



Uptake of metals and metalloids by plants growing in a lead–zinc mine area, Northern Vietnam

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ABSTRACT

This study was conducted to evaluate the phytoremediation and phytomining potential of 10 plant species growing naturally at one of the largest lead–zinc mines in Northern Vietnam. Total concentrations of heavy metals and arsenic were determined in the plant and in associated soil and water in and outside of the mine area. The results indicate that hyperaccumulation levels (mg kg^{-1} dry weight) were obtained in *Houttuynia cordata* Thunb. (1140) and *Pteris vittata* L. (3750) for arsenic, and in *Ageratum houstonianum* Mill. (1130), *Potamogeton oxyphyllus* Miq. (4210), and *P. vittata* (1020) for lead. To the best of our knowledge, the present paper is the first report on metal accumulation and hyperaccumulation by *H. cordata*, *A. houstonianum*, and *P. oxyphyllus*. Based on the obtained concentrations of metals, bioconcentration and translocation factors, as well as the biomass of these plants, the two latter species and *P. vittata* are good candidates for phytoremediation of sites contaminated with arsenic and multi-metals. None of the collected plants was suitable for phytomining, given their low concentrations of useful metals (e.g., silver, gallium, and indium).

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1. Introduction

Mining activities generate a large amount of tailings that are generally deposited upon the ground surface [1]. Tailings usually provide an unfavorable substrate for plant growth because of their low pH, high concentrations of toxic metals, and low nutrient content [2].

At the present study site, one of the largest Pb–Zn mines in Northern Vietnam, mining activity started in the 18th century and has continued until the present. Long-term mining operations have generated considerable amounts of sulfide-rich waste materials that have been released directly to the surrounding area without treatment. As a result, soil and water are contaminated with heavy metals and As. Of particular concern, water from the main stream in the study area is directly used for irrigation and domestic supply by rural communities located around the mine [3]. This problem gives rise to the need to remediate the mine tailings and drainage contaminated with heavy metals and As.

Soil remediation is primarily accomplished by the physical removal of soils from contaminated sites for landfilling, incineration, or *in situ* stabilization by chemical treatment [4].

These technologies are generally costly and in many cases result in significant secondary damage to the environment [4]. In contrast, phytoremediation is considered a cost-effective and environment-friendly technology for the treatment of soils and water contaminated by heavy metals/metalloids [5–7]. Criteria related to the concentration of metals in plant shoots are used to identify those plants with the greatest potential in phytoremediation [8]. Hyperaccumulators are defined as plants with leaves able to accumulate at least 100 mg kg^{-1} of Cd; 1000 mg kg^{-1} of As, Cu, Pb, Ni, Co, Se, or Cr; or $10,000 \text{ mg kg}^{-1}$ of Mn or Zn (dry weight) when grown in a metal-rich environment [9,10].

Phytomining has also emerged as an environment-friendly technology to allow economic exploitation of low-grade surface ores or mineralized soils that are too metal-poor for conventional mining [11,12]. The use of plant species for both phytoremediation and phytomining appears to be a sustainable approach that would ensure the commercialization of these technologies.

It is important to use native plants for phytoremediation because such plants respond better to the stress conditions at the site than would plants introduced from other environments [13]. Previous studies have investigated the concentrations of heavy metals/metalloids in natural vegetation in and around mining areas, as well as the possible use of such plants for phytoremediation [13–19]. However, few studies have evaluated accumulation of useful metals (e.g., In, Ag, and Ga) in plants and the possible use of these plants for the combined phytoremediation and phytomining.

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The objectives of this research are to (1) determine the concentrations of multiple heavy metals and As in plant species growing on a contaminated site, and (2) assess the feasibility of using these plants for phytoremediation and phytomining.

2. Materials and methods

2.1. Sampling

Plant samples, together with associated soil and water samples in and outside of the mine area, mine drainage, and along the main stream, were collected in March and November of 2009 (Fig. 1). The plants were sampled based on their coverage at the site. A total of 168 plant samples of 10 plant species were collected and identified from seven sites in the mine area and at one site outside of the mine for comparison (Table 1; Fig. 1). The plant species collected were *Ageratum houstonianum* Mill. (Asteraceae), *Commelina communis* L. (Commelinaceae), *Diplazium esculenta* (Retz.) Sw. (Aspleniaceae), *Equisetum diffusum* D. Don (Equisetaceae), *Houttuynia cordata* Thunb. (Saururaceae), *Kyllingia nemoralis* (Cyperaceae), *Leersia hexandra* Sw. (Poaceae), *Potamogeton oxyphyllus* Miq. (Potamogetonaceae), *Pteris vittata* L. (Pteridaceae), and *Selaginella delicatula* (Desv.) Alst (Selaginellaceae) (Table 1).

2.2. Analytical methods

Soil samples were dried at 80 °C for 3 days, ground to a fine size, and homogenized for analysis by X-ray fluorescence (Epsilon

Table 1

Family, species composition, and number of plant samples in and outside of the mine area.

Code name	Family	Species	n
Age	Asteraceae	<i>Ageratum houstonianum</i> Mill.	12
Com	Commelinaceae	<i>Commelina communis</i> L.	15
Dip	Aspleniaceae	<i>Diplazium esculenta</i> (Retz.) Sw.	15
Equ	Equisetaceae	<i>Equisetum diffusum</i> D. Don	15
Hou	Saururaceae	<i>Houttuynia cordata</i> Thunb.	18
Kyl	Cyperaceae	<i>Kyllingia nemoralis</i>	9
Lee	Poaceae	<i>Leersia hexandra</i> Sw.	3
Pot	Potamogetonaceae	<i>Potamogeton oxyphyllus</i> Miq.	12
Pte	Pteridaceae	<i>Pteris vittata</i> L.	63
Sel	Selaginellaceae	<i>Selaginella delicatula</i> (Desv.) Alst	6

5) at Ehime University, Japan, to determine the concentrations of elements in the soil.

Plant samples were separated into roots and shoots, and thoroughly rinsed with deionized water using an ultrasonic cleaner to remove soil particles attached to the plant surfaces. After rinsing, the samples were dried in a ventilated oven at 80 °C for 2 days. The dried samples were ground into fine powder using a mortar mill. Plant samples (20 mg per each) were digested with mixture (H₂O₂:HF:HNO₃ = 2:5:10) for inductively coupled plasma–mass spectrometer (ICP–MS) analysis. Elemental analyses of plant and water samples were performed by ICP–MS (Varian 820-MS) at the Integrated Center for Sciences, Ehime University, Japan.

Reagent blanks and internal standards were used where appropriate to ensure accuracy and precision in the ICP–MS anal-

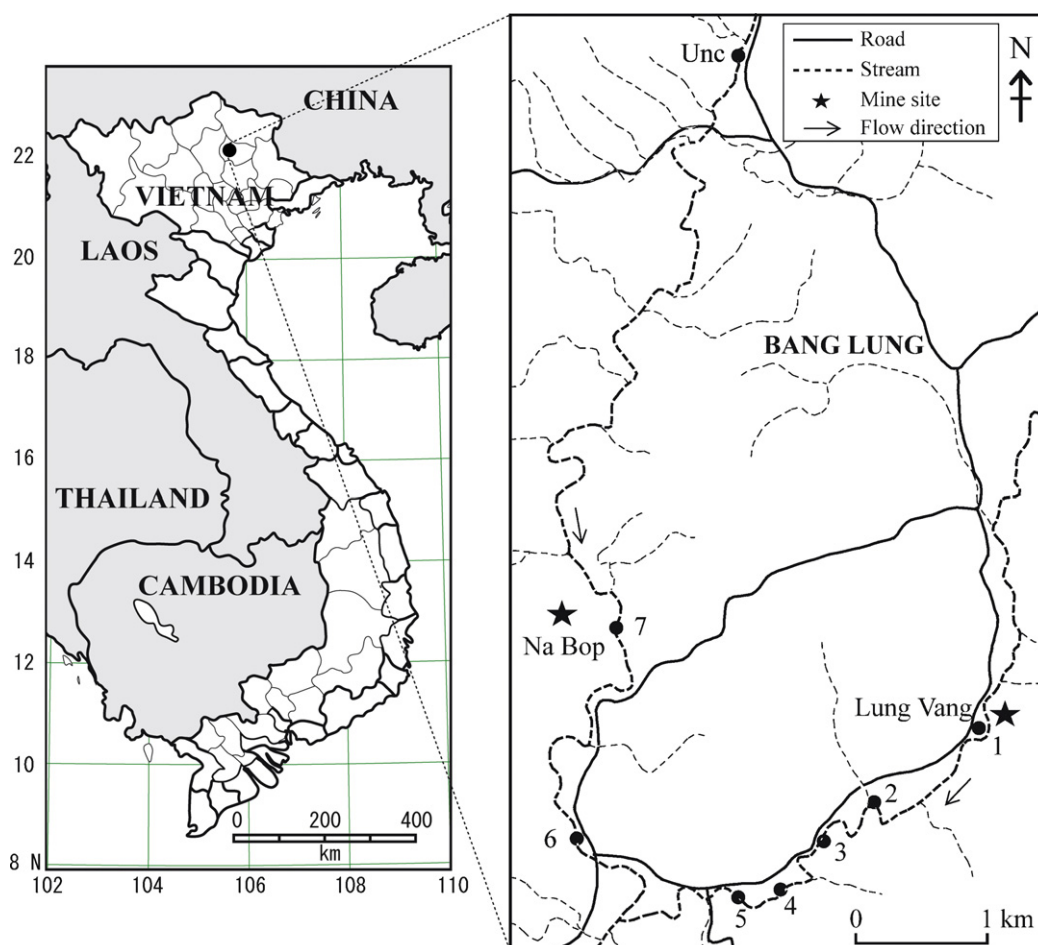


Fig. 1. Map showing the location of the sampling sites. Unc: uncontaminated site.

yses of elements. Certified reference materials NIES CRM No. 1 (National Institute for Environmental Studies, Japan) and SRM 1643e (National Institute of Standards Technology, U.S.A.) were used for quality control of the analytical procedure employed for plant and water samples, respectively, and the recoveries of heavy metals and As were 91–101%.

2.3. Bioconcentration and translocation factors

The bioconcentration factor for soil (BCFs) is defined as the ratio of metal concentration in shoots to that in the soil [10,20]. The bioconcentration factor for water (BCFW) is defined as the ratio of the total concentration of the element in the whole plant to that in the growing solution [21].

The translocation factor (TF), which indicates the effectiveness of a plant in translocation, is defined as the ratio of element concentrations in the shoots to that in the roots [22].

2.4. Statistical analysis

Statistical analyses of experimental data were performed using the SPSS 15.0 package for Windows. All data were tested for goodness of fit to a normal distribution, using a Kolmogorov–Smirnov one-sample test. Data were log transformed where necessary to achieve homogeneity of variance. Student's *t* tests were used to detect significant differences in plant concentrations of heavy metals and As between samples collected in March and November 2009, and between plant roots and shoots. Evaluation of significant differences among means was performed using one-way ANOVA followed by Tukey's post-hoc test, with $p < 0.05$ indicating statistical significance. Pearson product moment correlation coefficients (*r*) were used to express the associations of quantitative variables.

3. Results and discussion

3.1. Concentrations of heavy metals and As in soil and water

Analyses of soil samples revealed very high concentrations of Pb, As, Zn, Mn, and Cd (Table 2). Concentrations of Pb, As, and Zn in all samples from the mine site were significantly higher than those in the sample from outside of the mine site ($p < 0.001$) (Table 2). The highest concentrations (mg kg^{-1}) of Pb, Zn, Mn, Co, Cd, and In were 94,300, 84,700, 74,800, 894, 284, and 101, respectively, as obtained in a sample collected from site 1; the highest concentrations of As, Cu, Ag, Cr, and Ni were 35,900 (site 5), 1050 (site 7), 240 (site 7), 135 (site 2), and 55.6 mg kg^{-1} (site 6), respectively (Table 2). All the concentrations of Cu, Zn, As, Cd, and Pb in soil samples collected from the mine site exceeded Vietnamese standard limits for industrial soil, which are 100, 300, 12, 10, and 300 mg kg^{-1} , respectively [23]. The highest concentrations of As, Pb, Zn, Cd, and Cu in soil were higher than the maximum allowable limits of heavy metals in industrial soil by factors of 2990, 314, 282, 28, and 11, respectively [23]. The concentrations of heavy metals and As in the soil samples were correlated, with $r(41) = 0.34\text{--}0.81$ ($p < 0.05$) for Mn, $0.51\text{--}0.91$ ($p < 0.001$) for Cu, $0.66\text{--}0.93$ ($p < 0.001$) for Zn, $0.35\text{--}0.81$ ($p < 0.05$) for As, $0.34\text{--}0.84$ ($p < 0.05$) for Ag, $0.45\text{--}0.84$ ($p < 0.01$) for Cd, $0.39\text{--}0.89$ ($p < 0.01$) for In, and $0.54\text{--}0.91$ ($p < 0.001$) for Pb. This finding may indicate that all these metals and As were derived from similar sources [13].

Whereas the soil was mainly contaminated by Pb, As, Zn, Mn, and Cd, the water environment in the study area was contaminated by Mn, As, and Pb, with concentrations exceeding WHO standards for drinking water by factors ranging from 2 to 90 (Table 3). The highest concentrations of Mn, Pb, Zn, As, Cu, Ni, and Cd from mine drainage water were 1920, 566, 134, 93.5, 4.77, 3.78, and

Table 2
Mean (range) concentrations (mg kg^{-1}) of heavy metals and As in the soil in and outside of the mine area ($n = 3\text{--}15$).

Element	Sites							Unc ^b
	1	2	3	4	5	6	7	
Cr	n.d. ^c	117 ^{**} (102–135)	45.2 (36.7–52.7)	31.4 (26.6–34.3)	48.2 (25.0–74.3)	49.9 (46.8–52.5)	76.5 (62.5–84.1)	64.8 (59.8–70.2)
Mn	73300 ^{***} (71200–74800)	9320 [*] (5230–13800)	5600 (5430–5930)	14300 [*] (14100–14500)	24200 ^{**} (2630–51500)	1820 (1780–1880)	3470 (1420–6240)	1030 (917–1310)
Co	848 (802–894)	n.d.	n.d.	301 (259–343)	331 (305–357)	81.2 (79.3–83.1)	153 (141–165)	n.d.
Ni	n.d.	26.9 (24.6–30.8)	33.3 (27.4–39.1)	33.7 (31.3–36.5)	48.4 (38.7–57.8)	51.2 (47.1–55.6)	47.9 (7.52–76.9)	33.6 (24.1–44.6)
Cu	715 ^{***} (705–723)	493 ^{***} (195–811)	252 ^{**} (244–265)	210 [*] (202–216)	149 ^{**} (65.8–242)	114 (110–118)	468 ^{***} (124–1050)	40.9 (33.6–47.4)
Zn	82100 ^{***} (79300–84700)	3220 (1840–4730)	7070 ^{***} (6860–7460)	6650 ^{***} (6560–6680)	3810 ^{**} (1490–7780)	1260 ^{**} (1230–1290)	4590 ^{***} (846–10300)	89.5 (79.7–109)
As	9290 ^{***} (8780–9670)	11100 ^{***} (8900–13300)	5830 ^{***} (5580–6180)	10900 ^{***} (10800–11000)	12600 ^{***} (2490–35900)	309 ^{**} (290–319)	1280 ^{***} (307–2560)	4.69 (4.43–5.39)
Ag	186 ^{***} (175–196)	33.8 ^{***} (22.3–48.9)	22.5 [*] (21.8–23.9)	22.5 [*] (18.8–26.2)	7.52 (5.02–10.0)	15.3 (9.31–18.8)	106 ^{***} (41.5–240)	3.08 (2.08–4.79)
Cd	269 ^{**} (257–284)	11.8 ^{**} (8.23–15.2)	39.0 ^{**} (37.9–41.1)	28.8 ^{**} (28.6–29.9)	18.2 ^{**} (5.71–37.4)	4.47 (3.93–5.06)	28.8 ^{**} (1.67–38.2)	1.03 (0.97–1.12)
In	96.7 ^{***} (94.6–101)	12.9 ^{***} (9.42–16.9)	14.4 ^{**} (13.6–15.8)	10.6 ^{***} (9.75–11.4)	3.30 ^{***} (1.37–5.29)	7.42 ^{***} (6.00–9.90)	13.5 ^{***} (2.25–24.9)	0.85 (0.51–1.45)
Pb	91800 ^{***} (89100–94300)	15000 ^{***} (10300–19800)	7600 ^{***} (7260–8030)	6650 ^{***} (6570–6710)	2630 ^{***} (2190–3540)	3350 ^{***} (3210–3450)	30700 ^{***} (16900–77900)	83.1 (58.4–123)

Differentiations between concentrations of each element in the soil at contaminated and uncontaminated sites are significant.

^a Element.

^b Uncontaminated site.

^c Not determined.

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

Table 3
Concentrations ($\mu\text{g l}^{-1}$) of heavy metals and As in the water from mine drainages and stream.

Element	Sites							Unc ^b
	2	3	4	5	6	7		
Cr	3.21 ± 1.37 ^a	2.06 ± 0.09	4.32 ± 0.55	3.51 ± 1.08	3.68 ± 1.67	5.18 ± 1.56	3.55 ± 1.80	
Mn	1920 ± 113 ^{***}	1460 ± 95 ^{***}	75.7 ± 7.4 [*]	346 ± 216 [*]	0.69 ± 0.14	393 ± 62	0.76 ± 0.30	
Co	0.47 ± 0.26	0.45 ± 0.09	0.22 ± 0.03	0.75 ± 0.77	0.16 ± 0.07	0.96 ± 0.01	0.29 ± 0.17	
Ni	3.15 ± 1.42 ^{***}	3.78 ± 0.28 ^{***}	2.30 ± 0.04 ^{***}	2.17 ± 0.30 ^{***}	1.59 ± 0.39 ^{**}	3.75 ± 0.76 ^{***}	0.56 ± 0.48	
Cu	4.77 ± 1.47 ^{**}	1.71 ± 0.13	6.77 ± 5.51	0.94 ± 0.69	0.87 ± 0.29	1.70 ± 0.07	1.47 ± 1.67	
Zn	134 ± 30 ^{**}	134 ± 20 ^{**}	9.20 ± 0.69	7.50 ± 5.30	16.2 ± 14.5	121 ± 10 [*]	1.65 ± 0.55	
Ga	0.10 ± 0.04	0.06 ± 0.01	0.16 ± 0.02	0.03 ± 0.02 ^{***}	0.03 ± 0.04 ^{***}	0.06 ± 0.03	0.25 ± 0.17	
As	13.7 ± 9.1 ^{***}	12.3 ± 1.1 ^{***}	93.5 ± 10.1 ^{***}	80.2 ± 25.8 ^{***}	21.3 ± 12.7 ^{***}	7.73 ± 0.22 ^{***}	0.88 ± 0.36	
Ag	0.09 ± 0.01	0.05 ± 0.01	0.50 ± 0.77	0.04 ± 0.01 ^{**}	0.10 ± 0.15 [*]	0.05 ± 0.01 [†]	0.87 ± 1.04	
Cd	1.01 ± 0.20 ^{**}	0.47 ± 0.15	0.04 ± 0.01 [†]	0.02 ± 0.01 ^{***}	0.11 ± 0.08 [†]	0.75 ± 0.01	0.27 ± 0.16	
In	0.03 ± 0.01	0.04 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	
Pb	566 ± 351 ^{***}	3.09 ± 0.85	0.24 ± 0.04	0.19 ± 0.17	4.58 ± 7.14 [*]	183 ± 23 ^{***}	0.62 ± 0.35	

Differentiations between concentrations of each element in the water at contaminated and uncontaminated sites are significant.

^a Means ± standard deviations ($n=3-9$).

^b Uncontaminated site.

^{*} $p < 0.05$.

^{**} $p < 0.01$.

^{***} $p < 0.001$.

1.01 $\mu\text{g l}^{-1}$, respectively, which are significantly higher than concentrations in water from the uncontaminated site ($p < 0.01$). The concentrations of Cu, As, and Pb in the soil and water samples were correlated, with $r(45) = 0.68$ ($p < 0.001$), 0.60 ($p < 0.001$), and 0.48 ($p < 0.01$), respectively. This finding may indicate that these metals in water were leached from the associated soils.

3.2. Plant accumulation and transport of heavy metals and As

There were no significant differences ($p > 0.05$) in metal concentrations in plants collected in March and November 2009 (Student's t test); therefore, the results presented here are based on the combined data. High concentrations of heavy metals and As in the soil and water may result in high levels of these elements in the collected plant samples. The concentrations of all heavy metals and As varied widely among sites and plant species [24]. The highest concentrations of heavy metals and As (mg kg^{-1} dry weight) in the plant roots were found in *P. vittata* for Pb (12,700), Zn (6190), Cu (160), Ag (35.3), and In (5.66); in *E. diffusum* for Mn (10,100), As (3660), Co (30.2), and Ga (8.70); in *C. communis* for Cr (715) and Ni (191); and in *H. cordata* for Cd (52.8). The highest concentrations in the shoots were found in *P. oxyphyllus* for Mn (5010), Pb (4210), Zn (1810), Ag (13.5), and Co (8.48); in *H. cordata* for Cu (87.5) and Ga (6.75); in *L. hexandra* for Cr (205) and Ni (81.9); in *P. vittata* for As (3750); in *A. houstonianum* for Cd (20.1); and in *S. delicatula* for In (4.28) (Tables 4–6).

Metal concentrations in the plants were poorly correlated with total metal concentrations in the soil. This result was expected because total metal concentrations are considered to be poor indicators of metal availability to plants [15,25]. However, the concentrations of Cu ($r = 0.31$, $p < 0.05$, $n = 51$), Ag ($r = 0.49$, $p < 0.001$, $n = 49$), and In ($r = 0.42$, $p < 0.01$, $n = 49$) in the plant roots were correlated with those in the soil. The concentrations of Zn ($r = 0.70$, $p < 0.001$, $n = 42$) and Cd ($r = 0.81$, $p < 0.001$, $n = 45$) in the plant roots were highly correlated with those in water. Correlations between the concentrations of heavy metals in the plant shoots and those in water were also found for Mn ($r = 0.38$, $p < 0.05$, $n = 45$), Zn ($r = 0.50$, $p < 0.01$, $n = 42$), and Cd ($r = 0.31$, $p < 0.05$, $n = 45$).

Normal and toxic concentrations of heavy metals and As (mg kg^{-1}) are respectively considered to be 0.1–0.5 and 5–30 for Cr, 20–300 and 300–500 for Mn, 0.02–0.1 and 15–30 for Co, 0.1–5.0 and 10–100 for Ni, 5–30 and 20–100 for Cu, 27–150 and 100–400 for Zn, 1.0–1.7 and 5–20 for As, 0.05–0.2 and 5–30 for Cd, and 5–10 and 30–300 for Pb [25]. Most of the collected plant species showed

concentrations higher than these toxic levels for Cr, Mn, Zn, As, and Pb, whereas they showed normal levels for Co, Ni, Cu, and Cd. In addition, all of the plant species were able to adapt very well to growth in soil that was highly contaminated by As and multiple heavy metals, especially Pb, Zn, Mn, and Cd (Table 2). These results may indicate that the plant species growing on the present site, contaminated by heavy metals and As, are tolerant of these metals.

In the previous study, Yoon et al. [13] reported concentrations (mg kg^{-1}) of undetectable to 1183, 6–460, and 17–598 for Pb, Cu, and Zn, respectively, in native plants growing on a contaminated site. MorenoJimenez et al. [15] reported concentrations (mg kg^{-1}) of Mn, Cu, Zn, and Cd of 14.9–400.6, 2.68–70.2, 9.5–1048, and undetectable to 22.04, respectively, in shoots of plants growing in an area surrounding a mine site. Stoltz and Greger [16] reported concentrations of Cu, Zn, As, Cd, and Pb of 6.4–160, 68–1630, 0.7–276, 0.1–12.5, and 3.4–920 mg kg^{-1} , respectively in wetland plant species growing on submerged mine tailings. Rio et al. [17] reported concentrations (mg kg^{-1}) of Pb, Zn, Cu, Cd, and As of undetectable to 450, 13–1138, 1.2–152, undetectable to 9.7, and 0.8–120, respectively, in wild vegetation in a river area after a toxic spill at a mine site. In an analysis of wetland plant species collected from mine tailings, Deng et al. [18] reported concentrations of up to 11,116, 1249, and 1090 mg kg^{-1} for Zn, Pb, and Cd, respectively, in *Sedum alfredii* growing on tailings at a Pb–Zn mine. Chehregani et al. [19] reported concentrations (mg kg^{-1}) of undetectable to 14.6, 9.60–84.0, 4.00–18.5, 4.00–1485, and 20.0–1987 for Cd, Cu, Ni, Pb, and Zn, respectively, in shoots and leaves of plants collected in a waste pool at a Pb–Zn mine. In the present study, the concentrations of Pb, Cu, Zn, As, Cd, Mn, and Ni are higher than those in the plants reported by Yoon et al. [13], Moreno-Jimenez et al. [15], Stoltz and Greger [16], Rio et al. [17], Deng et al. [18], and Chehregani et al. [19], but lower than the concentrations of Cu and Cd in the plants assessed by Stoltz and Greger [16] and Deng et al. [18], respectively.

3.3. Potential plant species for phytoremediation and phytomining

An ideal plant for phytoremediation should have the following characteristics: (1) an inherent capacity to hyperaccumulate and tolerate metals and metalloids in aboveground tissues; (2) a high and fast-growing biomass and be repulsive to herbivores (to prevent the escape of accumulated metals and metalloids to the food chain); (3) BCFs and TF values higher than 1; (4) a widely dis-

Table 4Mean (range) concentrations of Cr, Mn, Co, and Ni (mg kg⁻¹ dry weight) in plant samples in and outside of the mine area (n = 3–63).

Code name	Cr		Mn		Co		Ni	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
Age	25.3 (24.3–27.1)	46.8 ^{**} (45.1–54.9)	704 (683–739)	1030 (970–1130)	0.51 (0.49–0.53)	0.83 (0.75–0.94)	9.14 (8.52–10.4)	12.7 [*] (11.5–14.1)
Com	215 (5.93–715)	22.3 (4.91–36.1)	1080 (244–2110)	672 (160–1570)	3.87 ^{***} (1.77–7.33)	1.12 (0.53–1.73)	74.3 (1.86–191)	7.11 (1.62–10.9)
Dip	69.9 [*] (31.9–109)	5.67 (4.80–6.86)	4600 ^{**} (184–9630)	215 (78.8–434)	8.64 ^{***} (1.16–17.3)	0.61 (0.27–1.37)	39.9 ^{***} (12.0–74.1)	1.82 (1.02–3.48)
Equ	21.6 (9.69–55.5)	63.1 [*] (35.1–105)	7800 ^{***} (3460–10100)	580 (189–1540)	16.5 ^{***} (6.32–30.2)	1.20 (0.37–1.79)	9.56 (4.52–19.2)	21.6 (0.49–35.6)
Hou	7.72 (6.01–9.53)	9.06 (4.81–17.9)	1560 (339–3060)	672 (224–1310)	4.92 [*] (1.68–9.18)	2.21 (0.30–4.55)	3.77 (2.12–4.98)	3.63 (1.02–8.75)
Kyl	21.7 (13.7–41.4)	44.9 ^{**} (40.0–54.4)	1820 (871–4230)	1440 (1080–2110)	5.86 (2.67–11.2)	3.12 (0.88–5.06)	10.7 (7.57–17.4)	13.9 [*] (9.69–18.4)
Lee	112 (111–114)	192 ^{**} (179–205)	3040 ^{**} (2980–3140)	676 (647–727)	10.6 ^{***} (10.2–11.2)	2.01 (1.87–2.23)	48.0 (44.7–54.4)	72.5 [*] (64.4–81.9)
Pot	11.2 (7.23–14.8)	11.5 (6.00–15.3)	3680 (2930–5740)	3140 (2190–5010)	6.92 (4.72–8.63)	6.20 (4.25–8.48)	11.3 (9.41–13.0)	13.8 (8.24–18.9)
Pte	22.9 (4.57–121)	12.7 (4.27–67.9)	1430 (142–1600)	227 (76.3–808)	3.90 (0.81–17.3)	0.61 (0.20–2.54)	9.58 (1.25–43.7)	3.65 (0.49–20.8)
Sel	38.8 (36.6–40.4)	47.9 [*] (40.4–63.2)	712 ^{***} (673–735)	392 (330–430)	4.67 (4.58–4.78)	4.11 (0.89–7.29)	16.9 (15.6–19.2)	15.6 (14.1–19.1)

Differentiations between root and shoot of each element of the same plant species are significant.

^{*} p < 0.05.^{**} p < 0.01.^{***} p < 0.001.**Table 5**Mean (range) concentrations of Cu, Zn, Ga, and As (mg kg⁻¹ dry weight) in plant samples in and outside of the mine area (n = 3–63).

Code name	Cu		Zn		Ga		As	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
Age	19.0 (18.7–19.6)	22.8 (21.8–24.1)	1130 (1110–1180)	1210 (1200–1220)	0.52 (0.37–0.61)	0.89 (0.68–1.28)	162 (145–195)	209 (166–280)
Com	33.0 (25.7–39.1)	26.3 (14.1–42.7)	448 (341–696)	289 (158–463)	1.84 ^{***} (1.50–2.64)	1.05 (0.42–1.52)	117 (64.4–204)	75.8 (13.1–128)
Dip	32.4 ^{***} (28.4–37.8)	12.0 (8.58–15.8)	1220 [*] (530–2050)	176 (88.9–268)	3.11 ^{***} (1.51–5.74)	0.68 (0.29–1.30)	82.5 [*] (71.2–104)	17.2 (9.86–106)
Equ	56.5 ^{***} (36.1–84.6)	16.4 (12.7–22.3)	986 ^{***} (306–2200)	139 (61.8–244)	6.43 ^{***} (3.36–8.70)	0.82 (0.13–1.19)	2230 ^{***} (539–3660)	167 (23.4–308)
Hou	51.4 [*] (43.5–79.0)	36.8 (14.4–87.5)	898 [*] (448–2600)	252 (130–498)	2.97 [*] (1.40–4.51)	2.57 (0.35–6.75)	428 (146–1080)	325 (32.0– 1140)
Kyl	30.4 ^{**} (21.6–40.3)	18.4 (11.3–26.9)	453 [*] (260–819)	239 (172–298)	2.52 [*] (1.30–3.00)	1.20 (0.72–2.14)	630 (80.8–1620)	324 (28.9–938)
Lee	44.6 ^{***} (43.1–47.4)	10.6 (10.3–11.2)	844 ^{***} (821–889)	197 (183–208)	6.23 ^{**} (4.92–7.04)	0.36 (0.23–0.58)	458 ^{***} (436–494)	9.25 (9.08–9.56)
Pot	32.3 (20.3–50.6)	36.4 (20.0–63.1)	877 (612–1450)	1120 (601–1810)	3.92 (1.06–5.51)	3.38 (0.92–5.97)	508 [*] (33.8–857)	151 (34.7–222)
Pte	76.7 (22.1–160)	13.8 (8.56–28.7)	1360 (117–6190)	196 (60.8–951)	3.98 (0.34–7.45)	0.68 (0.21–2.03)	454 (124–1740)	1750 (627– 3750)
Sel	32.9 ^{**} (32.4–33.6)	19.0 (13.9–23.5)	352 ^{***} (343–369)	250 (229–270)	3.17 ^{**} (2.13–3.71)	1.36 (0.46–1.91)	272 ^{***} (255–284)	57.6 (30.3–82.0)

Hyperaccumulation values are bold. Differentiations between root and shoot of each element of the same plant species are significant.

^{*} p < 0.05.^{**} p < 0.01.^{***} p < 0.001.

Table 6
Mean (range) concentrations of Ag, Cd, In, and Pb (mg kg⁻¹ dry weight) in plant samples in and outside of the mine area (n = 3–63).

Code name	Ag		Cd		In		Pb	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
Age	3.58 (3.23–4.22)	3.68 (3.20–4.25)	12.6 (11.6–14.3)	19.0 (11.7–20.1)	1.06 (0.27–1.47)	0.87 (0.51–1.54)	1050 (988–1160)	1070 (968–1130)
Com	4.11 (3.04–6.87)	2.76 (0.87–6.64)	17.0 [*] (4.53–41.4)	1.90 (0.41–3.53)	0.28 (0.21–0.44)	0.32 (0.06–0.48)	464 (239–727)	384 (92.2–955)
Dip	2.55 [*] (1.45–4.12)	1.34 (0.27–2.22)	10.9 [*] (8.22–14.7)	0.71 (0.50–1.08)	0.83 (0.24–1.68)	2.13 (1.03–3.19)	1310 [*] (932–1720)	150 (47.2–261)
Equ	5.40 ^{***} (0.88–15.0)	0.85 (0.22–2.24)	6.88 ^{***} (1.65–16.6)	0.70 (0.17–1.31)	0.57 ^{***} (0.24–1.10)	0.14 (0.01–0.45)	1590 ^{***} (287–4830)	234 (19.1–851)
Hou	3.26 (0.79–9.32)	2.75 (0.42–9.31)	16.9 (8.07–52.8)	4.92 (0.95–13.3)	0.31 (0.10–0.92)	1.14 (0.07–2.32)	222 (122–270)	99.4 (81.5–130)
Kyl	3.44 (1.21–7.94)	2.26 (0.47–3.80)	4.17 ^{***} (2.94–5.71)	2.18 (1.68–2.99)	0.33 (0.22–0.74)	0.56 (0.14–1.69)	556 (275–720)	386 (111–700)
Lee	5.25 ^{***} (4.74–5.80)	0.33 (0.22–0.39)	13.3 ^{***} (12.4–14.8)	0.56 (0.54–0.59)	1.32 [*] (1.05–1.51)	0.23 (0.03–0.32)	2880 ^{***} (2870–2910)	111 (106–116)
Pot	4.97 (0.80–11.3)	6.59 (0.82–13.5)	7.23 (4.42–11.6)	10.6 ^{**} (6.98–14.3)	0.60 (0.12–0.91)	1.07 (0.26–2.22)	2260 (490–4620)	1710 (489–4210)
Pte	8.43 (0.71–35.3)	2.48 (0.29–13.3)	5.36 (0.50–22.2)	0.75 (0.20–3.46)	1.59 (0.13–5.66)	0.98 (0.04–5.14)	2980 (270–12700)	296 (49.1–1020)
Sel	1.61 (1.51–1.81)	3.91 (0.64–7.01)	2.40 ^{***} (2.28–2.64)	2.04 (0.52–3.50)	0.40 (0.28–0.64)	3.89 (3.12–4.28)	234 ^{**} (214–245)	136 (129–150)

Hyperaccumulation values are bold. Differentiations between root and shoot of each element of the same plant species are significant.

* p < 0.05.

** p < 0.01.

*** p < 0.001.

tributed, highly branched root system; (5) easy to cultivate and with a wide geographic distribution; and (6) relatively easy to harvest [6]. In contrast, phytomining is constrained by the need to produce a commercially viable metal crop [26]. Whether phytomining can become a reality depends on the price of the target metal [10]. In other words, the goal of phytoremediation is to clean contaminated media, whereas that of phytomining is economic return.

In the present study, the plants had accumulated very low concentrations of Ag, Ga, and In. Considering the present market prices of these metals [27] and the concentrations of these elements in the plants analyzed in the present study, none of the plant species collected from the mine shows potential for phytomining of these useful metals.

The data presented in this study indicate that hyperaccumulation levels were obtained for *H. cordata* and *P. vittata* for As (Table 5), and for *A. houstonianum*, *P. oxyphyllus*, and *P. vittata* for Pb (Table 6). To the best of our knowledge, the present study is the first to report on the accumulation of As and multiple heavy metals and the hyperaccumulation in *A. Houstonianum*, *P. oxyphyllus*, and *H. cordata*.

Of the four hyperaccumulators identified in the present study, *A. houstonianum* appeals as the best plant species for translocating heavy metals and As from the roots to shoots. BCFs values varied markedly among the elements, ranging from 0.001 (Co) to 2.32 (Cr) (Fig. 2a). The BCFs values for *A. houstonianum* for Cr and Ni, which exceeded 1, reflected the ability of this plant species to accumulate these metals from the soil and to transport them from the roots to shoots. High BCFw values were obtained for all heavy metals, ranging from 964 (As) to 148,000 (Mn) (Fig. 2b). TF values exceeding 1 were obtained for Cr, Mn, Co, Ni, Zn, Ga, As, Ag, Cd, Ag, and In; values close to 1 were obtained for Cu (0.92) and Pb (0.91) (Fig. 2c). Moreover, *A. Houstonianum*, a cool season annual plant that requires dry or moist soil, has a relatively high biomass, shows rapid growth, is easy to propagate, and is widely distributed in the study area, making it a good candidate for the phytoremediation of soil contaminated with As and multi-metals, especially Pb.

Among the plant species analyzed in the present study, *P. vittata* is the most widely distributed species. The results of the present study are in agreement with a previous study that found *P. vittata* to be an efficient As hyperaccumulator [28]. Low BCFs values were obtained for the plant, ranging from 0.002 (Co) to 0.85 (As) (Fig. 2a). This result is in line with the finding by Stoltz and Greger [16] that most of the plant species growing on mine tailings are restricted in terms of the translocation of metals and As to the shoots. The limited upward movement of elements from the roots to shoots can be considered as a tolerance mechanism [29]. In contrast, BCFw values were very high, ranging from 6190 (Cr) to 762,900 (Pb) (Fig. 2b). Very high BCFw values were obtained for Pb and Mn (310,500), reflecting the strong ability of *P. vittata* to accumulate these heavy metals from water. TF values exceeding 1 were obtained for As and In. The TF value obtained for *P. vittata* for As was significantly higher than the value for other hyperaccumulators identified in the present study (p < 0.001) (Fig. 2c). In addition, *P. vittata* is mesophytic and widely naturalized in many areas with a mild climate, has a high biomass, shows rapid growth, and propagates easily [21,28]; therefore, this plant has high potential for the phytoremediation of As and multi-metals, especially Pb. This finding is in line with previous reports that *P. vittata* has potential for the phytoremediation of soils contaminated by As [21], Zn and As [30], Cd and As [31], and As, Pb, and Zn [32].

Among the 10 plant species collected in the study area, *P. oxyphyllus*, a submerged aquatic plant that grows naturally in ponds, shallow rivers, and streams, usually in slightly acid water, appears to be the best hyperaccumulator of Pb. This plant accumulated higher concentrations of Mn, Co, Cu, Ga, and Pb than did other species analyzed in the present study. The BCFs values of *P. oxyphyl-*

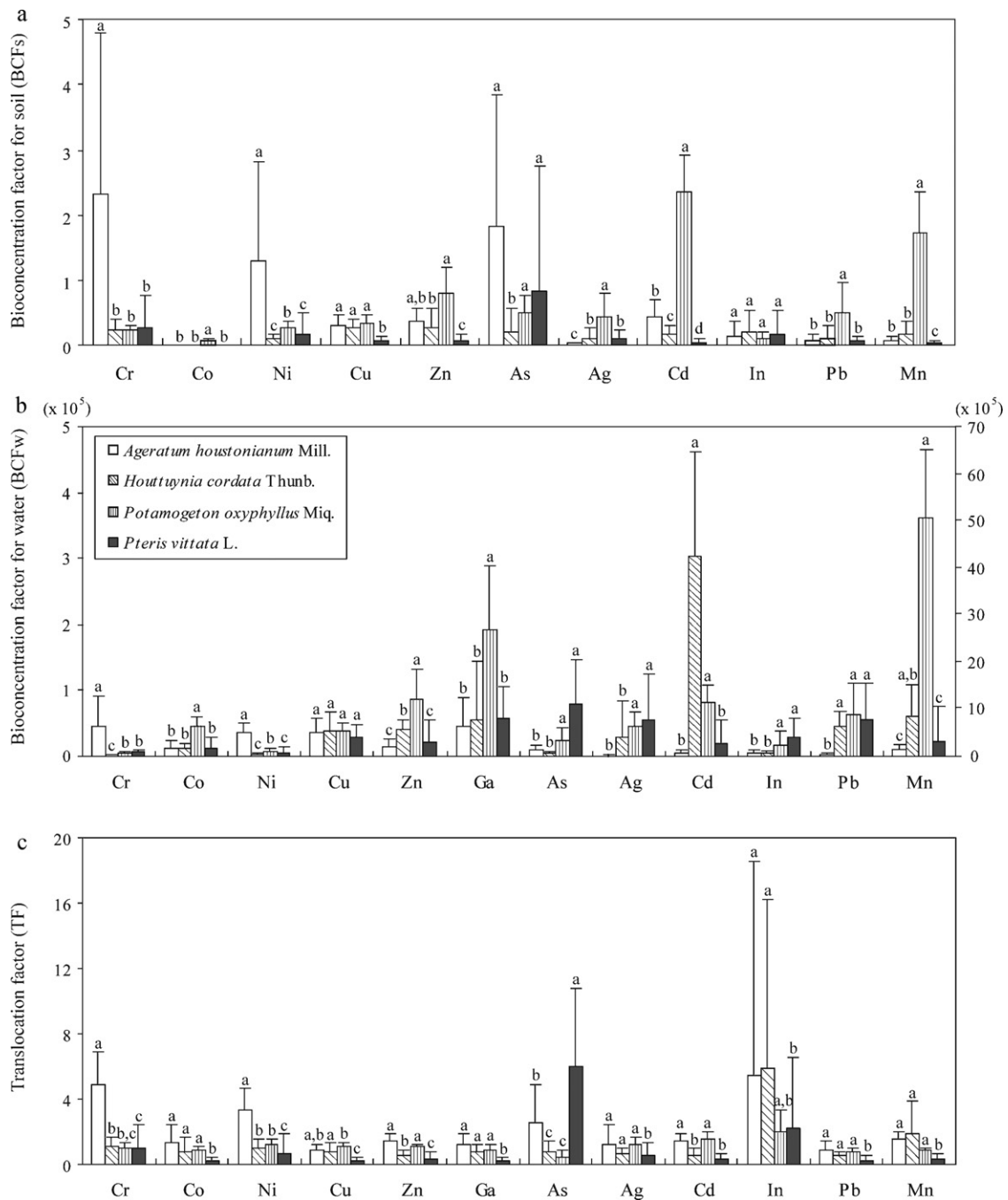


Fig. 2. Bioconcentration factor for soil (a) and for water (b), and translocation factor (c) of four plant species around and outside of the mine. Error bars on columns are standard deviations ($n=6-15$). Error bars with difference letters indicate significant differences among plant species at $p < 0.05$. The Y axis on the right of (b) is used for Pb and Mn.

lus varied greatly from 0.08 (Co) to 2.37 (Cd) (Fig. 2a). In contrast, BCFw values were much higher than BCFs values, ranging widely from 4010 (Cr) to 4,966,000 (Mn) (Fig. 2b). Very high BCFw values were obtained for Mn, Pb (865,000), and Ga (192,000), reflecting the strong ability of *P. oxyphyllus* to accumulate these heavy metals from water. *P. oxyphyllus* also appeals as a useful species in translocating heavy metals from the roots to shoots. TF values exceeding 1 were obtained for this plant for Cr, Ni, Cu, Zn, Ag, Cd, and In; values close to 1 were obtained for Mn, Co, and Ga (Fig. 2c). Though the biomass of *P. oxyphyllus* is lower than that of *A. houstonianum* and *P. vittata*, its high concentrations of heavy metals and rapid growth make it a candidate for the phytoremediation of water contaminated by As and multi-metals, especially Pb and Mn.

Though *H. cordata* is a hyperaccumulator of As, its low BCFs and TF values (Fig. 2a and c), and small biomass mean that it has less potential for phytoremediation than do *A. houstonianum*, *P. vittata*, and *P. oxyphyllus*.

4. Conclusions

Results of this study indicate that *H. cordata*, *A. houstonianum*, and *P. oxyphyllus* were identified as metal hyperaccumulators for the first time. *P. vittata*, *A. Houstonianum*, and *P. oxyphyllus* are good candidates for phytoremediation of sites contaminated with As and multi-metals. None of the collected plants was suitable for phytomining. To fully investigate the potential for phytoremedia-

tion, further studies (both greenhouse and field experiments) are needed to confirm the phytoremediation potential of these plant species and to establish their agronomic requirements and optimal management practices.

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