RESEARCH ARTICLE

Heavy metal accumulation and phytostabilization potential of dominant plant species growing on manganese mine tailings

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Abstract Screening plants that are hypertolerant to and excluders of certain heavy metals plays a fundamental role in a remediation strategy for metalliferous mine tailings. A field survey of terrestrial higher plants growing on Mn mine tailings at Huayuan, Hunan Province, China was conducted to identify candidate species for application in phytostabilization of the tailings in this region. In total, 51 species belonging to 21 families were recorded and the 12 dominant plants were investigated for their potential in phytostabilization of heavy metals. Eight plant species, Alternanthera philoxeroides, Artemisia princeps, Bidens frondosa, Bidens pilosa, Cynodon dactylon, Digitaria sanguinalis, Erigeron canadensis, and Setaria plicata accumulated much lower concentrations of heavy metals in shoots and roots than the associated soils and bioconcentration factors (BFs) for Cd, Mn, Pb and Zn were all < 1 , demonstrating a high tolerance to heavy metals and poor metals translocation ability. The field investigation also found that these species grew fast, accumulated biomass rapidly and developed a vegetation cover in a relatively short time. Therefore, they are good candidates for phytostabilization purposes and could be used as pioneer species in phytoremediation of Mn mine tailings in this region of South China.

Keywords Mn mine tailings, heavy metal accumulation, phytostabilization

1 Introduction

Mining and smelting processes often generate large

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amounts of waste materials. These wastes are usually deposited on the ground as tailings which occupy a huge area of land surface. In many cases, the mine tailings are characterized by high metal and metalloid concentrations, poor substrate structure, low nutrient content and water retention capacity [\[1\]](#page-9-0). These properties make tailings susceptible to wind and water erosion and act as a continuous source of environmental contamination to the surroundings terrestrial and aquatic ecosystems [[2\]](#page-9-0).

As public awareness of the adverse effects of the tailings on the environment and human health has grown, an interest in developing remediation techniques for mine tailings among the scientific community and government departments has also increased in recent years. Conventional methods of clean-up based on the excavation, transport and landfilling of contaminated soils and wastes are too expensive to implement due to extensive areas of mine tailings involved. A viable approach to overcome or minimize the adverse effects of the tailings is phytoremediation, which is defined as the use of green plants and their associated microbiota, soil amendments, and agronomic techniques to remove, contain, or render harmless environmental contaminants [\[3](#page-9-0)]. In the last few decades, phytoremediation has become attractive as it can fulfill the objectives of stabilization, pollution control, visual improvement and removal of threats to human health [\[4\]](#page-9-0). Phytoremediation of heavy metal-contaminated soils provides two major process options, phytoextraction and phytostabilization. Phytoextraction refers to the use of plants for removal or reduction of metal contamination in metal-contaminated sites. This is done by accumulation of metals in the above-ground plant biomass and then plants are harvested and either incinerated or composted to recycle the metals [[5](#page-9-0)]. In general, suitable hyperaccumulator plants are relatively rare and most hyperaccumulators

can only accumulate one or two metals and often maintain only a slow growth rate. When soils are heavily contaminated (e.g., mine tailings), the removal of metals using plants would take an unrealistic amount of time. Therefore, alternatives such as phytostabilization have to be considered. Phytostabilization focuses on the formation of a vegetation cover where sequestration (binding and sorption) processes immobilize metals within the plant rhizosphere reducing metal bioavailability and, thus, livestock, wildlife, and human exposure [[6](#page-9-0)]. The plant canopy serves to reduce aeolian dispersion, while plant roots help to prevent water erosion, immobilize heavy metals by adsorption or accumulation and provide a rhizosphere wherein metals precipitate and stabilize. Consequently, phytostabilization has great practical significance and flexibility in ecological restoration of mine tailings and remediation of soil polluted by heavy metals.

There are some important considerations when selecting plants for phytostabilization. First, plants should be tolerant of the soil metal levels and the other unfavorable edaphic conditions such as drought, compaction, extreme acidity/alkalinity, excess salinity and low/no nutrients. Secondly, plants should also be poor translocators of metal contaminants to above-ground tissues that could be consumed by humans or animals. Thirdly, plants must grow quickly to establish ground cover, have dense rooting systems and a large biomass [[2](#page-9-0),[7\]](#page-9-0). In addition, plants chosen for use in phytostabilization should ideally be native species that can establish, grow and colonize the metal-contaminated sites. In spite of the potential usefulness of phytostabilization for use on tailings of heavy metal mines, information about the behavior of these plants is scarce and little knowledge exists on suitable plant species to stabilize manganese mine tailings.

To examine the potential for effectively stabilizing heavy metals, an on-site survey of Mn mine tailings in Huayuan County, Hunan Province was conducted in 2011. Fifty-one plant species belonging to 21 families were recorded, and 12 dominant plant species were found growing well and with a wide distribution in this area. The main objectives of this study were to evaluate metal accumulation potentials in dominant plants and identify candidate species for application in phytostabilization of these Mn mine tailings. It was expected that the results generated from this study will be useful for the complete understanding of the restoration potential of dominant plants in the phytostabilization of Mn mine tailings.

2 Materials and methods

2.1 Site description

This study was carried out at Huayuan Mn mine tailings ponds (27°44′–29°47′N, 109°11′–110°55′E), located in Xiangxi Tujia and Miao Autonomous District, Hunan Province. The area has a subtropical moist monsoonal climate with an average temperature of 16.7°C and an annual rainfall of about 1421 mm.

This area has an abundance of manganese reserves and the scale of electrolytic Mn production ranks second (following Guangxi) in China. Mine tailings slurries produced from the milling and electro-refining process have been deposited on the ground as ponds or lagoons. So far, over 100 tailings ponds have been abandoned each covering an area of $20-2000000 \text{ m}^2$ (Huanyuan Environmental Protection Bureau). These tailings are almost completely devoid of vegetation and have resulted in the pollution of nearby waters and soils due to the dispersal of metal-contaminated particles by water and wind erosion. A remediation project was initiated by the local government in 2010 and implemented annually. The remediation procedures are conducted as follows: 1) surface of tailings ponds are leveled; 2) drainage ditches (20 \times 20 cm) are constructed with cemented barriers, and 3) a cover of about 50 cm topsoil from an adjacent unmined site is used to cap the surface of the tailings. After this initial remedial work, some native plant species provided from the existing soil seed bank and propagules arriving spontaneously colonize the mine tailings.

2.2 Sample collection

Three Mn tailings ponds (Zhenxing, Gaoke and Xingyin) were selected as study sites. These sites differed in the time of capping soil; Gaoke Mn tailings pond had been capped soil for one year (GK[I]), and Xingyin for two years (XY [II]). Zhenxing Mn tailings pond was divided into two parts, one half for one year (ZX[I]) and the other for two years (ZX[II]). Sampling was carried out in November 2011.

Soil samples were taken from three depths (0–15 cm, 15–30 cm, and 30–50 cm) for ZX[I] and GK[I], and at two depths $(0-15 \text{ cm and } 15-30 \text{ cm})$ for $ZX[II]$ and $XY[II]$. A total of 228 soil samples were collected, including ZX[I] 27, GK[I] 21, ZX[II] 18, XY[II] 24 at each depth, respectively. All vascular plants growing on the tailings ponds were recorded and the relative abundance of each species was estimated visually and then described as dominant, frequent, occasional or rare. The dominant species were collected; usually 3–5 subsamples nearby were gathered and mixed into one composite sample. The associated soils (0–30 cm) of the sampled plants were also collected for total metal analysis. All the soil and plant samples were sealed in polythene bags in the field and transported to the laboratory.

2.3 Sample analysis

Soil samples were air-dried and ground to pass through a 2 mm sieve. Soil pH and electrical conductivity (EC) were measured in a 1:2.5 (w/v) aqueous suspension. Organic matter (OM) was analyzed by dichromate oxidation and titration with ferrous sulfate [[8\]](#page-9-0). Total nitrogen (TN) was determined by the semi-micro Kjeldahl method [\[9\]](#page-9-0). Total phosphorus (TP) was estimated according to the molybdenum blue method [\[10\]](#page-9-0). Soil total heavy metals (Cd, Mn, Pb and Zn) and K (TK) were determined by Inductivelycoupled Optical Emission Spectrometry (ICP-OES: iCAP6300, Thermo Electron, USA) after digestion in 4 mL of aqua regia [\[11](#page-9-0)]. Soil bioavailable metals were extracted with a diethylene-triamine-pentaacetic acid (DTPA) extracting solution procedure [[12](#page-9-0)]. Ten grams of sieved soil ($<$ 2 mm) were added to 20 mL DTPA solution $(0.005 \text{ mol} \cdot \text{L}^{-1} \text{ DTPA} + 0.01 \text{ mol} \cdot \text{L}^{-1} \text{CaCl}_2 + 0.1 \text{ mol}$ $\cdot L^{-1}$ triethanolamine, pH = 7.3), shaken for 2 h on a horizontal shaker and centrifuged for 20 min at 3000 r ·min⁻¹. The supernatants were analyzed for Cd, Mn, Pb and Zn by ICP-OES.

Plant samples were thoroughly washed with running tap water, rinsed three times with deionized water, separated into shoots and roots, and then oven-dried at 105°C for 30 min and 70°C, to constant weight. Approximately 0.5 g of finely-ground plant samples were digested with a mixture of concentrated HNO₃ and concentrated HClO₄ at 5:1 (v/v) [\[13\]](#page-9-0). The concentrations of Zn, Pb and Cu in the plant materials were determined by ICP-OES analysis of the digests.

2.4 Statistical analysis

All data were analyzed using the statistical package SPSS

15.0 for Windows (SPSS Inc., USA). One-way ANOVA was carried out to assess the significance of differences between means. Differences between individual means were tested by the least significant difference (LSD) test. Pearson's correlation coefficients were calculated between extractable metal concentrations at different soil depths and plant metal concentrations.

For all collected dominant plants, the bioconcentration factor (BF) was calculated for each metal by dividing the metal concentration in shoots by the total metal concentration in soil [\[14\]](#page-9-0). The translocation factor (TF) was also obtained by dividing the metal concentration in shoots by the metal concentration in roots [[14](#page-9-0)].

3 Results

3.1 General properties of Mn mine tailings and capped soil

The general properties of the four Mn mine tailings and capped soil are presented in Table 1. The pH of the four Mn tailings ranged from 5.4 to 6.6, indicating a slightly acid nature. The EC values of the Mn tailings were relatively high (2.4 to 3.0 $dS \cdot m^{-1}$) compared to the capped soil $(0.22 \text{ dS} \cdot \text{m}^{-1})$. In general, the four Mn tailings contained high concentrations of total and DTPA-extractable heavy metals (Cd, Mn, Pb, and Zn) and low levels of major nutrient elements (N, P, and K) and organic matter. In contrast, the capped soil has higher levels of nutrients and organic matter but low concentrations of heavy metals.

Table 1 Physico-chemical properties of the four Mn mine tailings and capped soil (means \pm SE, $n = 10$)

parameters	ZX[I]	ZX[II]	GK[I]	XY[II]	capped soil		
$area/hm^2$	15	8	5	10	N _D		
${\rm cover}/\%$	50	80	50	80	ND		
pH	5.99 ± 0.11	5.41 ± 0.31	5.80 ± 0.21	6.62 ± 0.08	5.34 ± 0.09		
$EC/(dS \cdot m^{-1})$	2.57 ± 0.52	3.33 ± 0.67	2.43 ± 0.77	2.99 ± 0.47	0.22 ± 0.01		
$OM\%$	0.13 ± 0.03	0.23 ± 0.01	0.18 ± 0.02	0.31 ± 0.06	$0.89 + 0.09$		
$TN/(mg \cdot kg^{-1})$	0.83 ± 0.00	1.41 ± 0.01	0.69 ± 0.00	1.06 ± 0.02	2.28 ± 0.03		
$TP/(mg \cdot kg^{-1})$	20.69 ± 2.32	32.44 ± 3.43	39.46±2.91	28.08 ± 1.34	276.35±25.09		
$TK/(mg \cdot kg^{-1})$	482.28±14.42	520.89±21.18	503.17±30.08	468.41 ± 19.30	852.46±38.34		
total $Cd/(mg \cdot kg^{-1})$	16.20 ± 3.83	20.15 ± 4.04	26.05 ± 3.12	18.65 ± 2.90	1.87 ± 0.05		
$DTPA-Cd/(mg \cdot kg^{-1})$	0.63 ± 0.20	1.24 ± 0.13	0.58 ± 0.09	1.43 ± 0.23	0.21 ± 0.00		
total $Mn/(mg \cdot kg^{-1})$	8591.75±676.37	9006.95±499.25	6832.19±501.82	7044.46±756.55	1588.73 ± 63.48		
$DTPA-Mn/(mg \cdot kg^{-1})$	782.44±56.32	703.85±56.21	807.47±49.24	831.62±42.38	38.79 ± 2.94		
total $Pb/(mg \cdot kg^{-1})$	850.50±150.09	813.51 ± 266.61	750.60±244.66	936.36±241.42	127.46 ± 6.63		
$DTPA-Pb/(mg \cdot kg^{-1})$	59.26±11.84	65.38 ± 17.21	85.46±15.16	70.84±20.06	16.33 ± 3.92		
total $Zn/(mg \cdot kg^{-1})$	1024.25±321.74	956.45±289.51	990.50±461.88	1111.25±356.19	359.47±26.25		
$DTPA-Zn/(mg \cdot kg^{-1})$	202.69±28.36	219.58±32.69	156.07±36.19	192.42 ± 22.05	28.34±6.92		

Notes: ZX[I], Zhenxing Mn tailings pond capped soil for one year; ZX[II], Zhenxing Mn tailings pond capped soil for two years; GK[I], Gaoke Mn tailings pond capped soil for one year;XY[II], Xinyin Mn tailings pond capped soil for two years; ND: not detected

3.2 Species composition and abundance in the four Mn mine tailings ponds

The species recorded on the four Mn tailings ponds are listed in Table 2. There were 51 species belonging to 46 genera and 21 families, of which 8 belong to the Poaceae and 10 species belong to the Asteraceae. These two families were the dominant components of the natural vegetation on all four Mn mine tailings ponds. Overall, vegetation cover improved with remediation time, with a total cover of 50% on ZX[I] and GK[I] and reaching 80% on ZX[II] and XY[II] (Table 1). There were 34, 49, 31 and 48 plant species observed on ZX[I], ZX[II], GK[I], and XY [II], respectively. The most common species were grasses

(annuals 15, biennials 4 and perennials 18) accounting for 72.5% of the total, shrubs and tree only appeared on ZX[II] and XY[II], indicating that the grass species had wide ecological amplitude and high tolerance to the prevailing edaphic conditions. The dominant species recorded on the four Mn tailings ponds were: Alternanthera philoxeroides (A. philoxeroides), Alopecurus japonicus (A. japonicus), Artemisia princeps (A. princeps), Bidens frondosa (B. frondosa), Bidens pilosa (B. pilosa), Commelina communis (C. communis), Cynodon dactylon (C. dactylon), Chrysanthemum indicum (Ch. indicum), Digitaria sanguinalis (D. sanguinalis), Erigeron canadensis (E. canadensis), Phytolacca acinosa (P. acinosa) and Setaria plicata (S. plicata).

Table 2 Plant species growing on the four Mn tailings ponds in Huayuan, Hunan Province

family	species	ZX[I]	ZX[II]	GK[I]	XY[II]	life form
Amaranthaceae	Alternanthera philoxeroides (Mart.) Griseb.	D	D	$\bar{ }$	Ω	Perennial grass
	Amaranthus hybridus Linn.		Ω	F	$\overline{}$	Annual grass
Anacardiaceae	Rhus chinensis Mill.	$\overline{}$	F	$\overline{}$	F	Shurb
Asteraceae	Artemisia princeps Pamp.	F	F	D	F	Perennial grass
	Bidens frondosa Linn.	D	F	F	F	Annual grass
	B. pilosa Linn.	D	D	F	D	Annual grass
	Chrysanthemum indicum (Linn.) Des Moul.	\overline{O}	D	\mathbb{R}	D	Perennial grass
	Erigeron Canadensis (Linn.) Cronq.	D	D	D	D	Biennial grass
	Gnaphalium affine D. Don.	$\overline{}$	F	$\overline{}$	F	Biennial grass
	Hemistepta lyrata (Bunge) Bunge	\mathbb{R}	Ω	Ľ.	Ω	Biennial grass
	Ixeris sonchifolia (Maxium). Shih	\overline{O}	F	\equiv	F	Biennial grass
	Senecio scandens Buch.-Ham. Ex D. Don	L.	R	\equiv	Ω	Perennial grass
	Xanthium sibiricum Patrin ex Widder	F	F	F	F	Annual grass
Betulaceae	Alnus cremastogyne Burk.		Ω	$\overline{}$	F	Tree
Caryophyllaceae	Arenaria serpyllifolia Linn.		$\overline{}$	Ω	\mathbf{F}	Annual grass
	Myosoton aquaticum (Linn.) Cyr.	\overline{O}	F		\mathbb{R}	Perennial grass
	Stellaria media (Linn.) Cyr.	F	F	F	F	Annual grass
Commelinaceae	Commelina communis Linn.	F	D	F	F	Annual grass
Convolvulaceae	Calystegia hederacea Wall.	R	$\overline{}$	Ω	F	Annual grass
Euphorbiaceae	Acalypha australi Linn.	\overline{O}	F	\mathbb{R}	\sim	Annual grass
	Alchornea trewioides (Benth.) Muell. Arg.		Ω	Ľ.	\mathbf{F}	Shurb
	Discocleidion rufescens Franch.		\mathbb{R}	÷	Ω	Shurb
	Mallotus apelta (Lour.) Muell. Arg.		Ω	-	F	Shurb
Fabaceae	Robinia pseudoacacia Linn.		Ω	Ľ.	F	Tree
	Medicago hispida Linn.	\overline{O}	Ω	Ω	$\overline{}$	Biennial grass
Malvaceae	Urena lobata Linn.	\overline{O}	F	R	F	Shurb
Moraceae	Broussonetia kazinoki Sieb.	$\overline{}$	F	F	F	Shurb
Oxalidaceae	Oxalis acetosella Linn.	F	F	F	F	Perennial grass
Phytolaccaceae	Phytolacca acinosa Roxb.	D	D	D	D	Perennial grass

Notes: D, dominant; F, frequent; O, occasional; R, rare; –, not existent

3.3 Bioavailable heavy metal concentrations in the four Mn mine tailings

The bioavailable heavy metal concentrations at different soil depths of the four Mn tailings are shown in Fig. 1. In general, the concentrations of DTPA-extractable metals at all soil depths were very low with the range 0.1–0.7 mg \cdot kg⁻¹ for Cd, 26.6–121.8 mg \cdot kg⁻¹ for Mn, 2.8–9.6 mg $k_{\rm g}$ ⁻¹ for Pb and 11.1–76.3 mg $k_{\rm g}$ ⁻¹ for Zn. There were no significant variations $(P > 0.05)$ in metal concentrations between different soil depths from the same tailings and within the same depth at different tailings.

3.4 Heavy metal accumulation and translocation in dominant plants

Heavy metals (Cd, Mn, Pb, and Zn) concentrations in the 12 dominant plants and the associated soils are presented in Table 3. They show that heavy metals in both shoot and root tissues of most plants were significantly lower than those in their associated soils. Exceptions occurred only for P. acinosa (Cd and Mn), A. japonicus, C. communis and

Ch. indicum (Mn). In general, metal concentrations in plant tissues differed between species indicating their different strategies for metal accumulation. For example, A. philoxeroides, A. princeps, B. frondosa, B. pilosa, C. dactylon, E. canadensis, D. sanguinalis and S. plicata accumulated lower concentrations of Cd, Mn, Pb, and Zn than other species. Moreover, metal concentrations in the shoots were much lower than those in the roots, demonstrating low accumulation of heavy metals and poor translocation ability (metal exclusion, sensu Baker [[15](#page-9-0)]). Contrastingly, A. japonicus, C. communis, Ch. indicum and P. acinosa tended to accumulate higher concentrations of heavy metals in the shoots than roots, presenting relatively high metal transport ability (accumulation, sensu Baker [[15](#page-9-0)]).

Table 4 shows the derived bioconcentration factors (BF) and translocation factors (TF) for the 12 dominant plants. Overall, BF values were < 1 except for P. acinosa (Cd and Mn) and A. japonicus, C. communis and Ch. indicum (Mn). With regard to TF, most plants had relatively higher TF values than their BFs for the same metal; TF values for A. japonicus, C. communis, Ch. indicum and P. acinosa for Cd, Mn, Pb, and Zn were generally > 1 .

Fig. 1 DTPA-extractable metal concentrations at different soil depths for the four Mn tailings ($n = 27$ in each soil depth for ZX[I]; $n = 18$ in each soil depth for $ZX[II]$; $n = 21$ in each soil depth for $GK[I]$; $n = 22$ in each soil depth for $XY[II]$: (a) DTPA-Cd; (b) DTPA-Mn; (c) DTPA-Pb; (d) DTPA-Zn. Different letters in the same group indicate significant differences at $P < 0.05$ according to a LSD test

3.5 Plant–soil relationships

Pearson's correlation analyses between metal concentrations in the shoots of dominant plants and DTPAextractable metal concentrations at different soil depths for the four mine tailings are shown in Table 5. No significant correlations were apparent between metal concentrations in plant shoots and extractable metal concentrations for all soil depths except for positive corrections found between Cd concentrations in plants and DTPA-Cd concentrations at 15–30 cm in ZX[I] ($r = 0.62$) and Mn concentrations in plants and DTPA-Mn concentrations at 15–30 cm in GK[I] ($r = 0.73$).

4 Discussion

4.1 Metal accumulation and translocation in dominant plants

Our study shows that many native plant species can colonize Mn mine tailings after capping the substrate with soil. A total of 51 vascular species representing 46 genera and 21 families was recorded (Table 1) and the 12 dominant plants were investigated for their ability to translocate and accumulate metals (Tables 3 and 4). In general, plants growing in metalliferous mine soils have two basic tolerance strategies: metal accumulation and exclusion [\[15\]](#page-9-0). In our study, most dominant plants tended to accumulate much lower concentrations of heavy metals in both shoots and roots than their associated soils (Table 3), suggesting that these plant species tolerated heavy metals by the exclusion strategy. From the viewpoint of stabilizing metals in contaminated sites, metal excluders are desirable because they have a high tolerance to heavy metals but low translocation to the above-ground tissues, thereby reducing the risk of heavy metals entering the ecosystem through the food chain [\[16](#page-9-0)]. Eight plant species, A. philoxeroides, A. princeps, B. frondosa, B. pilosa, C. dactylon, D. sanguinalis, E. canadensis and S. plicata accumulated relatively lower concentrations of Cd, Mn, Pb, and Zn than the other species. Moreover, metal concentrations in the shoots were lower than those in the roots, indicating they could be metal excluders and good

Table 4 Bioconcentration factors (BF) and translocation factors (TF) of the dominant plants from the four Mn tailings ponds

		$\ensuremath{\mathrm{Cd}}$		Mn		Pb		Zn	
sites	species	BF	TF	BF	TF	\rm{BF}	TF	BF	TF
ZX[I]	A. philoxeroides	0.25	0.57	0.10	0.51	0.06	0.62	0.15	0.59
	B. frondosa	0.72	0.34	0.18	5.37	0.12	1.71	0.19	2.64
	B. pilosa	0.16	0.93	0.09	0.91	0.03	0.75	0.07	1.06
	D. sanguinalis	0.54	1.10	0.16	0.72	0.07	0.79	0.21	0.44
	E. canadensis	0.14	0.06	0.06	0.17	0.02	0.35	0.08	0.61
	P. acinosa	0.62	1.93	1.48	10.49	0.05	4.07	0.21	2.68
GK[I]	A. princeps	0.70	0.79	0.33	0.90	0.15	0.57	0.17	0.59
	C. dactylon	0.45	0.75	0.10	1.56	0.02	0.95	0.17	1.92
	E. canadensis	0.87	0.49	0.04	0.14	0.03	0.34	0.21	1.02
	P. acinosa	1.33	1.06	1.11	11.59	0.03	2.02	0.20	2.43
	S. plicata	0.49	1.74	0.09	2.28	0.03	1.13	0.22	2.24
ZX[II]	A. japonicus	0.35	1.56	0.81	1.55	0.16	0.82	0.44	1.06
	A. philoxeroides	0.16	0.28	0.03	0.24	0.02	0.33	0.36	0.52
	B. pilosa	0.27	0.52	0.06	0.59	0.02	0.50	0.12	0.62
	C. communis	0.31	0.52	1.02	3.07	0.16	1.11	0.57	0.73
	C. dactylon	0.25	0.58	0.07	0.42	0.05	0.55	0.09	0.50
	Ch. indicum	0.20	0.29	1.05	1.39	0.10	1.39	0.70	0.75
	E. canadensis	0.28	0.19	0.04	0.13	0.20	1.15	0.31	1.16
	P. acinosa	1.00	1.62	1.41	9.72	0.02	2.02	0.92	5.04
XY[II]	A. japonicus	0.61	1.75	1.14	1.20	0.09	1.30	0.29	0.78
	B. pilosa	0.31	0.31	0.10	0.61	0.02	0.33	0.11	0.65
	C. dactylon	0.41	0.95	0.11	0.61	0.08	0.98	0.28	0.81
	Ch. indicum	0.17	0.26	0.44	1.15	0.03	2.08	0.20	3.07
	D. sanguinalis	0.25	0.94	0.16	2.05	0.12	1.21	0.40	1.44
	E. canadensis	0.38	0.13	0.02	0.17	0.33	1.29	0.41	1.89
	P. acinosa	0.94	1.76	0.98	8.71	0.05	3.70	0.79	3.56
	S. plicata	0.38	2.01	0.08	5.64	0.05	1.23	0.43	1.50

candidates for phytostabilization of mine tailings. In contrast, A. japonicus, C. communis, Ch. indicum and P. acinosa accumulated higher concentrations of heavy metals in the shoots than roots and the TFs for Cd, Mn, Pb, and Zn were > 1 , demonstrating high metal translocation and accumulation ability. In particular, for P. acinosa, a reported Mn hyperaccumulator [\[17\]](#page-9-0), its maximum Mn concentration in shoots reached 8044 mg \cdot kg⁻¹ in this study and average values of BF and TF for Mn were 1.2 and 10.1.

In a revegetation program for metal-contaminated sites, metal concentrations in plant above-ground tissues are a major concern. The US domestic animal toxicity limits for cattle grazing are: $Cd \le 10$ mg \cdot kg⁻¹, Mn ≤ 2000 mg \cdot kg⁻¹, $Pb \le 100$ mg \cdot kg⁻¹, and $Zn \le 500$ mg \cdot kg⁻¹ [\[18\]](#page-9-0). All concentrations of Cd, Pb, and Zn in shoots of the dominant plants were far below these regulatory limits. However,

shoot Mn concentrations in A. japonicus, C. communis, Ch. indicum and P. acinosa exceeded toxicity limits which could potentially pose a toxic hazard to any wildlife grazing in the vicinity of the Mn tailings. Protective measures are therefore required to avoid future metal contaminants entering into the grazing food chain.

4.2 Relationships between plants and substrata

Plants grown in metal-enriched substrata take up metals to differing degrees. This uptake is largely influenced by the bioavailability of the metals. Many previous studies have shown significant correlations between metal uptake by plants and "available" metal concentrations in substrata (extracted by DTPA, $Ca(NO₃)₂$ or deionized water, etc.) [[19,](#page-9-0)[20](#page-10-0)]. In the present study, Pearson's correlation analyses suggested that the metal concentrations in plant

Table 5 Bioconcentration factors (BF) and translocation factors (TF) of the dominant plants from the four Mn tailings ponds

sites	plants -	$0-15$ cm			$15 - 30$ cm			$30 - 50$ cm					
			DTPA-Cd DTPA-Mn DTPA-Pb DTPA-Zn				DTPA-Cd DTPA-Mn DTPA-Pb DTPA-Zn				DTPA-Cd DTPA-Mn DTPA-Pb DTPA-Zn		
ZX[I]	C _d	0.073	-0.323	0.393	-0.387	$0.616*$	0.165	0.145	0.205	0.081	-0.311	0.143	0.290
	Mn	-0.186	-0.025	0.092	-0.358	0.377	-0.022	0.133	0.330	-0.195	-0.364	0.239	0.130
	Pb	-0.217	0.288	-0.381	0.109	0.170	0.310	0.380	0.242	-0.235	0.242	0.437	0.299
	Zn	-0.008	-0.085	0.057	0.278	0.232	0.067	0.015	0.044	0.075	0.312	0.256	0.570
GK[I]	Cd	-0.212	-0.383	-0.258	0.163	-0.169	0.171	-0.306	0.145	-0.121	-0.352	-0.396	0.504
	Mn	-0.225	-0.277	0.274	-0.192	-0.202	$0.726*$	-0.429	-0.461	0.247	0.229	-0.451	-0.340
	Pb	-0.178	-0.356	-0.183	0.326	0.162	0.082	-0.101	0.117	-0.164	-0.472	-0.314	0.476
	Zn	-0.457	0.000	0.210	-0.467	-0.306	0.362	-0.014	-0.307	0.342	0.543	-0.263	-0.475
ZX[II]	Cd	0.272	-0.100	0.368	0.202	-0.324	0.442	-0.472	0.260				
	Mn	0.388	0.316	0.271	-0.295	0.078	0.094	-0.276	0.359				
	Pb	-0.381	-0.373	-0.005	0.384	0.264	0.025	0.078	0.205				
	Zn	0.158	0.222	0.505	-0.131	0.246	0.226	-0.389	0.291				
XY[II]	Cd	-0.063	-0.080	-0.140	-0.230	0.399	-0.230	0.177	0.286				
	Mn	-0.001	-0.007	-0.274	-0.477	0.427	-0.427	0.410	0.102				
	Pb	0.253	-0.063	0.347	0.432	-0.115	0.125	-0.052	0.341				
	Zn	-0.136	-0.294	0.087	-0.240	0.496	-0.262	0.556	0.314				

Note: *, correlation is significant at the 0.05 level (2-tailed).

shoots were poorly correlated with DTPA-extractable metal concentrations at all soil depths (Table 5). Similar results were also found in another study by our group in which a revegetation cover was established at an extreme, metal-toxic wasteland in Dabaoshan, Guangdong Province, using a combination of four native grass species and one non-native woody species [\[21](#page-10-0)]. The poor correlation found in the present study is most likely caused by rhizospheric processes and microbial activity [[22](#page-10-0)]. In addition, other soil factors, such as pH, soil nutrients and the competition between metal ions and protons at the plant–soil interface, also affects the metal uptake by dominant plants [\[23\]](#page-10-0).

4.3 Potential use of dominant plants in phytostabilization

Selection of appropriate plant species is a very important aspect to consider in a phytostabilization-based technique for site restoration [\[2,4\]](#page-9-0). Plants should possess an extensive root system and a large biomass in the presence of high concentrations of heavy metals, and to ensure that the translocation of metals from roots to shoots is as low as possible [[3](#page-9-0),[24](#page-10-0)]. Of the 12 dominant plant species in this study, A. philoxeroides, A. princeps, B. frondosa, B. pilosa, C. dactylon, D. sanguinalis, E. canadensis and S. plicata are fast-growing annual or biennial grasses with high biomass and proliferating root systems, which can establish, grow and colonize successfully in Mn mine tailings and develop a good cover within a relatively short time period. In addition, these species accumulated much lower concentrations of heavy metals in shoots and roots than their associated soils with the BFs for Cd, Mn, Pb, and $Zn < 1$ (Tables 3 and 4), indicating that they could be good candidates for phytostabilization purposes. Similar results have been reported by other authors, e.g., C. *dactylon* and D. sanguinalis have proved successful for initial colonization of pure tailings and are commonly used as good pioneer species for revegetation of Pb/Zn and Mn mine tailings in South China [[25,26\]](#page-10-0). In another restoration design of Mn mine wasteland in Lipu, Guangxi, C. dactylon, D. sanguinalis and E. canadensis were employed to colonize Mn wasteland after amelioration [\[27\]](#page-10-0). In addition, it is notable that A. philoxeroides, a creeping grass, contained normal levels of Cd, Mn, Pb and Zn in above-ground tissues; it was a good stabilizer of the loose mine soils, as well as mine tailings. During field investigation, it was noteworthy to find several communities composed of the same single dominant species or the same combination of dominant species that were frequently recorded at the different Mn tailings ponds, such as A. philoxeroides, C. dactylon, D. sanguinalis, B. pilosa $+$ C. dactylon, and E. canadensis $+ C$. dactylon. In general, these single or combinations of species can rapidly colonize by propagules and form small islands of vegetation in microsites with relatively low concentrations of metals but high levels of nutrients, which created opportunities for migration of other tolerant species. From the viewpoint of vegetation establishment in a restoration design of Mn tailings, A. philoxeroides, B. pilosa, C. dactylon, D. sanguinalis and E. canadensis are prime species, followed by A. princeps, B. frondosa and S. plicata.

There is growing evidence that phytostabilization can be achieved by selective planting in combination with various soil amendments including zeolites, steel shots, phosphates, biosolids, sewage sludge and manure composts [\[28,29\]](#page-10-0). Removing topsoil from an adjacent uncontaminated site for capping mine tailings is a quick and simple approach. However, importing soil may bring about ecological damage to another site and sometimes the imported soil is not easily obtainable [[30](#page-10-0)]. Therefore, alternative materials obtained locally can be developed as soil amendments such as municipal solid wastes, spent mushroom compost, pig and/or chicken manure. In addition, various agronomic practices such as normal cropping or inter-cropping, firing, flooding, root nodulation, and application of metal chelates, can be added to a program to improve the remediation efficacy.

5 Conclusions

The present field investigation demonstrated that many dominant plant species can colonize Mn mine tailings after capping with soil. Of the 12 dominant plant species found in our study, A. philoxeroides, A. princeps, B. frondosa, B. pilosa, C. dactylon, D. sanguinalis, E. canadensis and S. plicata accumulated much lower concentrations of heavy metals in shoots and roots than their associated soils and the BFs for Cd, Mn, Pb, and Zn were all < 1 , indicating that they tolerated heavy metals by exclusion strategy and could be used for phytostabilization of Mn mine tailings. On the other hand, these species are also fast-growing native grasses with high biomass and proliferating root systems, which can colonize Mn mine tailings by single or combination of species and created good habits for other tolerant species. In a restoration design of Mn tailings, the prime species are A. philoxeroides, B. pilosa, C. dactylon, D. sanguinalis and E. Canadensis, following by A. princeps, B. frondosa and S. plicata.

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