Bioavailability of cadmium adsorbed on various oxides minerals to wetland plant species *Phragmites australis*

He Wang [a,b], Yongfeng Jia [a,*], Shaofeng Wang [a], Huijie Zhu [a,b], Xing Wu [a,b]

[a] *Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, No. 72 Wenhua Road, Shenyang 110016, China*
[b] *Graduate School, Chinese Academy of Sciences, Beijing 100049, China*

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ABSTRACT

The bioavailability of heavy metals strongly depends on their speciation in the environment. The effect of different chemical speciations of cadmium ions (i.e. adsorbed on different oxide minerals) on its bioavailability to wetland plant *Phragmites australis* was studied. Goethite, magnetite, gibbsite, alumina, and manganese oxide were chosen as representatives of metal (hydr)oxides commonly present in sediment. The cultivar system with Hoagland solution as nutrition supply, and single metal oxide with adsorbed Cd as contaminant was applied to study Cd accumulation by *P. australis*. The bioaccumulation degree in root after the 45-day treatment followed the order: $Al(OH)_3 > Al_2O_3 > Fe_3O_4 > MnO_2 > FeOOH$. The concentration of Cd in stem and leaf followed a similar order although it was considerably lower than that in root. Low-molecular-weight organic acids (LMWOAs), acetic acid, malic acid and citric acid were used to evaluate the desorbability of Cd from different oxides, which can be indicative of Cd-oxide bonding strength and Cd bioavailability. Desorption of Cd by acetic acid and malic acid followed the order: $Al(OH)_3 > Fe_3O_4 > Al_2O_3 > FeOOH > MnO_2$, while by citric acid: $Al(OH)_3 \geq Al_2O_3 > Fe_3O_4 > FeOOH > MnO_2$. This was consistent with the Cd accumulation degree in the plant. Cd adsorbed on $Al(OH)_3$ was the most easily desorbable species and most bioavailable to *P. australis* among the oxide minerals, whereas MnO_2 adsorbed Cd was least desorbable by LMWOAs hence constituted the least bioavailable Cd species adsorbed on the oxide minerals.

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1. Introduction

Cadmium is one of the most toxic and non-degradable contaminants in aquatic systems. The flux of cadmium released from anthropogenic activities such as mining, smelting, waste disposal, electroplating etc. is nearly 10 times that of all natural sources [1]. Since it cannot be removed from water by self-purification and could be accumulated through food chain, it poses a serious threat to human health.

In aquatic systems, cadmium ions are generally associated with particulate matter and settle and accumulate in the bottom sediments which in turn become important sinks and sources of heavy metal pollution [2]. Cadmium concentrations in sediment are often several orders of magnitude higher than those in ambient water [3]. When some environmental conditions such as pH, dissolved oxygen are changed, Cd may be transported from sediments back to the sediment–water interface through diffusion, sediment re-suspension, or biological activity such as bioturbation. Once at the

sediment–water interface or in the water column, Cd is very likely to be transported and to enter the food web. It is well known that sediment is a heterogeneous mixture of dissimilar particles which have been considered a complex assemblage of different organic and inorganic components [4], including organic matters and various minerals. Trace metal behavior (bioavailability, toxicity and distribution) in sediments is controlled by some factors or processes, including adsorption/desorption processes, ion strength, pH, the presence of organic matter, sulfur and carbonates in the environment [5–7]. In these impacts, adsorption/desorption is a ubiquitous process in water–sediment interface that notably govern the fate of trace metal. Many metal (hydr)oxides occur as a discrete phase or as coatings on other mineral surfaces in sediments [8]. Because these oxides usually have large surface areas, porous structures (for some amorphous phases), and an abundance of binding sites, Cd ions are easily bound to them [9].

Goethite (FeOOH), magnetite (Fe_3O_4), gibbsite ($Al(OH)_3$), alumina (Al_2O_3) and manganese oxide (MnO_2) are major (hydr)oxide minerals in sediment which fatefully influence the adsorption, fixation, and transportation of Cd in sediment [10]. The (im)mobility and bioavailability of heavy metals in sediments depend to a large extent on the binding forms and stability. Because of the difference in surface area, active site density and

* Corresponding author. Tel.: +86 24 8397 0503; fax: +86 24 8397 0436.
E-mail addresses: he.wangworld@yahoo.com.cn (H. Wang),
yongfeng.jia@iae.ac.cn (Y. Jia).

surface geometry, the bonding strength of Cd ions with these minerals may vary significantly. Hence the bioavailability of different (hydr)oxide minerals adsorbed Cd may be appreciably different.

Low-molecular-weight organic acids (LMWOAs) are major components in rhizosphere that can initiate the mobilization and uptake by plants of the adsorbed heavy metal ions. The stability of adsorbed Cd ions on various (hydr)oxide minerals in the media containing LMWOAs can be indicative of dissimilar bioavailability of various Cd species. Moreover, due to different adsorption capacity and stability of Cd on (hydr)oxides, when some environmental conditions change, desorption of Cd from surfaces of (hydr)oxides would be variable, leading to variation in bioavailability. Thus, it is of environmental significance to achieve comprehensive understanding of adsorption/desorption behaviors of Cd ions adsorbed on various (hydr)oxide minerals and consequently the effects on its bioavailability.

Selective extraction using a series of chemicals was commonly used to evaluate the bioavailability of heavy metals in soils and sediments, e.g. Tessier or BCR method [11,12]. The bioavailability of heavy metal ions adsorbed on different minerals at environment-relevant levels has not been reported although it may be reasonably assumed that different speciation exhibits different bioavailability. The objectives of the present study were (1) to investigate from molecular level the dependency of bioavailability on metal speciation by analyzing the bioaccumulation characteristics of Cd adsorbed on different oxides by hygrophyte *Phragmites australis* and (2) to evaluate the difference of bioavailability by desorption treatment using LMWOAs. *P. australis* was used as a testing plant because it is a common hygrophyte and has been widely applied to construct artificial wetlands for the treatment of wastewaters and submerged mine tailings [13] due to its excellent tolerances to various contaminants and the ability to uptake toxic elements and nutrient [14,15].

2. Experimental

2.1. Materials

All chemicals were of analytical reagent grade. The metal oxides were provided by Sinopharm Chemical Reagent Co., Ltd. Cadmium stock solution was prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ in distilled water at 100 mg/L prior to adsorption. All bottles and vessels were treated prior to use by soaking in 0.1 mol/L HNO_3 for at least 24 h. The modified Hoagland solution (pH 5.5 ± 0.2) was prepared with the following salts: $Ca(NO_3)_2 \cdot 4H_2O$, 3.57×10^{-4} mol/L; H_3BO_3, 2.31×10^{-5} mol/L; $CaCl_2 \cdot 2H_2O$, 2.14×10^{-3} mol/L; KH_2PO_4, 9.68×10^{-4} mol/L; KNO_3, 2.55×10^{-4} mol/L; $MgSO_4$, 1.04×10^{-3} mol/L; $FeCl_3$, 6.83×10^{-5} mol/L; $MnSO_4 \cdot H_2O$, 7.69×10^{-6} mol/L; MoO_3, 1×10^{-5} mol/L; $Cu(NO_3)_2 \cdot 5H_2O$, 1×10^{-5} mol/L; and $Zn(NO_3)_2 \cdot 6H_2O$, 1×10^{-5} mol/L.

2.2. Adsorption of Cd on metal oxides

The cadmium adsorption experiments were conducted in 2.5 L reactors containing 2 L Hoagland solution. 100 g of metal oxide solid was mixed with the Hoagland solution and the mixture was allowed to equilibrate for 1 h. 50 mL of cadmium stock solution (100 mg/L) was added by titration while vigorously stirring to achieve the terminal concentration of 50 mg/kg solid. The system was left to equilibrate in a shaker at 25 °C for 24 h. 10 mL of solution was taken and filtered through 0.2 μm membrane for the analysis of residual cadmium concentration. The pH of the solutions was controlled constant at 5.5, by means of HCl or NaOH. Then the slurry was then ready for the bioaccumulation tests.

2.3. Cultivation experiments

Two-year-old seedlings of *P. australis* grown in 'clean' wetland were purchased from LJTH Flower Co. China. The roots of the seedlings were washed twice with tap water and then distilled water and cultured into ceramic buckets ($D \times H$, 10 cm × 30 cm, each containing 2 L 10% Hoagland solution without addition of heavy metals) for acclimation. Three weeks later, uniform (approximately 25 cm height) healthy seedlings were selected and transplanted into ceramic buckets each containing 2 L of the previously prepared metal oxides–Hoagland solution slurry.

Four seedlings were grown in each of three replicate buckets for each of the substrates. The vessels were arranged in a randomized design. Seedlings were grown in a greenhouse with natural illumination. The media pH was left to drift but monitored once a week after the plant was introduced.

2.4. Dithionite–citrate–bicarbonate extraction

Iron plaque and other metals coating on fresh root surfaces were extracted using a modified DCB method [16]. After 45 days cultivation, each seedling was washed gently once with tap water, and three times with deionized water. The entire root system of each seedling was firstly incubated in 30 mL of DCB solution containing 0.03 mol/L sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), 0.125 mol/L sodium bicarbonate ($NaHCO_3$) and 0.11 mol/L sodium dithionite ($Na_2S_2O_4$) at 25 °C for 60 min. The extract was filtered through 0.2 μm membrane for analysis. Cd concentration in DCB extraction was calculated by dividing the Cd content (mg) in extract and the entire root dry weight (kg, dry weight).

2.5. Analysis of metal concentrations in plant samples

After DCB extraction, the stems and roots were oven-dried at 80 °C to constant weight, and ground to fine powders. The powder materials were digested in a mixture of $HNO_3/HClO_4$ (3/1, v/v), at 150 °C for 2 h and 210 °C for 1 h, and then dissolved in HNO_3 (5%). A reagent blank and a standard reference material (peach leaves, GBW08501, Chinese National Certified Reference Material) were included to verify the accuracy and precision of the digestion procedure and subsequent analysis. The measured value of Cd content in the reference material was 16.8×10^{-3} mg/kg, with the recovery of 93.3%.

Root bio-concentration factor (BCF) was calculated using the following equation to assess the concentrations in root tissue relative to environmental loadings, BCF = C_{root}/C_{solid}, where C_{root}: Cd concentration in the root; C_{solid}: Cd concentration in the oxide.

2.6. Cadmium desorption with LMWOAs

25 g of metal oxides minerals with adsorbed Cd (50 mg/kg) was introduced into 500 mL of Hoagland solution containing 30 or 50 mmol/L citric, acetic or malic acid (pH adjusted to 5.5 using NaOH solution). The slurry was agitated at 25 °C with the pH of solutions controlled constant at 5.5. The concentration of Cd was monitored as a function of time by taking a 2-mL of aliquot of slurry at various time intervals and filtering using 0.2 μm membrane followed by FAAS analysis.

2.7. Analysis of aqueous cadmium concentration

The concentration of cadmium in aqueous solution was measured on a flame atomic absorption spectrophotometer (FAAS, Varian AA240) at 228.8 nm with the detection limit of 0.05 mg/L. The instrument was operated as recommended by the manufacturer.
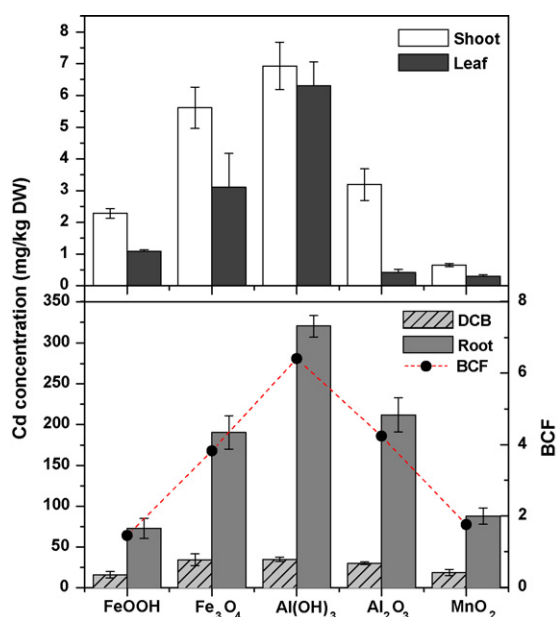
Fig. 1. Cd concentration and bio-concentration factor (BCF) in *P. australis*. (mean ± S.D.).

3. Results and discussion

3.1. Uptake of Cd by P. australis from different oxides

In the adsorption experiments, after 24 h equilibration of the oxide minerals with Cd solution, almost all the added Cd was uptaken by the oxides (data of Cd residual concentration not shown in paper). The concentration of loaded Cd on oxides was ~50 mg/kg. The pH values of the systems were adjusted to 5.5 at the initiation of the treatments and were left to drift during the 45-day cultivation of *P. australis*. The pHs in all cultivation systems were found to increase slightly but no marked difference was observed for different media.

It is obvious that the bioavailability of adsorbed Cd to *P. australis* highly depended upon the type of substrate oxide (Fig. 1). The *P. australis* cultivated in Cd–Al(OH)$_3$ medium was found to have accumulated the largest amount of Cd, followed by those in Cd–Al$_2$O$_3$ and Cd–Fe$_3$O$_4$. Lowest concentration of Cd was observed in the plants cultivated in Cd–FeOOH and Cd–MnO$_2$. The concentration of Cd in the *P. australis* grown in Cd–Al(OH)$_3$ media is ~1.6 times that in Cd–Fe$_3$O$_4$ and Cd–Al$_2$O$_3$ systems and ~5 times that in Cd–FeOOH and MnO$_2$ systems. This indicates that cadmium associated with aluminum (hydr)oxides was more available than that adsorbed on Fe- and Mn-oxides, which is probably attributed to the weak adsorption capability and stability of Al (hydr)oxides. It was reported that FeOOH adsorbed more Cd than Al$_2$O$_3$ (~175 mg/kg vs. ~42 mg/kg) under similar conditions [17,18]. It is the nature of metal (hydr)oxides that results in the discrepancy of adsorption capacity and stability which in turn would cause the difference of Cd bioavailability.

The adsorption capacity and bonding strength of metal oxides for Cd ions are governed by various factors. Cd ions are associated with metal (hydr)oxides via inner-sphere complexation with hydroxyls, so the adsorption is dependent on the density of active sites in the metal (hydr)oxides. Specific surface area is another important factor controlling Cd adsorption. Metal (hydr)oxides with relative larger specific surface area generally have larger adsorption capabilities. pH of zero point charge (pH$_{ZPC}$) of metal (hydr)oxides also has close relationship with metal adsorption. The surfaces of metal (hydr)oxides would be negatively charged at pH above pH$_{ZPC}$ and positively charged at pH below pH$_{ZPC}$, resulting in

increased electrostatic attraction or repulsion with metal cations respectively, hence leading to more or less readily adsorption. Iron oxides in present study (goethite and magnetite) exhibit greater specific surface areas (76–110 m^2/g vs. 18–40 m^2/g, as measured by the N$_2$-BET method) and adsorption sites density (16.8 sites/nm^2 vs. 8.0–8.5 sites/nm^2), as calculated by surface crystal structure than aluminum oxides [19–23]. In addition, the pH$_{ZPC}$ of these three sets of metal oxides is different, i.e. pH 2.8–3.3 for Mn-oxides; pH 7–8 for Fe-oxides; and pH 9–9.5 for Al-oxides [20,21,24]. Hence, manganese oxides would show electrostatic attraction towards Cd cations as the pH$_{ZPC}$ is below the pH of the cultivation systems (5.5–6.4) in the present study. Iron oxides would show less electrostatic repulsion towards Cd cations than aluminum oxides at the cultivation media pH [25]. Despite being minor phase in sediment, manganese oxides are important oxide minerals and play an important role in controlling the bioavailability of Cd in sediments [26]. Mn-oxide tends to have greater adsorption capability for Cd ions due mainly to its relatively high specific surface area and low pH$_{ZPC}$ [27]. Turner et al. [26] found that for a given salinity, the conditional particle–water distribution coefficient, (K_D) of Mn-oxides was two orders of magnitude greater than that of Fe-oxides. Therefore, Cd adsorbed on the surface of Mn-oxides would be more stable against bioaccumulation.

In addition to the Cd-oxide interactions, the substrate oxide itself may also influence the bioaccumulation of Cd by *P. australis*. It was reported that excess aluminum can induce more exudates in rhizosphere [28] which contain organic acids, sugar, and amino acid thus increasing solubilization and mobilization of Cd. Therefore cadmium adsorbed on Al (hydr)oxides was more bioavailable than that on Mn- and Fe-oxides.

Due largely to the complexity in nature of the sediments or soils, the speciation of heavy metals in the environment is commonly determined by sequential extraction using various chemicals (e.g. Tessier method), which treats the sediment or soil as "a black box". Heavy metals are artificially divided into five bound forms and some of the fractions are classified as bioavailable forms. Although sequential extraction methods can be used to roughly estimate trace metal bioavailability as a whole, it cannot quantify trace metals associated with specific biogeochemical phases because the extracted phases are operationally defined. In the present work, the bioaccumulation characteristics by *P. australis* of Cd ions adsorbed on oxides were evaluated individually and distinct difference in bioavailability was observed for different oxide mineral associated Cd. This cannot be identified by sequential extraction as all metal oxide adsorbed Cd are classified into "bound to metal oxides", or by cultivating the plants directly in Cd contaminated sediments or soils.

Fig. 1 also shows Cd concentration in different part of the plant tissues. Cadmium accumulated in root tissue from various Cd-oxide systems was 72.7–320 mg/kg DW which was much higher than environmental concentrations (50 mg/kg), with the root bioconcentration factor was >1 (1.45–6.41). Moreover, Cd content accumulated in roots was nearly 10-fold than those in aboveground parts. Cd distribution in different parts of the plants followed the decreasing order: root > root surface (DCB) > stem > leaf. Vymazal et al. found the concentration of Cd in *P. australis* grown in constructed wetland decreased in the order of root > rhizome > stem ≥ leaf [29].

P. australis is a perennial emergent macrophyte that takes up elements from sediments through its roots, and most heavy metals are accumulated in roots [13], as has been found in the present study that little Cd (less than 5%) was translocated to the aboveground tissues [30]. Cadmium accumulation was comparable to previously reported values in *P. australis* or other wetland plant species. Some studies have shown higher bio-concentration factors in root of *P. australis* than the present work, probably due to different cultivation conditions such as hydroponics treatment, or longer exposing in previous works [13,15,29]. Similar root accumulation character-

istics of metal or metalloid was also found in *P. australis* for Cu, Zn, As, in *Eriophorum angustifolium* for Cd, Zn, Pb, in *Carex rostrata* for Cu, Zn, As, and in *Salix* for Cu, As [13]. These elite hydrophytes were widely used to treat wastewater [15] or mine tailings [13] due to outstanding metal tolerance and accumulation ability and limitation of shoot metal translocation which may lessen elements dispersed into the environment through herbivores or at senescence [31].

Iron (hydr)oxide precipitates, or plaques, occur on root surface of aquatic plants, likely resulting from radial oxygen diffusion and subsequent oxidation of ferrous iron. The component of iron plaque was reported as lepidocrocite (γ-FeOOH), a mixture of lepidocrocite and goethite (α-FeOOH) and ferric phosphate [32,33]. Root plaques may also contain a variety of metals including aluminum, arsenic, manganese, chromium, mercury, nickel, lead and zinc depending upon the chemical environment [34]. In the present study, Mn, Al, Fe ions in the cultivated systems would form oxides on the root surface of *P. australis*. Plaques present on root surfaces usually have high specific surface areas and possess –OH functional groups which are capable of reacting with metals and other cations and anions in the environment. Opinions differ regarding the function of plaques in regulating the toxic species in wetland. Some researchers suggested that it may act as a barrier to inhibit metal uptake by plants [34], whereas others thought that plaques may enrich heavy metals around roots. This fraction of metal would be mobilized or transformed to be bioavailable under some circumstances [35]. In present study, dithionite–citrate–bicarbonate (DCB) method was used to extract Cd associated with plaques. Cd concentration was found to vary for different metal (hydr)oxides: 30–35 mg kg^{-1} for Al(OH)$_3$, Fe$_3$O$_4$ and Al$_2$O$_3$; <20 mg/kg for FeOOH and MnO$_2$. Cd concentration in DCB extraction had positive correlation with Cd accumulation in root tissues ($p < 0.05$) indicating that plaques did not limit heavy metal uptake under the conditions in this study.

3.2. Cadmium desorption by low-molecular-weight organic acids

The bioavailability of Cd was strongly speciation-dependent and largely controlled by the adsorption ability and bonding stability of the metal (hydr)oxides. Three typical LMWOAs with one, two and three carboxyls respectively were chosen to evaluate the difference of Cd adsorption strength on different metal (hydr)oxides and to establish its relationship with the bioaccumulation characteristics by *P. australis*.

Figs. 2–4 show the desorption of Cd from different (hydr)oxides by acetic, malic and citric acid, respectively. The desorption behavior was markedly different for the Cd adsorbed on different (hydr)oxides indicating remarkable difference in the adsorption affinity and stability of these minerals for Cd ions. The desorption degree followed the decreasing order: Al(OH)$_3$ > Fe$_3$O$_4$ > Al$_2$O$_3$ > FeOOH > MnO$_2$ for the acetic and malic acid treatment systems, and Al(OH)$_3$ $\geq$ Al$_2$O$_3$ > Fe$_3$O$_4$ > FeOOH > MnO$_2$ for the citric acid treatment system. The results suggest that Al(OH)$_3$ adsorbed Cd is the most readily desorbable Cd species among the minerals considered in the present work, whereas the Cd bound to MnO$_2$ the least easily desorbable, in between remaining Al$_2$O$_3$ and Fe$_3$O$_4$. This is in good agreement with the uptake order of these minerals adsorbed Cd by *P. australis*, i.e. Cd bound to Al(OH)$_3$ is the most bioavailable form while MnO$_2$ adsorbed Cd is the least bioavailable species. LMWOAs produced at soil–root interface may play an important role in the mobilization and bioavailability of Cd to plants due to pH decreasing and metal–ligand complexation in rhizosphere [36]. The exudations from the root such as LMWOAs were found to transform Cd species in rhizosphere into bioavailable forms [37].
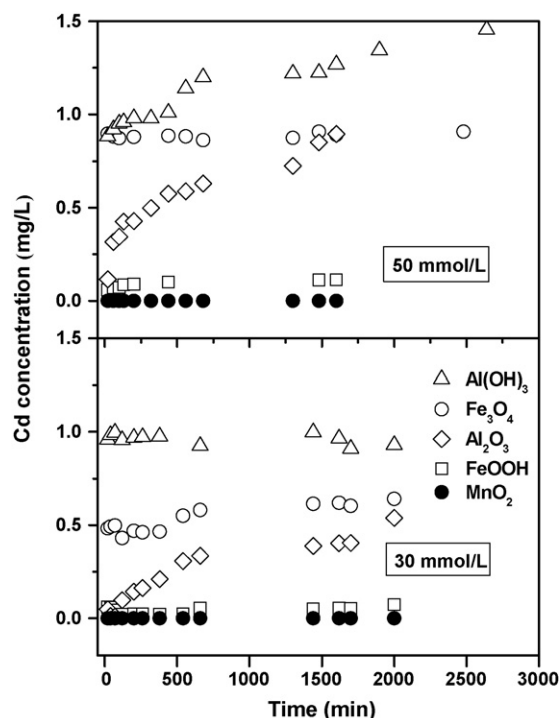

Fig. 2. Desorption of Cd associated with different oxide minerals by different concentrations of acetic acid at pH 5.5.

Cd desorption was observed to increase appreciably with increasing concentration and carboxyl groups of the LWMOAs. Desorption of Cd ions from the surface of metal oxide may have involved two mechanisms. LWMOAs may compete with Cd ions for similar binding sites in the oxides since carboxyl groups interact with oxide surface via inner-sphere complexation. In addition, the organics may also form complexes with Cd ions through their carboxyl
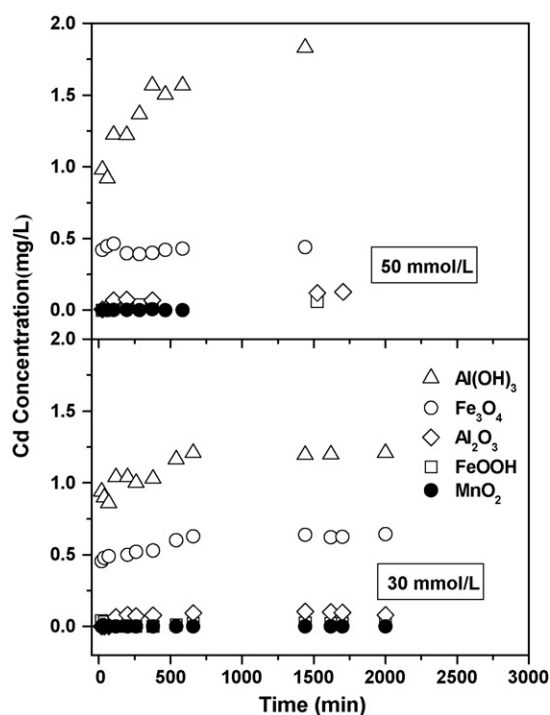

Fig. 3. Desorption of Cd associated with different oxide minerals by different concentrations of malic acid at pH 5.5.
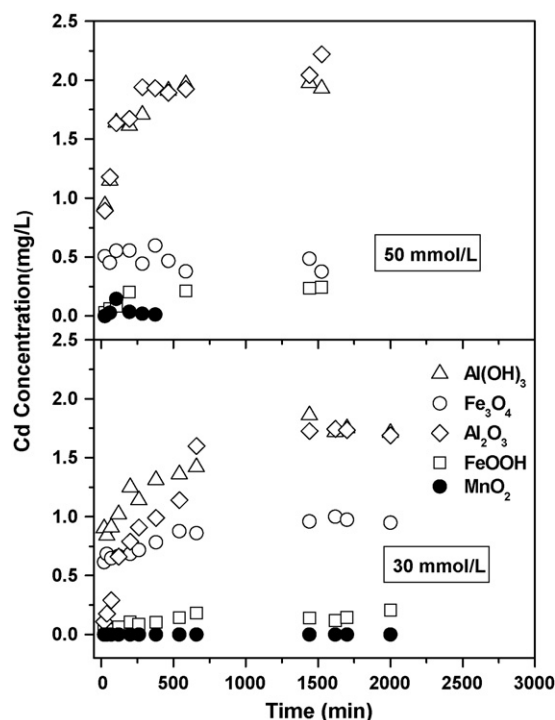
Fig. 4. Desorption of Cd associated with different oxide minerals by different concentrations of citric acid at pH 5.5.

groups. Both effects can initiate Cd desorption when oxides with previously adsorbed Cd ions are brought to contact with LMWOAs. Acetate can only form monodentate complexes with metals, while malate and citrate carrying two or three –COO groups can form chelates with five- or six-membered ring structure which are more stable than monodentate complexes, hence leading to enhanced Cd desorption from the oxides.

LMWOAs found in the environment (especially in rhizosphere where the concentration may be beyond 10 mmol/L) comprise mono-, di-, and tricarboxylic acids. They are exuded by plant roots and function as ligands increasing heavy metal desorption from soil, thus enhancing its mobility by complexing of metal cations or competition for binding sites [38]. Therefore desorption of Cd from metal oxides by LMWOAs can reasonably be indicative of its bioavailability to plants. The difference of Cd desorbability from different metal oxides is in good agreement with its bioaccumulation characteristics by *P. australis*.

4. Conclusions

The bioaccumulation characteristics of mineral-associated heavy metal ions strongly depend upon the type of the substrate minerals due to the difference of mineral–heavy metal interaction strength. This work investigated for the first time the bioavailability of various oxide minerals adsorbed Cd ions by a common wetland plant species *P. australis*. The adsorption strength of Cd on various oxides was evaluated by LMWOAs, the major components of plant root exudes which are proposed to be responsible the remobilization of heavy metals in rhizosphere. The major findings of the study are:

(1) The bioavailability of different oxides adsorbed Cd to *P. australis* was distinctly different. Cadmium associated with aluminum (hydr)oxides was more bioavailable than that adsorbed on Fe- and Mn-oxides probably attributing to the weak adsorption strength of Al(hydr)oxides–Cd. The discrepancy of the nature

of different metal oxides resulted in the diversity of adsorption capacity and oxide–Cd bonding strength which would overridingly influence the bioavailability of Cd.

(2) Desorbability of adsorbed Cd on various oxides by LMWOAs can be indicative of Cd-oxide bonding strength and Cd bioavailability. Desorption of Cd by acetic acid and malic acid followed the order: $Al(OH)_3 > Fe_3O_4 > Al_2O_3 > FeOOH > MnO_2$, while by citric acid: $Al(OH)_3 \geq Al_2O_3 > Fe_3O_4 > FeOOH > MnO_2$. This was consistent with the Cd accumulation degree in the plant.

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