hyperaccumulating ecotype (HE) of *S. alfredii* was collected from an old Pb/Zn mine area in Zhejiang Province, PR China, and the non-hyperaccumulating ecotype (NHE) of *S. alfredii* was obtained from a tea garden in Hangzhou, Zhejiang Province, PR China. Plants were grown in non-contaminated soil for several generations to minimize internal metal concentrations. The healthy and equal-sized plant shoots were selected and grown for three weeks in the greenhouse using a basic nutrient solution [22].

The paddy soil used in the pot experiment was collected from an abandoned site in Fuyang county of Hangzhou, Zhejiang Province, PR China. The site was heavily contaminated due to mining activities and not suitable for crop growth. Soil samples were air-dried, ground to pass through a 2-mm sieve, and stored in plastic bottles until use. Selected physical and chemical characteristics of this soil are shown in Table 1.

2.2. Experimental design

The experimental design has been described in detail previously by Li et al. [27]. In brief, the dimensions of the rhizobox were 150 × 140 × 200 (length × width × height in mm). It was divided into three sections, a central zone or rhizosphere zone (20 mm in width), which was surrounded by nylon cloth (300 mesh), and left and right non-rhizosphere zones (60 mm in width). Root growth was limited to the central compartment and within the nylon cloth. 0.5 kg of soil was placed in the rhizosphere zone and 3.0 kg was placed in the non-rhizosphere zones. One week before the study, the soil equilibrated at field capacity. After pre-culturing for three weeks in hydroponic solution, three plants were transplanted in rhizosphere zone and each treatment was replicated six times. The plants were watered throughout the study to keep the soil at approximately 65% of its field capacity. The plants were allowed to grow for 90 days in a greenhouse with natural light and an average night/day temperature of 30/24 °C, and day/night humidity of 70/85%. At the end of the experiment, the plants were harvested and each plant was separated into root and shoot. The plant were washed thoroughly with tap water and then rinsed with distilled water. Then were oven dried for three days at 65 °C, weighed, and ground to a 60-mesh fineness for chemical analysis. Rhizosphere soil (soil in rhizosphere zone) and bulk soil (soil in non-rhizosphere zones) were separated.

2.3. Extraction and fractionation of soil dissolved organic matter

The dissolved organic matter (DOM) was extracted according to the method of [28] with some modification. Both rhizosphere and bulk soils were extracted with deionized–distilled water using a solid: water ratio of 1:5 (w/v) on a dry weight basis and shake at 200 rpm for 16 h at 25 °C on a reciprocal shaker. The suspension was centrifuged at 10,000 × *g* for 25 min, and the supernatant was filtered through a 0.45 μm membrane filter and subsequently through a sodium cation exchanger to remove cations (e.g., Zn^{2+}, Cd^{2+}, Mg^{2+}). The filtrates were stored at 4 °C until use. The compositions of the DOM were fractionated into hydrophilic acid (HiA), hydrophilic base (HiB), hydrophilic neutral (HiN), hydrophobic acid (HOA), hydrophobic base (HoB) and hydrophobic neutral (HON) using the method developed by Leenheer [29].

2.4. Zinc and cadmium sorption experiments

Three different soils were used in the Zn and Cd sorption experiments (Table 1), a acidic silty loam (Typic Acrorthox, developed on quaternary red earths), a neutral clay loam (Inceptisol, derived from alluvial sediments) and a calcareous clay loam (yellow podzol). The soils were collected from the surface layer (0–20 cm) from Longyou, Jiaxing and Deqing County of Zhejiang province, PR China, respectively. A 1.0 g sample of each soil type was weighed into 50-ml polyethylene centrifuge tubes and equilibrated with 20 ml of mixed solution containing 10 concentration levels (0, 10, 25, 50, 100, 200, 300, 400, 500, 600 mg L^{-1}) of nitrate salts of Zn or Cd in a 0.01 M $NaNO_3$ background in the absence or presence of rhizosphere DOM. All the suspensions were adjusted to the pH of it original soils. Two drops of 1 M NaN_3 were added to each tube to inhibit DOM decomposition during the sorption experiments. The soil suspensions were shaken on a reciprocal shaker at 200 rpm and 25 °C for 4 h and then equilibrated in the dark for 2 h. The tubes were then centrifuged at 5000 × *g* and filtered. Zinc or cadmium concentrations in the filtrates were determined by flame atomic absorption spectrophotometry (FA-AAS, AA-6800, Shimadzu). The quantity of Zn or Cd adsorbed was calculated by subtracting the

Table 1
Selected physical and chemical properties of the soils.

Soils	pH[a]	OM[b]	Total N	Total P	CEC[c]	Sand	Silt	Clay	Total Zn	Total Cd
		g kg^{-1}			cmol kg^{-1}	%			mg kg^{-1}	
Paddy soil	6.83	27.6	1.43	0.84	8.72	26.5	33.6	39.9	2001.6	21.05
Acidic silty clay	4.75	25.9	0.93	0.61	10.86	11.9	46.3	41.8	81.6	0.26
Neutral clay loam	6.90	20.8	1.48	0.89	13.45	32.2	42.4	25.4	118.5	0.35
Calcareous clay loam	8.08	21.8	0.98	0.79	15.59	35.5	40.3	24.2	96.9	0.40

[a] 1:2.5 soil/water ratio.
[b] Organic matter.
[c] Cation exchange capacity.