

Bioaccumulation of zinc, lead, copper, and cadmium from contaminated sediments by native plant species and *Acrida cinerea* in South China

Chang Zhang · Na Song · Guang-Ming Zeng ·
Min Jiang · Jia-Chao Zhang · Xin-Jiang Hu ·
An-Wei Chen · Jia-Mei Zhen

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Abstract This research was conducted to search and identify spontaneously growing heavy metal-tolerant plant species that are potentially useful for phytoremediation in contaminated sediment. Five sites were selected for collection of plants growing on polluted shore (river bank) sediment of the Xiang River, China. The concentrations of Zn, Pb, Cu and Cd in plants, sediments, and grasshoppers were determined using flame atomic absorption spectrophotometer (AAS700, Perkin-Elmer, USA). Considering translocation factor and bioaccumulation factor, *Rumex crispus* (Polygonaceae), *Rumex dentatus* (Polygonaceae), and *Lagopsis supina* (Labiatae) could be potentially useful for phytostabilization of metals. *R. crispus* can be considered potentially useful for phytoextraction of Cd. In light of the biomagnification factors, grasshoppers are deconcentrators for Pb and Cd, microconcentrators for Zn and macroconcentrators for Cu to the plants, respectively. To the best of our knowledge, the present study is the first report on Zn, Pb, Cu and Cd accumulation in *R. crispus* and *L. supina*, providing a pioneer contribution to

the very small volume of data available on the potential use of native plant species from contaminated sediments in phytostabilization and phytoremediation technologies.

Keywords Sediment contamination · Phytoremediation · Hyperaccumulator · Heavy metals

Introduction

It is well-known that heavy metal pollution has reached to a promising toxic level due to consequences of anthropogenic activities and industrialization (Brown et al. 1995; Sainger et al. 2011). Even though some heavy metals are essential elements for a wide range of organisms and play structural roles in many proteins, excess in sediment has caused detrimental effects damaging plants, animal and human health. Heavy metals, such as cadmium, chromium, lead, etc., have been classified as carcinogenic to humans and wildlife by International Agency for Research on Cancer (Beyersmann & Hartwig 2008). Heavy metals not only affect plant growth and productivity but also enter the food chain (An et al. 2001; Sahi et al. 2002; Zrnčić et al. 2013) through water and contaminated plant products, as the plants easily become biomagnified in these organisms.

Extensive efforts have been made and strategies have been introduced to reduce the negative effects of heavy metal pollution on the environment and human health. Conventional techniques, such as vitrification, stabilization, and chemical oxidation, are costly, disruptive, and

C. Zhang · G.-M. Zeng · M. Jiang · J.-C. Zhang · X.-J. Hu ·
A.-W. Chen · J.-M. Zhen
College of Environmental Science and Engineering,
Hunan University,
Changsha 410082, China

C. Zhang (✉) · N. Song · G.-M. Zeng · J.-C. Zhang ·
X.-J. Hu · A.-W. Chen · J.-M. Zhen
Key Laboratory of Environmental Biology and Pollution
Control (Hunan University), Ministry of Education,
Changsha 410082, China
e-mail: zhangchang@hnu.edu.cn

labor-intensive (Butcher 2009; López et al. 2007). Phytoremediating organic xenobiotics are becoming increasingly popular as an unobtrusive, cost-effective remediation strategy for removing pollutants from soil. Recently, phytoremediation has been proved as a sustainable and cost-effective technology for environmental cleanup (Lelie et al. 2001; Xie et al. 2009). What's more, this technology is more environmentally friendly because the plants have a natural ability to absorb toxic chemicals from soil into above ground biomass. The contaminants can then be extracted from the harvested plants and processed appropriately (Xie et al. 2009). Currently, several specifically selected plant species, called hyperaccumulators, have been utilized to bioaccumulate excessively high amounts of heavy metals from sediment without leading to toxicity in the phytoremediation process. Phytostabilisation requires metal-tolerant species that are efficient in both rapid coverage of the contaminated sites and exclusion of toxic metals from plant parts that are consumed by herbivores (Mench et al. 2009; Vangronsveld et al. 2009).

Researchers have developed important indexes to assess the environmental parameters on metal bioavailability. Sainger et al. (2011) defined bioaccumulation factor (BAF) as the ratio of total metal concentration in shoots to that in soil (DW: dry weight). The translocation factor (TF) is defined as the ratio of total metal concentration in the plants shoot to that in the roots (Zu et al. 2005). Hyperaccumulators of Cu and Pb were defined as plants containing over $1,000 \mu\text{g}\cdot\text{g}^{-1}$ (ppm) of any of these elements in the dried matter; for Zn, the criterion is $10,000 \mu\text{g}\cdot\text{g}^{-1}$ (1 %) (Baker & Brooks 1989). Hyperaccumulation of heavy metals is possible in a total of over 500 plant species, reportedly comprising of 101 families [i.e., Asteraceae, Brassicaceae, Caryophyllaceae (Sarma 2011)]. Metal hyperaccumulation occurs in approximately 0.2 % of all Angiosperms and is particularly well represented in the Brassicaceae (Krämer 2010; Sarma 2011). Considerable attention has been attracted to the metal hyperaccumulating plant species during last decades because of their remarkable ability for cleaning up contaminated soils (Rascio & Navari-Izzo 2011).

The shore sediment in Zhuzhou section of the Xiang River, China was contaminated with significant heavy metals by industrial wastewater from Zhuzhou Smelter, Zhuzhou Chemical Industry Plant, Zhuzhou Electricity Plant et al. Industrial activity has resulted in significant heavy metal pollution, with the consequence that heavy metal concentrations in water and locally grown

vegetables and crops greatly exceed accepted standards and thus threaten the health of human beings (Wang & Arne 2003). Recently, public concern over heavy metals in contaminated soils and their bioaccumulation in living beings has been growing (Sainger et al. 2011; Zhuang et al. 2009). Therefore, searching for plant species with the potential application for phytoremediation is necessary because few metal-tolerant and metal hyperaccumulator plants in this sediment area have been reported. The grasshopper *Acrida cinerea* has a wide host range in Zhuzhou City and was chosen for this study because it is polyphagous. Soil contaminants are accumulated by terrestrial receptors through their diet or by direct ingestion of soil (Brink et al. 2011). A survey of bioaccumulation and translocation related to heavy metal, in this urban area, is important to find native hyperaccumulators of heavy metal and provide a basis for assessment of metal toxicity to insect. This study of the Zhuzhou/Xiang River shore area was undertaken: (1) to determine the concentration of heavy metals in soils, plants, and the grasshopper population of the contaminated area; (2) to compare toxic metal concentration in plant shoots or leaves to that found in roots and the surrounding soils; (3) to compare the concentration of metals in the grasshopper population to those found in the plants; and (4) to check the phytoremediation efficiency of plants dominating the polluted sediment sites.

Materials and methods

Site description

The site chosen for this study is located on the shore of the junction between the Xiang River and the Xiawan River from the Qingshitang district (Fig. 1). Zhuzhou City ($112^{\circ}57'30''$ – $114^{\circ}07'15''$ E, $26^{\circ}03'05''$ – $28^{\circ}01'27''$ N) is the second biggest city of Hunan Province, with a total area of $11,420 \text{ km}^2$ and a population of 3.68 million. The climate in this area is a subtropical moist monsoon climate with an average annual temperature of 17.5°C and the average annual rainfall of 1,408.3 mm. The Xiawan River has been heavily contaminated with heavy metals by emissions of wastewater from a large number of heavy industrialized companies, i.e., Zhuzhou Smelter and Zhuzhou Chemical Industry Plant, etc. The Xiawan River is a tributary of the Xiang River which is the domestic drinking water source for people in the Hunan province. This means the polluted



Fig. 1 Sample collection sites (1–5) at Qingshuitang district, Zhuzhou City, Hunan Province, China

water discharge not only leads to heavy metals accumulation in the sediments of the riverbank but also results in heavy metals entering into the general community because it is ingested by the animals and human.

Sample collection and preparation

Samples include living plants, insects and soil to a depth of 20 cm, i.e., the soil with intensive plants root exploration. *Rumex dentatus*, *Rumex crispus*, *Lagopsis supina*, and Grasshopper were collected in September 2011 along the upstream bank of the Xiang River junction with the Xiawan River. According to Yildirim et al. (2001), *R. crispus* is a perennial wild plant, and it has length of 30–150 cm. Its basal leaves are acute and narrowly lanceolate to oblanceolate. *R. dentatus* is an annual or biennial herb producing a slender, erect stem up to 70 or 80 cm in maximum height. The leaves are lance-shaped to oval with slightly wavy edges, growing to a maximum length around 12 cm. It has allelopathic activity of producing substances that inhibit the growth of other plants near it (Hussain, Mobeen, Kil, & Yoo 1997). *L. supina* is a perennial herb with erect stem length of 15–60 cm. Leaves is palmate with 3 full cracks, which have cog or small cracks. Both sides of the leaf are covered with thick fluff. All of them grow in moist areas, such as lakeshores and the edges of cultivated fields.

Heavy metal concentrations in the tissues of *R. dentatus*, *R. crispus*, and *L. supina* were investigated as these species dominated the studied sites. At least 3 to 5

individual samples of each plant species were randomly collected within the sampling areas. Fresh plant materials were selected by average size, and separated from the soil. All tissue samples of plants were washed thoroughly by the tap water, and cleaned with Milli-Q water twice before separating into roots and shoots. All plant parts were killed out for 5 minutes in an oven at 105 °C, and then dried at 70 °C to a consistent weight. Subsamples were ground through a 30-mesh screen using a stainless steel Wiley Mill before analyses.

The grasshoppers (average length 14–25 mm) were caught from the same sites of the plants. Wet tissue samples were rinsed with ultrapure water (Milli-Q), and then transferred to pre-weighed polypropylene vials, and dried at 60 °C to constant weight. Subsamples of the grasshoppers were also milled before analysis.

Soil samples around the plants roots were collected from the same plant sampling areas. For each site, 10–20 cm samples were randomly collected from three points and mixed into a composite sample. A total of 1 kg subsample of this composite sample per site was taken back to laboratory for further sample preparation and analysis. Finally, homogenized samples were dried at 105 °C to a constant mass and the dried homogenized samples ground into fine powder and sieved through a 200-mesh sieve.

Sample analysis

Soil samples were analyzed for pH and organic matter (Burt 2004). Soil acidity (pH) was measured

using a suspension of soil in water at a ratio of 1:2.5; additionally, this suspension was stirred for 5 min. Organic matter was measured by the Walkley-Black titration method (Walkley & Black 1934). The gravimetric soil moisture content (mass %) was measured by standardized oven-drying method (GB7172-87, National Standard 1987).

To determine the total metal concentrations in the plants and grasshopper components, 0.5 g subsamples of plants and grasshopper were digested in a 4:1 (v/v) mixture of nitric acid (HNO₃) and perchloric acid (HClO₄) using the hot block digestion procedure (USEPA 3050B, USEPA 1996). To determine the total metal concentrations in each soil sample, 0.1 g dried aliquots were weighed into 100 mL PTFE beakers to which nitric acid (20 mL), hydrofluoric acid (5 mL) and perchloric acid (5 mL) were added. The beakers were warmed for several hours, and then the acids were evaporated to incipient dryness. After cooling, the beaker sides were rinsed with ultrapure water, and then 2 mL of perchloric acid was added to the residue, and the contents evaporated once more. 25 mL of nitric acid (2 %, v/v) was added and heated until all the salts had dissolved. Once cooled, the solution was diluted to 100 mL with ultrapure water.

All the digestion solutions were treated as follows: filtrated through 0.45 µm filter, stored at -4 °C, and analyzed within a week. Loss of solution through evaporation was minimized by storage at low temperature. The heavy metal levels in all samples were measured by flame atomic absorption spectrophotometer (Perkin Elmer AA700, USA). To assess the analytical accuracy, three replicated for each sample, a certified reference material (from Sigma-Aldrich Company) and a reagent process blank were performed for each analytical batch.

Data processing and statistical analysis

All treatments were replicated three times in the experiment. The IBM SPSS Statistics 19 and Sigmaplot 12 were used for statistical analysis of data. Pearson product moment correlation coefficients (*r*) were used to express the correlation of quantitative variables, *t* test was used for comparison of means of roots and shoots of plants. ANOVA was conducted for all data, and multiple comparison was used to test the difference between heavy metals levels and evaluate whether the “means” were significantly different, taking *p*<0.05 and 0.01 as significant.

Results

Soil properties

The physicochemical properties of all the soils sampled from the sites are presented in Table 1. As shown, soil pH ranged from 6.47 to 7.94. The concentrations of organic matter in the soils were found to be high and site 1 registered a significantly lower value than the other four sites. The moisture content of soil samples from sites 2 and 3 were similar but different from those in sites 1, 4, and 5.

The soil was mainly contaminated with Zn and Pb although elevated concentrations of Cu and Cd were found. The concentrations of Zn in sediment collected from the sites varied from 423 to 1,992 mg·kg⁻¹. Total Pb and Cu concentrations of the five soil sample sites ranged from 165 to 390 mg·kg⁻¹ and from 76 to 147 mg·kg⁻¹, respectively. Total concentrations of Cd in soils ranged from 14 to 31 mg·kg⁻¹. In order to

Table 1 Characteristics of sediments from five studied sites

Characteristics	Site 1	Site 2	Site 3	Site 4	Site 5
pH (1:2.5)	7.94±0.09	7.58±0.05	6.82±0.00	6.47±0.02	7.35±0.02
MC (%) ^a	19.46±0.32	27.57±0.57	27.73±0.48	21.51±0.25	24.08±0.60
OM (g·kg ⁻¹) ^b	81.0±1.05	155.5±3.63	149.3±43.8	147.6±5.77	137.0±4.78
Total Zn (mg·kg ⁻¹)	1610±53.9	1992±63.5	1034±59.4	1936±87.1	423±18.4
Total Pb (mg·kg ⁻¹)	363±13.2	390±24.9	294±2.8	330±23.1	165±14.7
Total Cu (mg·kg ⁻¹)	147±4.3	137±4.2	76±8.4	101±4.7	87±1.7
Total Cd (mg·kg ⁻¹)	25±0.5	29±0.5	23±1.6	31±0.8	14±4.3

MC moisture content, OM organic matter

express the correlation of metal concentrations among the five sites, Pearson product moment correlation coefficients (r) were used. Total metal concentration in the sediment samples collected from the five different locations were highly correlated with $r=0.93$ (Zn-Pb, $p<0.05$, $N=5$), 0.97 (Cd-Zn, $p<0.01$, $N=5$), and 0.90 (Cd-Pb, $p<0.05$, $N=5$), respectively.

Metal concentrations in plants

Metal concentrations in the investigated plants were very variable. As shown in Fig. 2a, total Zn concentration in roots varied from 211.7 to 480.4 $\text{mg}\cdot\text{kg}^{-1}$, while it ranged from 134.9 to 901.7 $\text{mg}\cdot\text{kg}^{-1}$ in shoots. The maximum Zn concentration was found in the shoots and roots of *R. crispus* from site 4. In addition, the shoots and roots of *L. supina* from site 2 and *R. dentatus* from site 3 accumulated significant amount of Zn. As presented in Fig. 2b, the average Pb concentrations in roots varied from 7.4 to 22.13 $\text{mg}\cdot\text{kg}^{-1}$ and those in shoots were 7.8–46.6 $\text{mg}\cdot\text{kg}^{-1}$. The maximum

Pb concentration was found in shoots of *R. crispus* from site 4, while the maximum concentration in roots was found in *L. supina* from site 2. Pb concentrations in shoots from sites 3 and 4 were similar but nearly double the level of those from sites 1 and 2.

It can be seen from Fig. 2c that the average concentrations of Cu were lower than $50\text{ mg}\cdot\text{kg}^{-1}$. The average concentrations of Cd were lower than $40\text{ mg}\cdot\text{kg}^{-1}$ (Fig. 2d) in all investigated plants. The average Cu concentrations in shoots ranged from 13.3 to 28.6 $\text{mg}\cdot\text{kg}^{-1}$, and those in roots were from 12.4 to 46.0 $\text{mg}\cdot\text{kg}^{-1}$. There was only one plant specimen, i.e., *R. dentatus* from site 3 with similar value of concentrations in both shoot and root. The maximum Cu concentration was found in the root of *L. supina* from site 2, and a considerably high Cu concentration was also found in the root of *R. dentatus* from site 5. Fig. 2d showed that the average Cd concentrations in shoots varied from 3.2 to 37.0 $\text{mg}\cdot\text{kg}^{-1}$, and those in roots were from 2.3 to 20.8 $\text{mg}\cdot\text{kg}^{-1}$. The maximum Cd concentrations were found in shoots and roots of *R. crispus* from site 4. Zn concentrations among the

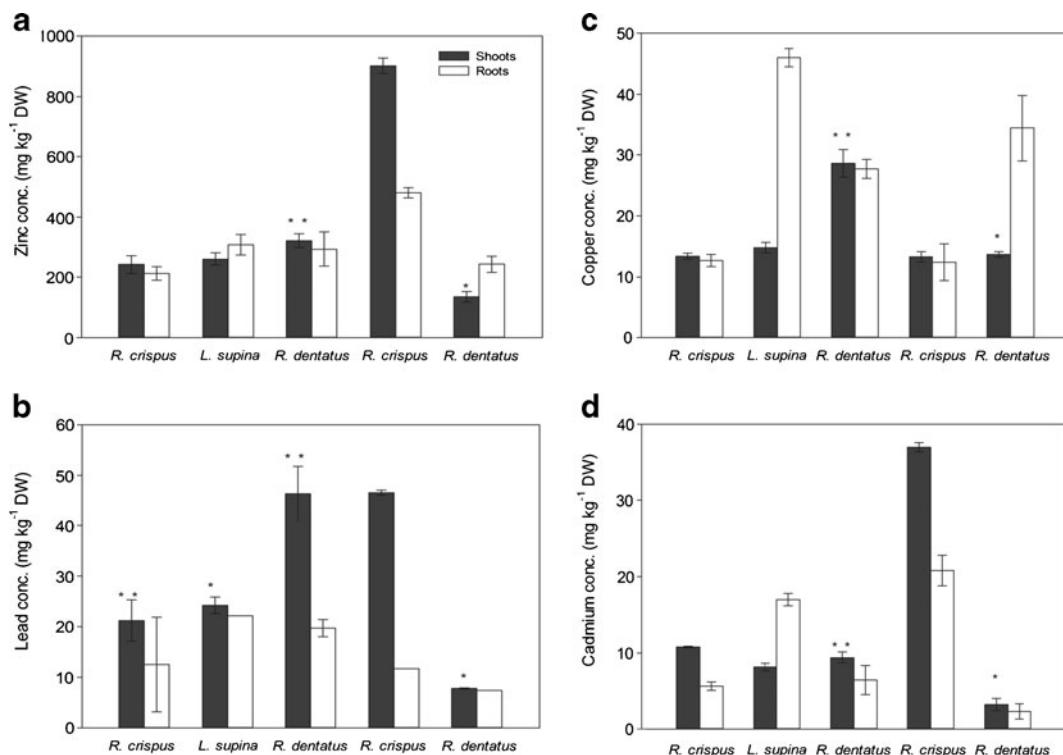


Fig. 2 Metal concentrations in shoots and roots of plant species from five sites: **a** zinc concentration, **b** lead concentration, **c** copper concentration, **d** cadmium concentration. Asterisks * and ** above bars indicate significant differences between shoot

and root for different sampling site at $p<0.05$ and $p<0.01$ according to the t test. Data were presented as the mean values of triplicates ($n=3$)

three plant species collected from five locations, only the plant *R. crispus* from site 4 accumulated Zn concentrations near to $1,000 \text{ mg} \cdot \text{kg}^{-1}$, although some plant species accumulated Zn in considerably high amount (Fig. 2).

Metal concentrations in grasshoppers

As shown in Fig. 3, heavy metals (Zn, Pb, Cu, and Cd) were found in remarkably high concentrations in the plant samples from all five sites. The concentrations of these heavy metals in grasshopper samples were in the order $\text{Zn} > \text{Cu} > \text{Pb} > \text{Cd}$. Concentrations in shoots vs. grasshopper showed that these toxic metals have been differently accumulated in different trophic levels in this ecosystem.

The shoot of *R. crispus* only from site 4 had Zn concentration significantly higher than those in the grasshopper. Both Pb concentration and Cu concentration of the shoots of sites 1–4 were higher than those of the grasshopper, while the shoot of *R. dentatus* from site 5 had concentrations of Pb and Cu lower than that of the grasshopper. In the case of Cu, the accumulation in food plants (producers) never exceeded that of grasshoppers (herbivores). In the grasshopper, the concentration of Cu was higher than those of Pb and Cd.

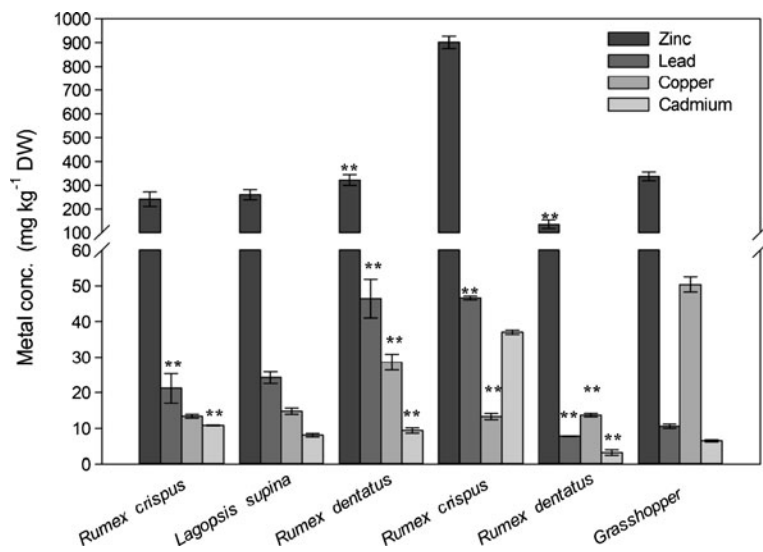
Bioaccumulation and translocation of heavy metals

Plant's potential for phytoextraction can be estimated by comparing, both the TF and the BAF. TF has been used to measure concentration in shoots and in roots

while the BAF has been used to measure the concentration in shoots and the concentration in soils. TF and BAF in plant species greater than 1 means that plant species are suitable for phytoextraction (Salt et al. 1998; Sainger et al. 2011). The TFs and BAFs of the collected plants for four metals are shown in Fig. 4. For Pb, *R. crispus* from site 4 had the highest TF (3.98) among all the plants screened and all the plant species had the TF greater than 1. This indicated that these plant species were efficient in translocating Pb in shoots, although BAF of all the species for Pb was less than 1 (Fig. 4b). But the results for Zn were different here, *R. crispus* from site 1 and 4 and *R. dentatus* from site 3 had the TF greater than 1, while the TF values of *L. supina* from site 2 and *R. dentatus* from site 5 were less than 1. What's more, the BAF of the total plants for Zn is less than 1 (Fig. 4b). Though the Cu and Cd concentrations in sediments were relatively lower compared to Zn and Pb, the results documented for Cu were the same as the Zn mentioned above. For Cd, plants from all the sites, except, *L. supina* from site 2 had TF greater than 1 and BAF greater than 1 for only one plant, i.e., *R. crispus* from site 4.

Biomagnification factor (BMF) of metals has been reported previously (Goodyear & McNeill 1999; Leita et al. 1991). Biomagnification factors were calculated as the ratio between the lipid normalized concentrations in the predator and prey (Yu et al. 2011). Fig. 5 shows that for Zn, only *R. crispus* from site 4 had the BMF less than 1, while all other plants from the four sites (1 to 4) registered the BMF greater than 1. All the

Fig. 3 Metals concentrations in shoots of plant species and grasshopper from five sites (mean \pm standard error, $n=3$). DW dry weight. Asterisks * and ** above bars indicate significant differences between plant species and grasshopper for different sampling site at $p < 0.05$ and $p < 0.01$ according to the *t* test



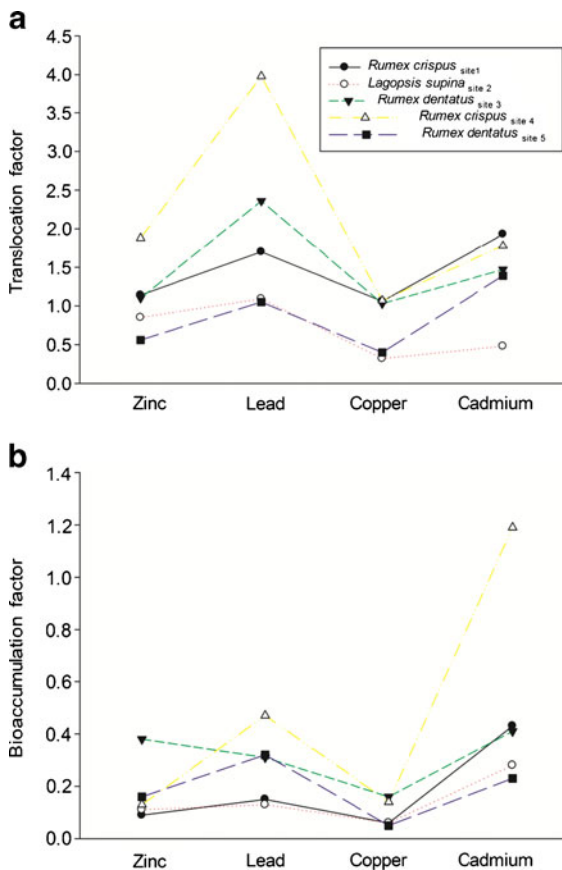


Fig. 4 **a** Translocation factors of the plant species from five sites on zinc, lead, copper, and cadmium; **b** Bioaccumulation factors of the plant species from five sites on zinc, lead, copper, and cadmium

plants species except *R. dentatus* from site 5 registered the BMF less than 1 for Pb and Cd. For Cu, all the plants species had the BMF greater than 1.

Discussion

It is well known that both the soil physicochemistry and metal labile pool for biological action are key factors to enhance the efficiency of phytotechnologies. Metal bioavailable forms are necessary for metal translocation from root to shoot in plants. One of the most influential parameters, controlling the conversion of metals from immobile solid-phase forms to bioavailable solution phase, is the pH of the soil (Sainger et al. 2011). Present studies reveal that high pH values could lead to low trace metal availability in plants. Organic matter is

an important factor that controls the bioavailability of heavy metals in the soil (Karaca 2004). Generally, the chemistry of heavy metal interacted with soil matrix is central to the phytoremediation concept. In the present study, it is evidenced that the heavy metals concentrations in sediments polluted with industrial effluent were above permissible limit prescribed by CPCB (1998) and USEPA (2002). Heavy metal concentrations in sediments increased in the following pattern $Cd < Cu < Pb < Zn$. Results of Pearson correlation coefficients showed that all sites had a high concentration of Cd also tended to have high concentrations of Zn and Pb, which may indicate that all the three metals come from similar sources of contamination. Among all the five sites, the second site was the most contaminated with Zn and Pb. Also to be noted, the first site and the fourth site were the most polluted with Cu and Cd, respectively.

Phytoremediation is the most suitable method for removing heavy metals from the contaminated sites (Sainger et al. 2011). But the potential of phytoremediation techniques using hyperaccumulators has raised some concerns related to the invasiveness and disruption of indigenous ecosystems (Angle et al. 2001), i.e., the ecosystem function change because of the introduction of alien plants. Therefore, alternate options were needed to find native hyperaccumulator plants from the polluted region for sediment remediation of that region (González & González-Chávez 2006). The three plant species that dominated the polluted areas were assessed for their phytoremediation efficiency. In previous studies, Wang and Arne (2003) reported that the normal heavy metal contents of terrestrial plants growing in

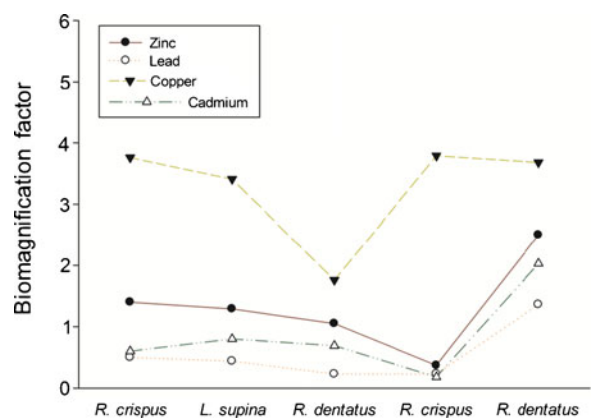


Fig. 5 Biomagnification factors of the grasshopper to the plant species from five sites

uncontaminated soils of Hunan province were found to be $18.0 \text{ mg} \cdot \text{kg}^{-1}$ for Zn, $0.09 \text{ mg} \cdot \text{kg}^{-1}$ for Pb, $2.3 \text{ mg} \cdot \text{kg}^{-1}$ for Cu, and $0.04 \text{ mg} \cdot \text{kg}^{-1}$ for Cd. Results of the study showed that concentrations of Zn, Pb, Cu, and Cd in the investigated species, in the contaminated sediment, were much higher than the normal plant grown in unpolluted sediment. This indicates these plants species have a strong ability to tolerate heavy metals. It was found that the shoots of all plant species accumulated a higher concentration of Pb than those of roots. This showed more translocation and accumulation of Pb in upper parts of plants. This is consistent with earlier reports on sunflower (*Helianthus annuus*), tobacco (*Nicotiana tabacum*), and vetiver (*Vetiveria zizanioides*) in which lead taken up by the plant species was concentrated in both shoots and roots with greater amounts found in the shoots portion (Boonyapookana et al. 2005). Sarret et al. (2001) studied lead accumulation in *Phaseolus vulgaris* and observed that Pb was mostly distributed in shoot tissues. High Pb accumulation in shoots indicates high mobility of Pb from roots to the shoots and mobilization of heavy metals in vacuoles of root cells. Pb is nonessential and toxic to plant growth, and it may be possible that plants have some specific mechanism of transportation Pb (Boonyapookana et al. 2005). As expected, the Cd concentration in shoots was greater than those in roots. This finding is in agreement with other observation reported in some Herbs (Xiao et al. 2010), *Thiaspia caerulea* (Brown et al. 1995), where maximum cadmium accumulated in shoots. In general, cadmium is compartmentalized in vacuole of *T. caerulea* (Ma et al. 2005) and vacuoles in leaf are found to be primary location for Cd sequestration in *Arabidopsis halleri* (Lindsay & Norvell 1978). In the case of Zn and Cu, they were predominantly present both in the roots and leaves of the plants. One reason to explain why these metals were translocated from roots to shoots is that they are essential trace elements for plants.

The high metal accumulation by some cultivars suggests that these plants may be used to clean up toxic metal-contaminated sites in a process termed phytoextraction (Kumar et al. 1995; Bech et al. 2012). As the best technology suited for phytoextraction, hyperaccumulators involve the uptake of trace metals and their accumulation in harvestable parts of plants to promote long-term soil cleaning (Sainger et al. 2011). Phytoextraction refers to the uptake and translocation of metal contaminants in the soil by plant roots into above-ground components of the plants (Padmavathiamma & Li 2007). Plants in this study were growing in contaminated sites and exhibited strong metal

adaptability to their environment, as metal concentrations greatly exceeded the levels considered harmful to normal plants. All kinds of standards have been set up for hyperaccumulator plants such as concentration of toxic metals in shoots is 10–500 times as much as those in normal plant, metal concentrations in shoots will always be greater than those in plants' roots (Zu et al. 2005). Other studies described many plant species that are capable of accumulating a mass of heavy metals in their tissues. For example, Barrutia et al. (2009) and Barrutia et al. (2010) considered *Rumex acetosa* suitable for reclamation of Pb, Zn, and Cd contaminated site. Similarly Huang et al. (2011) found that *R. dentatus* was a local accumulator of Cu in Cu-enriched mine soils.

The TFs in *R. crispus*_{site1}, *R. crispus*_{site4} and *R. dentatus*_{site3} were >1, while the BAF were <1 in all of them except BAF in *R. crispus*_{site4} were >1 for Cd. TFs in *R. dentatus*_{site5} were >1 for Pb and Cd but <1 in *L. supina*_{site2} for Cd, while the BAF were <1 in both species collected from contaminated sediments. On the basis of the above results, we can consider that *R. crispus* and *R. dentatus* may be potentially useful for phytostabilization of Zn, Pb, Cu, and Cd, and *L. supina* be useful for phytostabilization of Cd, due to their capacity to restrict the accumulation of elevated amounts to the roots. *R. crispus* could be utilized for phytoextraction technologies of Cd, i.e., the situation of the site 4, because it can store cadmium into vacuoles of the leaves to protect the plants from toxicity. Concentrations of metal uptake and accumulation observed in some plants species collected from different sites gave different indications. This may result from the effect of various factors: the metal concentration in the soil, pH, plant age, etc. Some of the investigated plant species may be metal-resistant or act as metal excluders, so further studies and experiments in lab are still required.

In grasshoppers, the value of biomagnification factor was in the order $\text{Cu} > \text{Zn} > \text{Cd} > \text{Pb}$, although Zn was in significantly higher concentrations than other three metals. Among these four elements, the concentration of Zn in the plant shoots was the highest (about 10–90, 10–70, and 20–100 times higher than Pb, Cu, and Cd, respectively). But it was comparatively low (10–49 times of Pb, 6–7 times of Cu, and only 5–6 times of Cd) in the grasshoppers. The higher bioaccumulations of Cu and Zn could be responsible for their higher toxicity, whereas the lower accumulations of Pb and

Cd in the organisms could be one cause of its less toxicity (Devkota & Schmidt 2000). Further, Cu and Zn are essential metals to the grasshopper, but Pb and Cd are not.

On the basis of BMF, grasshoppers can be compared to spiders that have been assigned to the group of deconcentrators, microconcentrators, or macroconcentrators if $BMF < 1$, $1 < BMF < 2$, or $BMF > 2$, respectively (Agnieszka et al. 2011). Mean value of BMF for Zn is 1.32, so grasshoppers are microconcentrators compared to the plants for Zn. Mean value of BMF for Cu is 3.28, and mean values of grasshoppers are one species of macroconcentrators for Cu. Moreover, BMF_{Cu} and BMF_{Cd} demonstrates clearly that grasshoppers process these two metals in two different ways. The mean values of BMF for Pb and Cd did not exceed 1. This means that the organisms are deconcentrators for Pb and Cd compared to the plants.

Conclusions

In conclusion, five sites contaminated with heavy metals (Zn, Pb, Cu, and Cd) were investigated. The results demonstrate that the heavy metals concentrations exceeded the normal range of sediment and organisms. Heavy metal concentrations of Cd and Pb steadily decreased along the soil–plant–grasshopper food chain, but the concentration of Zn slightly increased while Cu concentration significantly increased from plant to insect larva. *R. crispus* and *R. dentatus* can be considered potentially useful for phytostabilization of Zn, Pb, Cu, and Cd, and *L. supina* can be considered potentially useful for phytostabilization of Cd, due to their capacity to restrict the accumulation of elevated amounts to the roots. *R. crispus* could be utilized for phytoextraction technologies of Cd, i.e., the situation of the site 4. In light of the biomagnification factors, grasshoppers are deconcentrators for Pb and Cd, microconcentrators for Zn, and macroconcentrators for Cu compared to the plants, respectively.

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References

- Agnieszka, B., Grażyna, W., Piotr, W., Elżbieta, S., & Ilona, W. (2011). Metallothioneins and energy budget indices in cadmium and copper exposed spiders *Agelena labyrinthica* relation to their developmental stage, gender and origin. *Comparative Biochemistry and Physiology: Part C. Toxicology and Pharmacology*, 154(3), 161–171.
- An, H. K., Park, B. Y., & Kim, D. S. (2001). Crab shell for the removal of heavy metals from aqueous solution. *Water Research*, 35(15), 3551–3556.
- Angle, J., Chaney, R., Li, Y. M., & Baker, A. (2001). *The risk associated with the introduction of native and hyperaccumulator plants*. USDA, Agricultural Research Service, USA: Abstract.
- Baker, A. J. M., & Brooks, R. R. (1989). Terrestrial higher plants which hyperaccumulate metallic elements: A review of their distribution, ecology and phytochemistry. *Biorecovery*, 1(2), 81–126.
- Barrutia, O., Epelde, L., García-Plazaola, J. I., Garbisu, C., & Becerril, J. M. (2009). Phytoextraction potential of two *Rumex acetosa* L. accessions collected from metalliferous and non-metalliferous sites: Effect of fertilization. *Chemosphere*, 74(2), 259–264.
- Barrutia, O., Garbisu, C., Hernández-Allica, J., García-Plazaola, J. I., & Becerril, J. M. (2010). Differences in EDTA-assisted metal phytoextraction between metallicolous and non-metallicolous accessions of *Rumex acetosa* L. *Environmental Pollution*, 158(5), 1710–1715.
- Bech, J., Duran, P., Roca, N., Poma, W., Sánchez, I., Roca-Pérez, L., Boluda, R., Barceló, J., & Poschenrieder, C. (2012). Accumulation of Pb and Zn in *Bidens triplinervia* and *Senecio* sp. spontaneous species from mine spoils in Peru and their potential use in phytoremediation. *Journal of Geochemical Exploration*, 123, 109–113.
- Beyersmann, D., & Hartwig, A. (2008). Carcinogenic metal compounds: Recent insight into molecular and cellular mechanisms. *Archives of Toxicology*, 82(8), 493–512.
- Boonyapookana, B., Parkpian, P., Techapinyawat, S., Delaune, R. D., & Jugsujinda, A. (2005). Phytoaccumulation of lead by sunflower (*Helianthus annuus*), tobacco (*Nicotiana tabacum*), and vetiver (*Vetiveria zizanioides*). *Journal of Environmental Science and Health: Part A. Toxic/Hazardous Substances and Environmental Engineering*, 40(1), 117–137.
- Brink, N. W., Lammertsma, D. R., Dimmers, W. J., & Boerwinkel, M. C. (2011). Cadmium accumulation in small mammals: Species traits, soil properties and spatial habitat use. *Environmental Science and Technology*, 45(17), 7497–7502.
- Brown, S. L., Chaney, R. L., Angle, J. S., & Baker, A. J. M. (1995). Zinc and cadmium uptake by hyperaccumulator *Thlaspi caerulescens* and metal tolerant *Silene vulgaris* grown on sludge amended soils. *Environmental Science and Technology*, 29(6), 1581–1585.
- Burt, R. (2004). *Soil survey laboratory methods manual* (Soil Survey Investigations Report No. 42. Versión 4.0). USA: United States Department of Agriculture.
- Butcher, D. J. (2009). Phytoremediation of lead in soil: Recent applications and future prospects. *Applied Spectroscopy Reviews*, 44(2), 123–139.

- CPCB, Central Pollution Control Board (1998). *Permissible limit for the discharge of industrial effluents (inland water surface)*. New Delhi.
- Devkota, B., & Schmidt, G. H. (2000). Accumulation of heavy metals in food plants and grasshoppers from the Taigetos Mountains, Greece. *Agriculture, Ecosystems and Environment*, 78(1), 85–91.
- González, R. C., & González-Chávez, M. C. A. (2006). Metal accumulation in wild plants surrounding mining wastes. *Environmental Pollution*, 144(1), 84–92.
- Goodyear, K. L., & McNeill, S. (1999). Bioaccumulation of heavy metals by aquatic macro-invertebrates of different feeding guilds: A review. *The Science of the Total Environment*, 229(1–2), 1–19.
- Huang, W. X., Huang, Y., Ye, F. Y., Shan, S., & Xiong, Z. T. (2011). Effects of copper on phenology and reproduction in *Rumex dentatus* from metalliferous and non-metalliferous sites. *Ecotoxicology and Environmental Safety*, 74(4), 1043–1049.
- Hussain, F., Mobeen, F., Kil, B. S., & Yoo, S. O. (1997). Allelopathic suppression of wheat and mustard by *Rumex dentatus* ssp. Klotzschianus. *Journal of Plant Biology*, 40(2), 120–124.
- Karaca, A. (2004). Effect of organic wastes on the extractability of cadmium, copper, nickel and zinc in soil. *Geoderma*, 212(2–4), 297–303.
- Krämer, U. (2010). Metal hyperaccumulation in plants. *Annual Review of Plant Biology*, 61, 517–534.
- Kumar, P. B. A. N., Dushenkov, V., Motto, H., & Raskin, I. (1995). Phytoextraction: The use of plants to remove heavy metals from soils. *Environmental Science and Technology*, 29(5), 1232–1238.
- Leita, L., Enne, G., Nobili, M. D., Baldini, M., & Sequi, P. (1991). Heavy metal bioaccumulation in lamb and sheep bred in smelting and mining areas of S.W. Sardinia (Italy). *Bulletin of Environment Contamination and Toxicology*, 46(6), 887–893.
- Lelie, D. V. D., Schwitzguébel, J. P., Glass, D. J., Vangronsveld, J., & Baker, A. (2001). Peer reviewed: Assessing phytoremediation's progress in the United States and Europe. *Environmental Science and Technology*, 35(21), 446A–452A.
- Lindsay, W. L., & Norvell, W. A. (1978). Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Science Society of America Journal*, 42(3), 421–448.
- López, M. L., Peralta-Videa, J. R., Parsons, J. G., Benitez, T., & Gardea-Torresdey, J. L. (2007). Gibberellic acid, kinetin, and the mixture indole-3-acetic acid-kinetin assisted with EDTA-induced lead hyperaccumulation in alfalfa plants. *Environmental Science and Technology*, 41(23), 8165–8170.
- Ma, J. F., Ueno, D., Zhao, F. J., & McGrath, S. P. (2005). Subcellular localisation of Cd and Zn in the leaves of a Cd-hyperaccumulating ecotype of *Thlaspi caerulescens*. *Planta*, 220(5), 731–736.
- Mench, M., Schwitzguébel, J. P., Schroeder, P., Bert, B., Gawronski, S., & Gupta, S. (2009). Assessment of successful experiments and limitations of phytotechnologies: Contaminant uptake, detoxification and sequestration, and consequences for food safety. *Environmental Science and Pollution Research*, 16(7), 876–900.
- National Standard (1987). Method for the determination of soil water content, GB1712-87.
- Padmavathiamma, P. K., & Li, L. Y. (2007). Phytoremediation technology: Hyper-accumulation metals in plants. *Water, Air, and Soil Pollution*, 184(1–4), 105–126.
- Rascio, N., & Navari-Izzo, F. (2011). Heavy metal hyperaccumulating plants: How and why do they do it and what makes them so interesting? *Plant Science*, 180(2), 169–181.
- Sahi, S. V., Bryant, N. L., Sharma, N. C., & Singh, S. R. (2002). Characterization of a lead hyperaccumulator shrub, *Sesbania drummondii*. *Environmental Science and Technology*, 36(21), 4676–4680.
- Sainger, P. A., Dhankhar, R., Sainger, M., Kaushik, A., & Singh, R. P. (2011). Assessment of heavy metal tolerance in native plant species from soils contaminated with electroplating effluent. *Ecotoxicology and Environmental Safety*, 74(8), 2284–2291.
- Salt, D. E., Smith, R. D., & Raskin, I. (1998). Phytoremediation. *Annual Review of Plant Physiology and Plant Molecular Biology*, 49, 643–668.
- Sarma, H. (2011). Metal hyperaccumulation in plants: A review focusing on phytoremediation technology. *Journal of Environmental Science and Technology*, 4(2), 118–138.
- Sarret, G., Vangronsveld, J., Manceau, A., Musso, M., Haen, J. D., Menthonnex, J. J., & Hazemann, J. L. (2001). Accumulation forms of Zn and Pb in *Phaseolus vulgaris* in the presence and absence of EDTA. *Environmental Science and Technology*, 35(13), 2854–2859.
- USEPA, United States Environmental Protection Agency (2002). *Effluent Guidelines and Standards. Sub-Chapter N. Parts 400–424*. USA.
- USEPA. (1996). *Acid digestion of sludges, solids and soils, USEPA 3050B, In SW-846 Pt1. Office of Solid and Hazardous Wastes*. Cincinnati: USEPA.
- Vangronsveld, J., Herzig, R., Weynes, N., Boulet, J., Adriaensen, K., Ruttens, A., Thewys, T., Vassilev, A., Meers, E., Nehnevajova, van der Lelie, D., & Mench, M. (2009). Phytoremediation of contaminated soils and groundwater: Lessons from the field. *Environmental Science and Pollution Research*, 16(7), 765–794.
- Walkley, A., & Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter and proposed modification of the chromic acid titration method. *Soil Science*, 37(1), 29–38.
- Wang, H. Y., & Arne, O. S. (2003). Heavy metal pollution in air–water–soil–plant system of Zhuzhou City, Hunan Province, China. *Water, Air, and Soil Pollution*, 147(1–4), 79–107.
- Xiao, H., Zhou, N. B., & Tao, X. J. (2010). Determination of heavy metals in herbs in the Xinqiang River (in Chinese). *Journal of Analytical Science*, 26(1), 119–121.
- Xie, Q. E., Yan, X. L., Liao, X. Y., & Li, X. (2009). The arsenic hyperaccumulator fern *Pteris vittata* L. *Environmental Science and Technology*, 43(22), 8488–8495.
- Yildirim, A., Mavi, A., & Kara, A. A. (2001). Determination of antioxidant and antimicrobial activities of *Rumex crispus* L. extracts. *Journal of Agricultural and Food Chemistry*, 49(8), 4083–4089.
- Yu, L. H., Luo, X. J., Wu, J. P., Liu, L. Y., Song, J., Sun, Q. H., Zhang, X. L., Chen, D., & Mai, B. X. (2011). Biomagnification of higher brominated PBDE congeners in an urban terrestrial food web in north China based on field observation of prey deliveries. *Environmental Science and Technology*, 45(12), 5125–5131.

- Zhuang, P., Zou, H. L., & Shu, W. S. (2009). Biotransfer of heavy metals along a soil–plant–insect–chicken food chain: Field study. *Journal of Environmental Sciences*, 21(6), 849–853.
- Zrnčić, S., Oraić, D., Čaleta, M., Mihaljević, Ž., Zanella, D., & Bilandžić, N. (2013). Biomonitoring of heavy metals in fish from the Danube River. *Environmental Monitoring and Assessment*, 185(2), 1189–1198.
- Zu, Y. Q., Li, Y., Chen, J. J., Chen, H. Y., Qin, L., & Christian, S. (2005). Hyperaccumulation of Pb, Zn and Cd in herbaceous grown on lead–zinc mining area in Yunnan, China. *Environment International*, 31(5), 755–762.