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Metal solubility and speciation under the influence of waterlogged condition and the presence of wetland plants

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ABSTRACT

The effect of wetland plants on metal status in the rhizosphere is species specific. The present study aimed to address the effects of different chemical speciations on metal redistribution and verify changes in metal speciation in the rhizosphere caused by wetland plants based on different radial oxygen losses. The presence of wetland plants increased the redox potential and led to the redistribution of metals in the rhizosphere across different chemical speciations. Associated metals such as Pb and Zn were correspondingly released or co-precipitated, influencing their solubility. The higher the root oxidisation ability of the plant, the greater the effect. However, the presence of wetland plants also transformed metals (Pb and Zn) to a more stable fraction (residual), leading to a lower potential metal bioavailability and leaching process in the long run. Knowledge of these variables and the time-dependent metal behaviour revealed by this study is crucial for the remediation of mine tailings using wetland plants.

1. Introduction

The biogeochemical environment of waterlogged soils and sediments is generally favourable for the immobilisation of metals (Zheng et al., 2013). The general absence of metal tolerance evolution in wetland plants may be related to the attenuated metal toxicity induced by waterlogged conditions (Deng et al., 2006). Storage of mine tailings under water alleviates the potential hazard of dust blows and periodic metal leaching to the surroundings. Thus, constructed wetlands with macrophyte growth are increasingly being used to treat wastewater (Horne, 2000; Zurita et al., 2012; Wu et al., 2015) and rehabilitate mine wastes (McCabe and Otte, 2000; Ye et al., 2004; Rai, 2008). However, metal speciation in soil is often modified as a result of root-induced changes in soil properties (Tao et al., 2004; Hu et al., 2011). The presence of plants can enhance the leaching properties of metals, such as Cd and Zn, via the release of rhizosphere organic ligands (Zhu et al., 1999; Stoltz and Greger, 2002; Dong et al., 2007). As wetland plants can directly affect the metal mobility that regulates the redox potential (E*h*) and pH of soil factors (Wigand et al., 1997; Wright and Otte, 1999; Husson, 2013) via radial oxygen loss (ROL) into the medium surrounding roots (Armstrong et al., 1992; Yang et al., 2012), metals may be mobilised due to sulphide oxidisation and dissolution (Holmer et al., 1998; Jacob and Otte, 2004). In contrast, this ROL from the root may act to remove metals from pore water via ferrous oxidation reactions (Simpson et al., 1998) or the formation of Fe plaque on the root surface (Mendelssohn et al., 1995). However, the effect of wetland plants on the rhizosphere is species specific (Wright and Otte, 1999; Stoltz and Greger, 2002), possibly due to the varied ability of root oxygen release (Brix, 1993). Therefore, whether the metals are immobilised by waterlogged conditions or by the presence of wetland plants must be clarified.

The mechanisms according to which metal accumulates in soil indicate the presence of five major geochemical fractions (Tessier et al., 1979; Salomons et al., 1988): (i) exchangeable; (ii) bound to carbonate; (iii) bound to Fe/Mn oxides; (iv) bound to organic matter; and (v) residual metal. These fractions provide insights into the metal bioavailability phases and the potential mobility of heavy metals under changes in condition (notably pH or E*h*) (Kennedy et al., 1997; Li and Wong, 2010). Several methodologies, including consequential extraction, single extraction and soil leaching experiments, have commonly been used to determine the possible chemical associations of metals in soils and access the mobility and bioavailability of metal (Tessier et al., 1979; Krishnamurti et al., 1997; Zhu et al., 1999; Cukrowska et al., 2004). Although the influence of wetland vegetation on rhizosphere biogeochemistry has received increasing attention (Wright and Otte, 1999; Stoltz and Greger, 2002; Jacob and Otte, 2004; Hinsinger et al., 2009), few studies have addressed the effects of different chemical speciations on metal redistribution.

The effects of waterlogging and different wetland plants (varying by ROL) on metal solubility and chemical speciation (measured by both the sequential extraction procedure and single chemical

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extractant) of Pb/Zn mine tailings under greenhouse conditions were investigated in this study. The main objectives of the study were to (1) assess the effects of metal retention in Pb/Zn mine tailings under submerged conditions; (2) understand how the presence of wetland plants affects Pb, Zn and Fe (solubility) in pore water and their chemical speciations; and (3) compare changes in the metal speciations in the rhizosphere based on wetland plants with different ROLs. Three kinds of pots were used in the experiment: pots drained without vegetation, pots waterlogged without vegetation and pots waterlogged with different wetland plants. It was expected that metal solubility (indicated by pore water concentrations) would be lower under waterlogged conditions than under drained conditions. It was also expected that ROL-induced oxidation would lead to changes in the metal partitioned in different chemical fractions and soil solutions. Due to the different ROLs, various changes to the rhizosphere, such as changes to redox potential and metal solubility, were observed across different species.

2. Materials and methods

2.1. Soil and plant materials

A combination of Pb/Zn mine tailings and normal soil with different ratios (w/w) was prepared for plant growth with water level treatment. A surface soil (0–20 cm) from Loi Tung Village, Fang Ling, Hong Kong and a Pb/Zn mine tailing (rich in Pb, Zn, Fe and S) from Shaoguan, Guangdong Province, China were air-dried and sieved through a 2-mm sieve. Subsamples of air-dried normal soil and tailings (passed through 2 mm and 0.1 mm) were tested to determine the pH/EC (soil/water ratio 1:5), total S (CHNS Analyser), total metal concentration (ICP-AES following digestion with conc. HCl + conc. $HClO_4$ [4:1, v/v]) (McGrath and Cunliffe, 1985), DTPA extractable metal concentration (Page et al., 1982) and metal speciation (three-step sequential extraction; see the following) (Ure et al., 1993a; McGrath and Cegarra, 1992).

Cypercus flabelliformis, *Polypogon fugax* and *Panicum paludosum* were selected as the plants, as they were characterised by different spatial patterns of ROL (Deng et al., 2009). That is, *P. fugax* could release oxygen along the whole root, and *C. flabelliformis* and *P. paludosum* confined ROLs to root apical regions. Seeds of *C. flabelliformis* and *P. fugax* were germinated in sand for 1 week, and cuttings of *P. paludosum* were rooted in sand until new tillers emerged, whereupon they were transferred and subjected to clean and contaminated substrates in waterlogged conditions.

2.2. Experimental design

The Pb/Zn mine tailings and normal soil were thoroughly mixed in ratios (w/w) of 0:100% tailings:soil (T0), 12.5:87.5% (T12.5), 25:75% (T25) and 50:50% (T50). About 950 g of each mixture was packed into separate pots (1 L) with V-mark@ fertiliser (V-mark Resources Co. Ltd., Hong Kong) added to make the final nutrients 300 mg N, 92 mg P and 184 mg K/kg (based dry weight). To separate the rhizosphere from the bulk soil, a cubic water-permeable nylon bag (500 mesh, with the same bottom area as the pot) was placed on the upper layer, containing a 250-g soil-sediment mixture to support the plants (rhizosphere, grey part in Fig. 1). The remaining 700-g mixture placed just below was considered bulk soil (light part in Fig. 1). Nine seedlings of *C. flabelliformis*, *P. fugax* and *P. paludosum* were respectively grown in a waterlogged pot, with three replicates per treatment. Unvegetated pots were treated the same way under both drained and waterlogged conditions. For the drained treatment (without plants), soils were watered with soft tap water once daily to keep the moisture at a water holding capacity of about 70%. For the waterlogged treatment (both with and without plants), substrates were kept flooded with about 2 cm of water. The pot experiment lasted 50 d after the seedlings were transplanted. All of the pots were arranged in a randomised block design and maintained

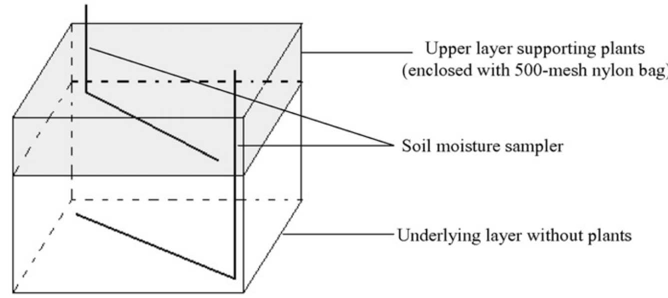

Fig. 1. Diagram of the pot compartments.

under natural light in a greenhouse. Temperature, light and humidity were not regulated. The temperature varied between 18 and 35 °C. During the experiment, pore water was extracted at days 15, 30 and 45 using a soil moisture sampler (Rhizon@ SMS, Rhizosphere Research Products, Netherlands), which was embedded in both the rhizosphere (upper layer) and bulk (underlying layer) soil (Fig. 1), and then acidified to pH 2 before metal (Pb, Zn and Fe) determination. Due to the relatively low concentration in the Pb/Zn mine tailing (314 mg kg^{-1}, Table 1), Mn was omitted from the present study. At the end of the experiment (50 d after onset), the pH and E*h* in both the rhizosphere (upper layer) and bulk (underlying layer) substrates were measured in situ using a portable pH/E*h* metre (ORION model 290). For each pot, about 1.0 g of fresh subsamples from both the rhizosphere (upper layer) and bulk (underlying layer) substrates were collected and subjected to sequential extraction instantly (see below). Soil moisture was determined at the same time. Soil subsamples from the three replicate pots of each treatment were then air-dried and ground (<2 mm) to determine their electronic conductivity (EC) and dissolved organic carbon (DOC) (soil/water ratio 1:5, dissolved organic carbon measured on a Shimadzu TOC-5000) and conduct a single chemical extraction of the metals (Pb and Zn). The dry weight of the plant root was recorded after Fe plaque extraction.

Table 1
The properties of the normal soil from Hong Kong and Pb/Zn mine tailings from Shaoguan, Guangdong of China.

		Normal soil	Pb/Zn mine tailing
pH		6.3	8.1
EC (μs m^{-1})		230	3690
S (%)			17.8
Total metal concentration (mg kg^{-1})	Pb	36	3590
	Zn	94	12,500
	Cu	15	53
	Cd	4.6	102
	Fe	14,170	133,750
	Mn	120	314
DTPA-extractable metal concentration (mg kg^{-1})	Pb	3.5	45
	Zn	3.9	286
	Cu	1.0	2.5
	Cd	0.08	0.38
	Fe	131	0.52
	Mn	8.6	0.47
HOAc soluble (%)	Pb		31.5
	Zn		10.5
Reducible (%)	Pb		14.5
	Zn		1.5
Oxidizable (%)	Pb		44
	Zn		66
Residual (%)	Pb		10
	Zn		22