

Influence of Vetiver Grass (*Vetiveria zizanioides*) on Rhizosphere Chemistry in Long-term Contaminated Soils

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A detailed understanding and appreciation of the important mechanisms operating at the soil:root interface, commonly identified as the rhizosphere, is critical for evaluating the potential for particular plant species to be successfully used as part of a phytoremediation technique. For specific plants, mechanisms may exist to overcome the inherent limitation of the phytoremediation technique when poorly mobile soil metals are of interest. In the present study, the influence of root exudates on the rhizosphere chemistry of soil and consequential metal uptake were investigated following culture of vetiver grass (*Vetiveria zizanioides*), recognized as a promising plant for land stabilization, in three different long-term contaminated soils and one non-contaminated control soil.

The soil solution pH increased (0.3-1.1 units) following vetiver grass culture and dissolved organic carbon (DOC) also significantly increased in all soils with the highest increase in PP02 (23 to 173 mg L⁻¹). Chemical changes are contributed to root exudation by vetiver grass when exposed to high concentration of heavy metals. Chemical changes, consequently, influenced metal (Cd, Cu, Pb, and Zn) solubility and speciation in the rhizosphere. The highest solubility was observed for soil Ko01 (eg. 2091 and 318 µg L⁻¹ for Cd and Pb, respectively). Initial heavy metal solubility in soils varied with soil and either increased or decreased following vetiver grass culture depending on the soil type.

An increase in pH following plant culture generally resulted in a decrease in metal solubility, while elevated DOC due to root exudation resulted in an increase in metal solubility via the formation of metal-DOC complexes. Donnan speciation demonstrated a significant decrease in free Cd and Zn in the rhizosphere and the concentration of Cd, Pb, and Zn in vetiver grass shoot was highly correlated with soluble concentration rather than total soil metal concentration.

Key words: Dissolved organic carbon (DOC), Heavy metals, Phytoremediation, Root exudates, Solubility, Donnan speciation

Introduction

When the soil environment becomes contaminated from either anthropogenic or geogenic sources the elevated contaminants in the soils threaten the sustainability of life and biota (Naidu et al., 2003). In particular, heavy metals are potential major cause of phytotoxicity and are hazardous to humans when the food chain becomes contaminated. For this reason, remediation of contaminated sites worldwide is one of the main duties of industrial societies.

Many remediation techniques have been developed and applied to contaminated site to clean up and for

rehabilitation (Ashley and Lottermoser, 1999; Cartwright et al., 1976; Clark et al., 2001; Pichtel et al., 1997). Among these techniques, phytoremediation is a promising technique to overcome the disadvantages of the conventional engineering-based techniques such as excavation and soil washing which are very expensive and ecologically intrusive. Phytoremediation has the advantages of being cost-effective, environmental friendly and less disruptive to the soil and therefore associated the site ecosystem (Salt et al., 1995). Research towards the successful application of phytoremediation has broadly been conducted in two major areas; a) screening of hyperaccumulators or potential plants having high biomass and resistance to high concentration of heavy metals (Brooks et al., 1997) and b) understanding

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the hyperaccumulation mechanism of the potential plants (Cobbett and Goldsbrough, 2000; Keller et al., 2003; Wang et al., 2002).

One of the potential phytoremediation plants identified is vetiver grass (*Vetiveria zizanioides*), known for its effectiveness in erosion and sediment control (Truong et al., 1995). While this plant is not a heavy metal hyperaccumulator, it has the potential to be applicable for phytoremediation because of its unique morphological, physiological and ecological characteristics including high biomass, massive and deep root system and tolerance for adverse environmental condition including high metal concentrations (Randloff et al., 1995; Xia, 2004). In Australia, vetiver grass was used to stabilize landfill and industrial waste site contaminated with heavy metals such as As, Cd, Cr, Ni, Cu, Pb and Hg (Truong et al., 1995). The maximum Pb accumulated in roots was 2,842 mg kg⁻¹ in the field study and 4,546 mg kg⁻¹ in the pot study. In the pot study, 573 and 773 mg kg⁻¹ were accumulated in the shoots when it was irrigated with 5 to 9 g L⁻¹ of Pb, respectively (Chantachon et al., 2004). In addition, Chen et al. (2000) found that the total above ground uptake of Cd by vetiver grass was even greater than that of the hyperaccumulator, *Thlaspi caerulescens* due to the high biomass of vetiver grass.

Up to date most studies have focused on examining the practical ability of vetiver grass to phytoremediate soils but a basic understanding of accumulation and tolerance mechanism for this species is still poor. In particular, vetiver grass root interactions with heavy metals in the rhizosphere and the associated rhizosphere soil properties are poorly understood. Given that plant roots can potentially influence the DOC/OAs (dissolved organic carbon/organic acids) concentrations and soil pH by exudation of organic compounds and counter ions there is a need to elucidate the consequent influences of these properties on metal availability and uptake (Hees et al., 2000; McBride et al., 1997; Sauvé et al., 1997; Temminghoff et al., 1998; Weng et al., 2002).

The objectives of the present study were 1) to

investigate root exudation by vetiver grass in response to high concentrations of heavy metals in long-term contaminated soils, 2) the effect of vetiver grass culture on metal solubility and soil solution speciation and 3) to estimate the subsequent metal uptake by vetiver grass.

Materials and Methods

Soil properties The soils used in the present study were all from long-term contaminated sites with two different contaminant sources to examine source dependence of heavy metal chemistry. The soils were either collected from the vicinity of a Pb and Zn smelter operating in Port Pirie, SA, Australia (PP02 and PP03) or from a military shooting range in The Republic of Korea (Ko02 and Ko03). The bulk soil properties were summarized in Table1.

Plant cultivation Air dried soil (500 g, <2 mm) was weighed into 600 mL opaque plastic pots and saturated with a NPK basal fertilizer nutrient solution (150 mg kg⁻¹ of N as NH₄NO₃, 75 mg kg⁻¹ of P as KH₂PO₄, and 95 mg kg⁻¹ of K as KH₂PO₄) described previously (Quartacci et al., 2005). The nutrient solution was supplied from the saucer through holes in the bottom of the pots to prevent the soil from erosion and leaching of heavy metals that would have occurred if the solution was added to the pots from above.

Soils were allowed to equilibrate for one week and then additional Milli-QTM water was added in the same manner (below from saucer watering) to compensate for moisture loss due to evaporation, and then equilibrated for a further 48 hrs prior to sowing seeds. The experiments were conducted in triplicate for each soil and included a control soil to which no plants were grown, but which was otherwise treated exactly the same way as all other soils studied.

Two slits of vetiver grass trimmed to 10 cm and 5 cm for shoot and root, respectively were transplanted to each saturated soil. The plants were watered every 4 days

Table1. Selected properties of bulk soils.

Soil	pH	O.M.	DOC	Clay	Cd	Cu	Pb	Zn
		%	mg L ⁻¹	%	----- mg kg ⁻¹ -----			
PP02	9.2	0.3	16	12	17.8	446	2427	6472
PP03	8.2	1.7	613	13	3.6	630	625	9759
Ko01	6.2	0.6	15	18	7.9	87	380	55
Ko02	6.4	1.1	58	7	0.1	3.4	24	18

before newly developed shoot is appeared from plant basal. After that it was watered every 3 days until harvest in the same way for initial saturation method described above. The vetiver grass was harvested 10 weeks after transplanting.

Pre-treatment of plant tissues At harvest shoots were cut 1 cm above the soil surface and rinsed twice with Milli-Q™ water. Roots were carefully removed from the surrounding soil and soil particles clinging to the roots removed with vigorous shaking prior to thoroughly rinsing the roots with tap water and a detergent solution prior to rinsing three times with Milli-Q™ water. Washed shoots and roots were dried at 65°C in a fan forced oven until there was no change in the dry weights. Plant tissue was finely ground using a commercial grinder and stored in “ziplock” plastic bags until digested.

Soil analysis

Routine laboratory analyses for characterization of soils

Soil pH and EC were determined in a 1:5 soil:water (w/v) suspension using a combination pH-EC meter (smartCHEM-LAB, TPS, Australia) following 1 hr equilibration. Soil organic matter content was determined using the Walkley-Black method (Nelson and Sommers, 1996) and soil texture was determined using a micro-pipette technique (Miller and Miller, 1987). Total dissolved organic carbon was analysed using an automatic total organic carbon analyser (Model 1010, O.I. Analytical, USA) after extracting soil solution.

Total metal content Heavy metal contents were determined by ICP-MS (7500 series, Agilent, USA) following microwave assisted *aqua regia* digestion. Air-dried soil (0.5 g, <2 mm) was weighed directly into a teflon digestion vessel and *aqua regia* (5 mL) added. The soil suspension was digested in amicro-wave digestion oven (MARS5, CEM, USA) in accordance with Method 3051H (USEPA, 1997). After digestion, the soil suspension was decanted into a 50 mL volumetric flask and made up to volume using Milli-Q water and filtering through 0.45 µm filters prior to analysis. Each batch for a microwave run included a standard reference material (Montana Soil SRM2711, Certificated by National Institute of Standards & Technology, USA) and blank to validate digestion procedures. The concentration of heavy metals determined by *aqua regia* digestion will hereafter be referred to as the total heavy metal

concentration.

Soil solution analysis

Soil solution extraction Following plant harvest, sub-samples of soils from each pot were air dried and soil solution extracted at 70% maximum water holding capacity (MWHC). Soil (20 g, <2mm) was weighed into 20 mL disposable plastic syringes plugged with acid washed glass wool. The syringe was inserted in 50 mL centrifuge tube separated from the base by a polyvinyl chloride (PVC) spacer (Thibault and Sheppard, 1992). Water was added to the soil to obtain 70% of MWHC and the soil was allowed to equilibrate for 24 hr. The resulting soil paste was centrifuged at 905 rcf (2500 rpm) for 25 min. and the isolated soil solutions were filtered through 0.45 µm cellulose acetate disposable filters (Mille™, Millipore). The filtered soil solutions were used for the determination of DOC, anions and cation concentrations, and Donnan Membrane Technique (DMT) speciation.

In order to secure enough soil solution (100 mL) for a single DMT speciation, 25 replicates of syringe extractions for each pot were required. Solutions from individual replicates were isolated and combined to obtain at least 100 mL of solution after filtration. DMT speciation was commenced within 2 hrs of collection.

Analysis of soil solution components Dissolved organic carbon in soil solution was determined directly using a total organic carbon analyser (Model 1010, O.I. Analytical) without any sample modification except filtration.

Organic acids were quantified via ion chromatography (IC) using a Dionex ISC-2000 fitted with an AS19

Table 2. IC operating conditions for organic acids analysis.

Organic acid analysis		
Column	AS19	
Flow rate	0.25 mL	
Column temperature	35°C	
Suppressor current	40 mA	
Elution	Multi-step	
	Time (min)	Eluent conc. (mM)
	0 to 10	7.5 (constant)
	to 11	to 35 (increase)
	to 20	35 (constant)
	to 20.5	to 58 (increase)
	to 30	58 (constant)
	to 30.5	to 10 (decrease)
	to 35	10 (constant)

column (Dionex). The IC conditions for organic acid determination are tabulated in Table 2. The identity of peaks attributed to organic acids in IC was confirmed using LC-MS (1100 series, Agilent, USA) (Chen et al., 2007).

Heavy metals and major cations were analyzed using ICP-MS relative to a Ru internal standard. Periodic determination of quality control standards and blanks ensured accurate metal concentrations were determined.

Speciation of heavy metals using DMT

The DMT system used in the present study was identical to the system used by Temminghoff (Temminghoff et al., 2000) including a negatively charged membrane (BDH, No. 55165 2U). In their study, the conditions of 500 mL donor and 17 mL acceptor were used. However, in this study 100 mL of donor and 8 mL of acceptor solution were used because of the small volume of soil solution collected using 70% MWHC extraction. Operation of the DMT using these conditions modified was validated using an artificial laboratory made solution as described previously (Kim et al., 2007a).

Results and Discussion

Soil solution pH Soil solution pH is one of the crucial chemical properties governing heavy metal solubility in soils. Generally, increases in soil pH resulted in decreased heavy metal solubility through adsorption of heavy metal on to negatively charged soil surface by deprotonation (Feng et al., 2005; Naidu and Harter, 1998). The soil pH can be influenced by plant root operation (Jones, 1998). In particular, the soil-root interface (rhizosphere) is the zone most highly affected by plant root exudation of organic compounds and counter ions where the extent of soil solution pH change is dependent on both soil and plant type (Hinsinger et al., 2005). It was suggested that the acidification of the rhizosphere by plant roots and the consequent increase in metal solubility was involved in the mechanism of hyperaccumulation. However, there has been lack of further information to support this. Instead, in many previous studies, it was observed that the soil pH actually increased after plant culture (Knight et al., 1997; Luo et al., 2000). In the present study, soil solution pH significantly increased (0.3 to 1.1 units) with vetiver grass cultivation as compared with the control soil in all soils examined (Table 3). Of all the possible

mechanisms the most likely explanation for this is exudation by plant roots of negative moieties such as hydroxide to balance charge in the root cell due to the increased uptake of nitrate and phosphate anions during plant growth. The increased pH suggests that vetiver grass does not exhibit a solution acidification mechanism in the rhizosphere and yet solubilize metals.

Table 3. Soil solution pH; extracted from control soils without plant culture and extracted from vetiver grass cultivated soils.

Soil	Control	Vetiver grass	Δ pH ^a
PP02	7.88 (0.06 ^b)	8.92 (0.03)	1.04
PP03	7.67 (0.09)	8.32 (0.07)	0.65
Ko01	5.5 (0.2)	5.8 (0.1)	0.3
Ko02	5.15 (0.08)	6.20 (0.06)	1.05

a. Δ pH = pH following plant culture - pH in control

b. Standard deviation

Dissolved organic carbon (DOC) Dissolved organic carbon in soil solutions can be operationally defined as the fraction of organic carbons that can pass a 0.45 μ m membrane filter (Herbert and Bertsch, 1995). Generally, the concentration of DOC is higher in the rhizosphere soil when compared to the bulk soil due to plant root exudation which consists of various organic compounds such as organic acids (Jones, 1998). The role of DOC in soil solution chemistry can be broadly divided into two categories, detoxification of metal ions and increase in cation solubility. The elevated DOC by root exudation induced when the roots are exposed to high concentration of toxic metals, forms metal-DOC complexes which are less toxic than the free metal ions (Asao et al., 2003; Nian et al., 2002). In addition, the root exuded DOC may contribute to increases in cation solubility via transportation of cations from the solid phase into the solution phase by metal-DOC complex formation when there is lack of nutrient elements in the rhizosphere (Awad et al., 1994; Jones, 1998).

As expected the concentration of DOC increased following vetiver grass culture in all soils examined. The highest increase was observed in PP02 soil (5 times compared to control) which was the most highly contaminated Cu, Pb, and Zn soil when compared to Ko01 and Ko02 (Fig. 1). While the reasons for the markedly greater DOC content of this soil relative to the acidic Korean soils are unclear, it is likely that this may be due to a combination of alkaline pH and the high metal content. At elevated pHs any exudates released are

more likely to be present in pore water when compared to the slightly acidic soil which may enhance binding of the dissolved organics to soil colloids. Higher DOC may also result from the greater exudation by plant roots when exposed to higher heavy metals in soil (Wenzel et al., 2003). The elevated DOC exuded by vetiver grass roots could be a potential detoxification mechanism. It might be observed that increases in DOC could also increase soluble heavy metal ions in soil solution making metals more accessible to the plant.

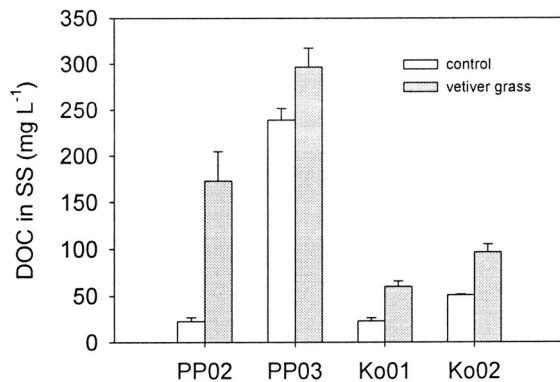


Fig. 1. The concentration of dissolved organic carbon (DOC) in soil solution extracted from control soils and vetiver grass cultivated soils.

Organic acids (OAs) Dissolved OAs contain mono- or multi-dentate functional groups that exhibit strong complex forming ability with heavy metals (Jones, 1998). Although OAs normally constitute less than 10% of the total DOC concentration in soil solution, organic acids have a significant effect on metal chelation and can cause an increase in dissolved heavy metal concentrations (Feng et al., 2005; Hees et al., 2000; Onyatta and Huang, 2003). In our previous hydroponic study, Indian mustard (*Brassica Juncea*) and sunflower (*Helianthus annuus* L.) exuded elevated concentrations of OAs as the concentration of applied Pb increased, while for vetiver grass there was a trend of OAs concentrations to decrease as the applied concentration increased (Kim et al., 2007c). The present pot trial with long-term contaminated soils showed a similar trend. Concentrations of OAs decreased in moderately contaminated Korean soils (Ko01 and Ko02) following plant culture and no significant change in OAs was observed in highly contaminated Australian soils (PP02 and PP03). This implied that for vetiver grass OAs exudation was not involved in increasing soluble metal

ions in soil solution (Fig. 2). This also indicated that the increase in DOC concentration was due to contributions from other organic compounds rather than organic acids (Walker et al., 2003).

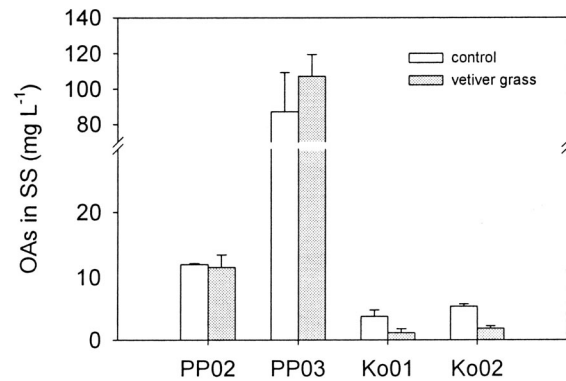


Fig. 2. The concentration of total organic acids (OAs) in soil solution extracted from control soils and vetiver grass cultivated soils.

Heavy metal solubility Overall, the concentration of soluble Cd, Cu, and Pb in soil solution increased in PP02 and Ko01 soils following vetiver grass culture but decreased in PP03 and Ko02 soils (Fig. 3) except Cu increased in Ko02.

The decrease of metal solubility in PP03 and Ko02 was attributed to increases in soil solution pH following vetiver grass culture. In contrast to this, significant increases in metal solubility in PP02 and Ko01 were likely due to significant increases in DOC concentration despite increases in soil solution pH following vetiver grass culture. The elevated DOC removed metal ions from the soil surface and transported them to soil solution by formation of metal-DOC complexes and consequently increased the concentration of metal ions in soil solution. In addition, the metals in these soils were present in a more labile form than the metals present in PP03 and Ko02 soils. Therefore, the elevated DOC efficiently enabled to release the metal ions from binding sites in PP02 and Ko01 soils. In contrast to this, for PP03 and Ko02 soils, the DOC did not exhibit a significant ability to release metal ions from the soil surface despite significant increases in DOC following plant culture. The reason is probably because the metal ions present in these soils are tightly bound to the soil surface and hardly desorbed by DOC complexation (Almas et al., 2000). Moreover, increase in soil solution pH following vetiver grass culture enhanced adsorption of metal ions onto the

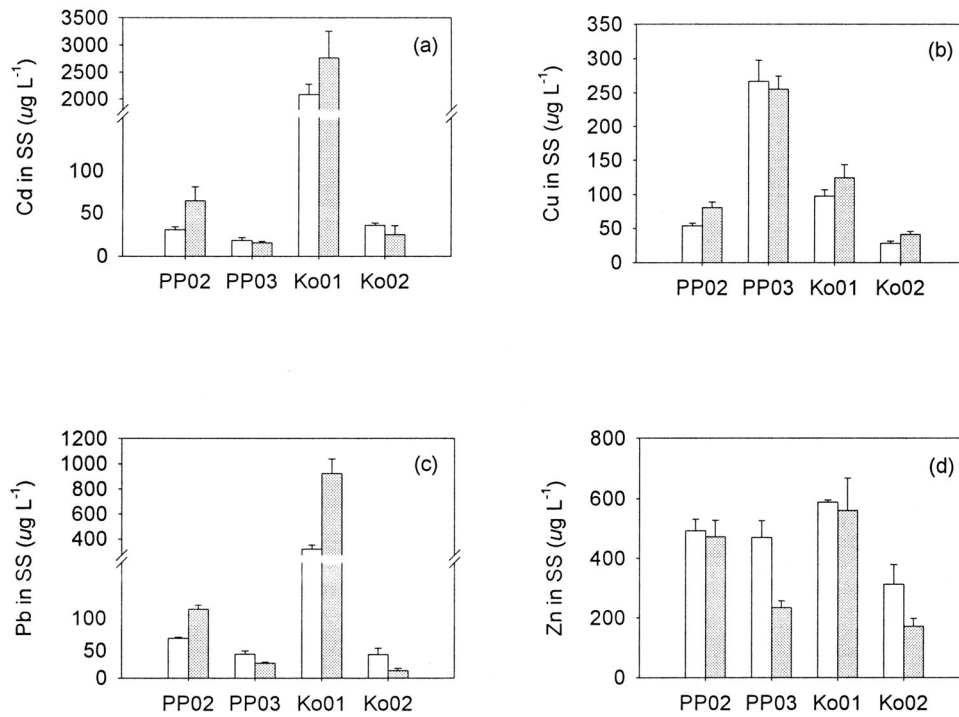


Fig. 3. The concentration of Cd (a), Cu (b), Pb (c) and Zn (d) in soil solution (SS) extracted from control soils and vetiver grass cultivated soils (white bar: control; grey bar: vetiver grass).

soil surface in these soils. This result indicated that the influence of DOC on Cd, Cu, and Pb solubility was considerably dependent on the soil type despite similar increases in DOC concentration by vetiver grass root exudation.

The solubility of Zn showed a different tendency when compared to the other metal ions, showing a decrease in Zn solubility in all the soils examined following vetiver grass culture (Fig. 3). This indicated that the Zn solubility was mainly governed by soil solution pH increased in the rhizosphere and was influenced by DOC significantly less than the other heavy metals. This is supported by the high proportion of free Zn in soil solution as described in the following section and is also expected since Zn is known to form fewer stable complexes with organic

acids relative to the other metals considered here.

Free metal ions in soil solution Despite the free metal ion fraction in soil solution still being identified as the most important species for plant uptake, there is still controversy in the literature as to whether plants uptake free metal ions only or metal ions complexed with ligands as well as free ions (Knight et al., 1997; Sauvé et al., 2000; Vulkan et al., 2000). Hence, investigation of metal speciation influenced by plant root is worthy to supply additional information to address this controversy.

Among the heavy metals tested, only free Cd and free Zn were measurable using DMT because most Cu and Pb ions exist as metal-organic complexes in the soil solution. This is supported by our previous simulation of metal

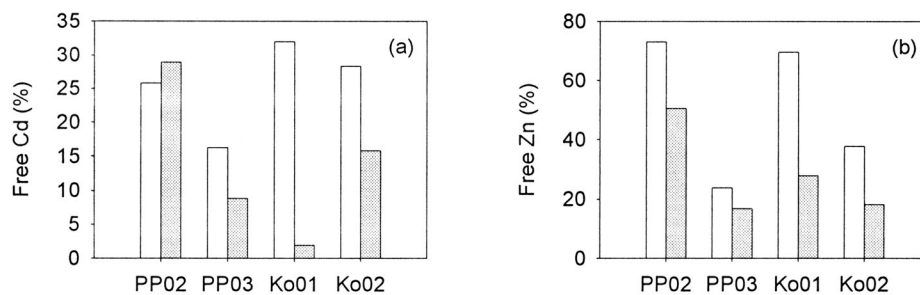


Fig. 4. The fraction of free Cd (a) and Zn (b) in soil solution extracted from control soils and vetiver grass cultivated soils (white bar: control; grey bar: vetiver grass).

speciation using MINTEQA2 (Kim et al., 2007b). For this reason, only Cd and Zn data are presented here.

The fraction of free Cd and free Zn constituted up to 32% and up to 73%, respectively of the corresponding metal concentrations in soils, and PP02 and Ko01 had higher fractions of free metals by DMT when compared to soils PP03 and Ko02 indicating more labile metals in these two soils (Fig. 4).

Following vetiver grass culture, for all soils, with the exception of free Cd in PP02 which increased (It could be an experimental error. Not able to be demonstrated with the current data), the fraction of free Cd and Zn was significantly decreased. The decrease in the fraction of free metal ions following vetiver grass culture is probably due to a) selective uptake of free Cd and Zn by vetiver grass, b) formation of organic complexes by elevated DOC, and c) enhanced metal-ligand complex formation at increased soil solution pH. Recently, it was shown that heavy metal uptake by plants is related with not only the free metal ion concentration but also the metal-ligand complex concentrations (Epstein et al., 1999; Vassil et al., 1998a; Vassil et al., 1998b). Therefore the fraction of free Cd or Zn alone is unlikely to fully explain the total uptake of metals by vetiver grass in the present study. However, it seems that vetiver grass transformed the Cd and Zn ions in soil solution to less toxic metal-organic complex by increasing soil solution pH and DOC, resulting in a decrease in free Cd and Zn despite increases in total soluble Cd and Zn concentrations in soil solution.

Metal uptake Vetiver grass accumulated the highest concentration of Cd from soil Ko01 being 13 times higher than the concentration of Cd from soil PP02 (Fig. 5), relative to the soil PP02 having 2.5 times higher total Cd. This implied that total Cd concentration was not a

good indicator of Cd uptake by vetiver grass and was strongly suggestive of a more labile fraction of Cd being accessed by vetiver grass in soil Ko01.

The results indicated that the soluble metal concentration is critical in determining metal uptake. Soluble Cd concentration was the highest in Ko01 being approximately 70 times higher than the soluble Cd concentrations observed in soil PP02. This hypothesis was also supported by the comparison between the soluble Cd results from PP03 and Ko02. Soil PP03 had a total Cd concentration 36 times greater than that of soil Ko02 and vetiver grass accumulated the same amount of Cd from these two soils even though soil Ko02 had twice the amount of soluble Cd compared to soil PP03. This supported the hypothesis that soluble Cd concentrations are more related with Cd uptake than total Cd concentration.

The importance of soluble metal concentration on metal uptake by plant was also observed with both Pb and Zn uptake. The highest concentration of Pb in vetiver grass shoot was observed in soil Ko01 where the initial soluble Pb concentration was 5 times higher than that in soil PP02 where total Pb was 6 times higher than that in Ko01. In addition, the concentration of soluble Pb in soil Ko02 was dramatically increased by DOC exuded from vetiver grass and might consequently influence Pb uptake. The total Zn concentrations in each soil were not related to the Zn accumulated in vetiver grass shoot. There was only a slight difference in Zn shoot concentrations between soils (Fig. 5) relative to the tremendous difference observed in total Zn concentrations in soils (Table 1). The soluble Zn in each soil was in good agreement with the total Zn accumulated in vetiver grass shoot (see Fig. 3).

The influence of soluble Cu on Cu accumulated in vetiver grass shoot was different from the other metals studied. The concentrations of both total and soluble Cu were the highest in PP03 but the accumulated Cu in vetiver grass shoot cultivated on this soil showed similar concentrations to vetiver grass shoots cultivated in other soils. This strongly suggested that there was another factor, distinct from Cu concentration in soil and soil solution, influencing Cu uptake and translocation. This other factor could potentially be the ability of a soil to resupply metals to the soil solution. For instance, we have surmised above that Cu in PP02 and Ko01 are present in more labile forms relative to that in other soils and that Cu exists in far less labile form in soil PP03. The concept

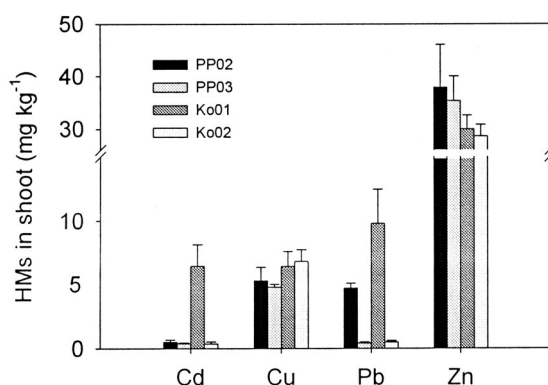


Fig. 5. The concentration of heavy metals (HMs) in vetiver grass shoot.

of an effective concentration (CE), which included soil solution concentrations as well as the concentration resupplied from the solid phase was first introduced by Zhang et al. (2001). They found that Cu concentrations in plant shoots were linearly related to CE and not to other Cu measurements (free Cu activity, EDTA extraction, and soil solution concentration) (Zhang et al., 2001). Based on this concept, we concluded that the Cu uptake relied not on the soil solution concentration alone but on the ability of the soil to resupply Cu to the soil solution as it became depleted.

Conclusion

When exposed to high concentrations of heavy metals present in long-term contaminated soils, vetiver grass increased rhizosphere soil solution pH and DOC concentrations. Consequently, the chemical changes induced by the vetiver grass root in the rhizosphere influenced both metal solubility and speciation. Vetiver grass induced increases in soil solution pH resulted in decreases of metal solubility, while increases in DOC concentrations attributed to root exudates resulted in a significant increase of metal solubility. The increase in both soil solution pH and DOC also influenced the speciation of metals in soil solution. While the fractions of Pb and Cu remained highly complexed prior to and following plant culture, the fraction of free Cd and Zn was decreased following plant culture. This could be either due to detoxification mechanism or a mechanism that increased metal solubility and subsequently enhanced metal uptake.

The extent to which pH and DOC influenced metal solubility was considerably dependent on soil type. The magnitude of increase in metal solubility due to elevated DOC was much greater in PP02 and Ko01 soils due to the presence of metal ions in a more labile form when compared to other soils, despite significant increase in soil solution pH following vetiver grass culture. The Cd, Pb and Zn uptake by vetiver grass was highly related to the solubility of these metals rather than total soil metal concentrations, and Cu uptake was influenced most significantly by the ability of the soil to resupply metal to the soil solution effectively.

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중금속으로 오염된 토양에서 근권부의 화학적 특성에 미치는 vetiver grass (*Vetiveria zizanioides*)의 영향

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일반적으로 근권부로 알려진, 토양과 뿌리 사이의 계면(soil-root interface)에서 일어나는 주요 기작에 대한 세부적 이해는 성공적인 phytoremediation 기술을 위해 특정 식물의 적용 가능성을 평가하는데 있어 매우 중요하다. 가령 어떤 식물은 토양중 낮은 중금속 유효도라는 제한인자를 극복하기 위해 근권부에서 특정 기작을 일으키기도 한다. 본 연구는 토양 고정 (land stabilization)에 탁월한 효과를 보이고 있는 vetiver grass(*Vetiveria zizanioides*)를 중금속으로 오염된 3가지의 다른 토양에 재배함으로써, 식물 뿌리가 근권부 토양의 화학적 특성에 미치는 영향과 이에 따른 식물의 중금속 흡수 특성을 조사하였다.

Vetiver grass 재배 후 근권부 토양의 토양수 pH는 시험에 이용된 모든 토양에서 0.3-1.1 만큼 증가하였고, 토양수 중 유기탄소의 함량도 23 mg L⁻¹ 에서 173 mg L⁻¹로 가장 많이 증가한 PP02 토양을 비롯해서 모든 토양에서 증가하였다. 이와 같은 근권부 토양수의 화학적 변화는 중금속 오염토양에 노출된 vetiver grass의 뿌리에서 나온 분비물(exudates)에서 비롯된 것이다.

결과적으로 근권부 토양수의 화학적 특성 변화는 중금속(카드뮴, 납, 구리, 아연) 유효도 및 화학종 변화에 영향을 미쳤다. 중금속의 최초 유효도는 시험에 이용된 토양의 종류에 따라 달랐으며 vetiver grass 재배 후 이 유효도의 변화 또한 토양 종류의 영향을 받아 증가 또는 감소하였다. 가장 높은 중금속 유효도를 보인 토양은 Ko01 토양으로 토양수 중 카드뮴과 납의 농도가 각각 2,091 µg L⁻¹, 318 µg L⁻¹ 이었다. 일반적으로 vetiver grass에 의해 증가한 pH는 중금속 유효도를 감소시켰고, 반면에 증가한 유기탄소는 토양중 중금속과 복합물질을 형성하면서 토양수 중 중금속의 농도를 높였다.

Donnan speciation 기술을 이용한 화학종 분리 결과 토양수 중 순이온으로 존재하는 카드뮴과 아연의 농도가 현저히 감소하였고, vetiver grass에 의하여 체내에 축적된 중금속의 함량은 토양중 중금속 총함량이 아닌 토양수 중 중금속 유효도와 깊은 관계를 보였다.