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Heavy Metal Contamination in Soils and Phytoaccumulation in a Manganese Mine Wasteland, South China

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Abstract: Heavy metal contamination of minesoils is a widespread problem in China. In Pingle manganese mineland in Guangxi (south China), heavy metal concentrations in soils and dominant plants were determined, and soil contamination was assessed with pollution index (Pi) and index of geoaccumulation (I-geo). Pi showed the minesoil was heavily polluted by Cd and slightly polluted by Cr. I-geo showed a severer pollution for all metals (except for Mn) than Pi because I-geo tended to overestimate the real pollution effect of minesoil. Fresh tailings dam had both the highest Pi and I-geo among the four sites indicating a high metal contamination. All the "bio-available" fractions of the studied metals were below 5% of the totals. Dominant plants tended to accumulate higher Cd and Cr, and showed higher Mn translocation to aboveground parts. Besides the agricultural reclamation, more diverse restoration goals with lower environmental risks should be considered for the Mn mine wastelands in South China.

Keywords: heavy metals, minesoil, pollution index, geoaccumulation index, phytoaccumulation, Pingle Mn mineland

Introduction

Human activities are greatly altering ecosystems worldwide at unprecedented rates and leading to accelerated loss of biodiversity (Raven, 2002) and environmental pollution. This was exactly the circumstance taking place in China for the last two decades. For instance, the mining industry, a primary contributor to the rapid economic boost, produced a huge area of wasteland and caused serious environmental problems. Mining has generated some 3.2 Mha wasteland in China by the end of 2000 (Li, 2006), and this figure is increasing at a rate of 46,700 ha annually. Pollution related to mining operations and their associated mine tailings caused a direct economic loss of over 9 billion RMB yuan (around 1.3 billion USD) and an indirect loss of about 30 billion (4.4 billion USD) each year.

Rehabilitation of mine wastelands was a priority issue to be addressed for many provincial governments in China because the shortage of cultivated land was increasingly outstanding, especially for the karst regions in the southwest part like Guangxi and Guizhou where are rich in the metallic ore resources. However, little progress has been made in raising the restoration rate of wastelands (currently 10%–12%) due to a matrix of reasons and the interlocked institutional management pattern (Andrews-Speed et al. 2003). A cutting-edge review on research and practice of ecological restoration of mineland in China was made by Li (2006) and one of the major raised concerns was the utilitarian reclamation of wastelands as growth field for edible agronomic crops. In fact, the input of heavy metals into food web generates another potentially more harmful problem (Ross, 1994) than the wasteland itself. Thus the assessment of heavy metal pollution of minesoils and evaluation of restoration goals would be important in determining the suitable restoration mode for a particular mine wasteland.

Among the recent studies about ecological restoration of metal-mined wastelands, a majority of them focused on the Pb/Zn and Cu minelands (Pugh et al. 2002; Shu et al. 2001, 2005; Ye et al. 2002; Yang et al. 2003; Yang et al. 2004b; Zu et al. 2005). Little attention has been paid to Mn minelands in China and worldwide possibly due to the common perception that Mn is a relatively non-toxic metal element. Mn is an essential trace element of life tissues, however, exposure to excessive Mn results in Mn toxicity, including Parkinson-like symptoms (Gerber et al. 2002; Erikson and Aschner, 2003), and abnormalities of the reproductive system (Zhu et al. 1999) and the immune system (Vartanian et al. 1999). So far, Mn toxicity has not been adequately investigated in comparison with Cd, Cu, Hg, Pb and Zn. Under natural conditions, Mn ores are generally accompanied with Pb, Cd, Zn, Ni, Co and Fe, and extraction of Mn

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will inevitably lead to release of the more toxic metals into the environment.

Guangxi, adjoining Guangdong Province in the east and bordering Vietnam to the southwest, ranks first of China in terms of Mn ore reserves (38.5% of the total) and mining scale. This region falls undeveloped economically in China and mining is the most important pillar industry. Due to its typical karst nature, the serious shortage of cultivable land in Guangxi is further worsened by mining operation, increasing soil erosion and rocky desertification. Currently 39 (out of 47 known) Mn mines are in operation (mostly opencast mining) and huge areas of wastelands await restoration. The objectives of this study, concerning the Pingle Mn mineland in northeast Guangxi, are to examine the heavy metal concentrations in minesoils and in the dominant plants. Based on these, the heavy metal contamination of soils is assessed and the potential plant species suitable for restoration of Mn mineland are screened. Research findings should provide some insights into the restoration pattern appropriate for the Mn mine wastelands in South China.

Materials and Methods

Site description

The Pingle Manganese mine (long 110°46’E, lat 24°39’N) is located in Pingle county, about 108 km southeast from Guilin (Fig. 1), a well-known world-class karst scenic city in South China. This medium-sized mine lies in a hilly land (<180 m elevation), firstly extracted with opencast mining in 1958 and now left with a severe destruction of natural environment. The mine area is located in the middle subtropical monsoon climatic zone. The annual average temperature in this region is 19.9 °C with yearly average rainfall of 1636 mm and mean relative humidity of 79%. The regional vegetation is the typical subtropical evergreen broadleaf forest, and zonal soil is loess, usually 8–15 m deep covering the mine surface.

Sample collection and preparation

Extensive ecological surveys and sampling were carried out in Pingle Mn mine from March 2005 to October 2006. According to the actual landform and vegetation the whole mineland was divided into four areas: the active mining area (MA), fresh tailings dam (FTD), reclaimed tailings dam (RTD) and restored area (RA). The active mining area is the highest among the first three covered with loose striped soil and overburden, but in the neighboring unexcavated area a good vegetation cover is seen with *Imperata cylindrical* var. *major* (a grass) dominating and some *Pinus massoniana* trees and *Schima superba* saplings standing out. Downward is a fresh tailings dam in use and some pioneer plants such as *Phytolacca acinosa* (herb) and *Amaranthus tricolor* (herb) colonizing. The reclaimed tailings dam (lowest in height) is a former tailings disposal pond but now reclaimed for use of orchard (mainly peach trees and Chinese chestnut). Underlain are natural herbaceous species, e.g. *Erigeron acer, Panicum repens* and *Cynodon dactylon* and the vegetation cover is about 80%. The restored area, a terraced hilly slope, is a large peach tree field (initiated by the local county government) and the overall vegetation coverage is around 30% with *P. acinosa, I. cylindrical* var. *major, Hedyotis auricularia* and *Digitaris sanguinalis* sparsely underlain. The peach was said (by growers) insipid, and the fruit size and annual yield smaller than usual.

Four soil sampling sites (MA, FTD, RTD and RA) were set up in the mineland, one site in each area. Samples with three replicates were collected from surface soil (0–20 cm) and usually 5 subsamples were merged into one single sample. Samples of major dominant plants (divided into leaf, shoot and root where appropriate) for each site were collected and 3–5 multi-point subsamples nearby were gathered and mixed into one sample. All soil and plant samples were sealed with polythene bags in the field and transported into the laboratory.

Soil samples were air-dried, homogenized and sieved through a 2-mm screen, then pulverized (with TAISITE FW100 stainless-steel pulverizer) and passed through a 100-mesh nylon sieve. Plant samples were gently washed with tap water, rinsed three times with deionized water, first dried at 105 °C for 30 min, and then at 70 °C to constant weight. Dried plant samples were ground in the same stainless steel pulverizer to fine powder.

Chemical analysis

Soil pH value (1:1 soil to distilled water, w/v) was measured using a pH meter. Soil organic matter (OM) was digested with H_2SO_4 + $K_2Cr_2O_7$ and determined with phenanthroline titration. Total nitrogen (TN) was determined by micro-Kjeldahl

Figure 1. Map of Guangxi, showing the study site (Pingle Mn mine) and a nearby Mn mine (Lipu) about 35 km west.

digestion followed by steam distillation. Total phosphate (TP) was determined colorimetrically by the molybdenum blue method. Soil samples were digested with concentrated HCl + concentrated HNO_3 HF + $HClO_4$ (10:5:5:3, v/v) and plant tissues digested with concentrated HNO_3 + $HClO_4$ (20:3–5, v/v) for metal determination (Li et al. 2007). The total metal concentrations (Cd, Cr, Cu, Pb, Zn and Mn) in digestates were determined by the atomic absorption spectrophotometer with flame atomizer (WFX-110, Beijing). The "plant—available" portion of metals in soil was extracted with 0.1 M HCl solution and determined with the same method. Quality assurance of metal analysis of soil and plant materials was performed using recovery rate (86%–115%) of the added certified reference materials (provided by Guangfu Fine Chemical Research Institute) into the digested solution.

Pollution assessment

The pollution index (Pi) and geo-accumulation index (I-geo) were employed to assess the pollution of individual metal in the Mn minesoils. Pollution index was calculated using the formula:

$$Pi = Ci/Si$$

where Ci represents the concentration of heavy metal *i* in soil while Si indicates the relevant standard value for this metal (see the next). Geo-accumulation index was determined by the following equation according to Müller (1969):

$$\text{I-geo} = \log_2 (Ci/1.5Bi)$$

where Bi is the soil background concentration of heavy metal *i* in Guangxi and 1.5 is a correction factor.

China Environmental Quality Standard for Soils (GB 15618-1995 Class II, $pH < 6.5$) was used as the assessment criteria (the standard values are: Pb, 250 mg/kg; Zn, 200; Cu, 150; Cr, 150; and Cd, 0.3) in this study since these figures indicate threshold levels of pollution warning. No value was given for Mn in this standard, thus Pi (Mn) was not calculated.

Based on Pi, soil contamination levels were classified into four grades: Pi < 1 (grade 1), unpolluted; $1 \leq$ Pi < 2 (grade 2), slight pollution; $2 \leq$ Pi < 3 (grade 3), medium pollution; Pi ≥ 3 (grade 4), heavy pollution. I-geo was classified into seven grades: I-geo ≤ 0 (grade 0), uncontaminated; $0 <$ I-geo ≤ 1 (grade 1), slightly moderately contaminated; $1 <$ I-geo ≤ 2 (grade 2), moderately contaminated; $2 <$ I-geo ≤ 3 (grade 3), moderately severely contaminated; $3 <$ I-geo ≤ 4 (grade 4), severely contaminated; $4 <$ I-geo ≤ 5 (grade 5), severely extremely contaminated; I-geo > 5 (grade 6), extremely contaminated (Müller, 1969).

Bioaccumulation factor and biological transfer factor

For each metal, Bioaccumulation Factor (BAF) of a plant is the heavy metal concentration in aboveground part (mainly leaf or leaf plus shoot where appropriate) divided by the metal concentration in soil, and this is used to evaluate the plant's uptake capacity of the metal from soil. Biological Transfer Factor (BTF) is the heavy metal content of aboveground tissues divided by the metal content in roots, which indicates the transfer efficiency of a metal to the aerial parts.

Statistical analysis

All statistical analyses were performed using SPSS 12 for Windows. One-way ANOVA was carried out to compare the difference of means from various sampling sites, followed by multiple comparisons using the least significant difference (LSD) test. The level of significance was set at $P < 0.05$ (two-tailed).

Results

Nutrient status and heavy metals in minesoil

The soil nutrients, total heavy metal concentrations and 0.1 M HCl-extractable fractions were presented in Table 1. Soil pH ranged from 4.65 to 5.59 and averaged 5.03, indicating an acid nature. Significant variations existed among the four sites for the macronutrients. The active mining area had the highest N and organic matter (OM) contents probably because this area was freshly excavated from hilly slope with a good vegetation cover. The mean soil TN and OM barely fell into "moderate" class (0.8–1.0 g/kg for TN and 10–15 g/kg for OM) according to China Soil Fertility Standard for Green Food Production (NY/T 391-2000). However, when TP was concerned, this minesoil was considered very low (averaged 0.41 g/kg) since soil TP less than 0.8–1.0 g/kg can limit plant growth (Zhejiang Agricultural University 1991).

The minesoils were characterized by elevated levels of all the studied metals compared with the local (Guilin) and China soil background concentrations. The highest total metal levels were observed in the fresh tailings dam for all metals, especially for Mn, Pb and Cd for which concentrations were 80.9, 11.8 and 96.1 times higher than their local soil background values respectively. Basically heavy metal concentrations followed the order of Mn $>$ Cr $>$ Pb $>$ Zn $>$ Cu $>$ Cd in the minesoil whereas in natural soil, the order was Mn $>$ Cr ~ Zn $>$ Cu ~ Pb $>$ Cd. All the extractable metal fractions were below 5% of their total concentrations, indicating a pretty low availability (exchangeable + potentially available) to higher plants. Among the metals, Cd, on average, had the highest percentage (3.55%) of extracted portions while Cr the lowest (0.19%). A correlation analysis between the total and extractable fractions revealed no significant correlation existed for Pb, Cr and Cd, but positive correlations ($p < 0.05$) found for Mn ($r = 0.81$), Zn ($r = 0.90$) and Cu ($r = 0.96$), respectively.

Pollution assessment of minesoil

The pollution assessment results with Pi and I-geo were shown in Table 2. Pi indicated that the minesoil was not polluted by Pb, Cu and Zn, but was slightly polluted by Cr and seriously polluted by Cd. Fresh tailings dam had the greatest Pi and I-geo values, demonstrating this site was more severely contaminated than others.

For the five metals, all I-geos showed severer pollution than Pi, but the pollution trend of different metals remained. For instance, slightly moderate to moderately severe contamination were identified with I-geo for Cu, Pb and Zn, while no pollution were assessed as with Pi, and conversely, a moderate contamination for Cr with I-geo while a slight pollution was indicated by Pi. For Cd, both assessments identified the heaviest grade of contamination (Table 2).

Table 1. The nutrients and heavy metal concentrations of minesoils (mean ± SE, $n = 3$) in Pingle Mn mineland. Data in parenthesis indicate the percentage of extracted fractions to the total metal concentrations.

Parameter	Sampling site				Guilin background value[a]	China background value
	Mining area (MA)	**Fresh tailings dam (FTD)**	**Reclaimed tailings dam (RTD)**	**Restored area (RA)**		
pH	4.65 ± 0.05a[b]	5.08 ± 0.17a	5.59 ± 0.27a	4.81 ± 0.14a		
Total N (g/kg)	1.09 ± 0.10a	0.89 ± 0.06b	0.47 ± 0.04c	0.65 ± 0.05c		
Total P (g/kg)	0.36 ± 0.01b	0.59 ± 0.08a	0.41 ± 0.04b	0.29 ± 0.06b		
Organic matter (g/kg)	24.82 ± 2.63a	11.67 ± 2.08b	5.96 ± 0.81b	8.64 ± 0.89b		
Total Mn (mg/kg)	10423.9 ± 68.5b	17839.7 ± 1841.5a	4648.4 ± 1696.1c	2095.6 ± 418.8c	220.45	482
Extracted Mn (mg/kg)	89.61 ± 7.09c (0.86%)	543.28 ± 65.26a (3.05%)	209.31 ± 33.61b (4.50%)	82.13 ± 15.46c (3.92%)		
Total Pb (mg/kg)	170.70 ± 7.07b	239.27 ± 26.20a	176.11 ± 5.88b	158.25 ± 10.29b	20.32	24.0
Extracted Pb (mg/kg)	2.04 ± 0.24a (1.2%)	2.79 ± 0.69a (1.17%)	3.58 ± 0.77a (2.03%)	1.99 ± 0.52a (1.26%)		
Total Zn (mg/kg)	136.65 ± 7.15a	198.24 ± 10.91a	144.37 ± 12.54a	161.12 ± 16.65a	62.33	67.4
Extracted Zn (mg/kg)	2.65 ± 0.61a (1.94%)	4.38 ± 1.53a (2.21%)	2.23 ± 0.18a (1.54%)	2.48 ± 0.53a (1.54%)		
Total Cu (mg/kg)	40.69 ± 2.89b	85.69 ± 14.51a	50.68 ± 7.59b	45.31 ± 5.26b	25.47	20.0
Extracted Cu (mg/kg)	1.14 ± 0.14a (2.8%)	2.40 ± 1.22a (2.8%)	1.04 ± 0.07a (2.05%)	0.94 ± 0.17a (2.07%)		
Total Cr (mg/kg)	196.65 ± 11.47a	256.84 ± 22.25a	253.95 ± 7.01a	235.11 ± 19.33a	64.63	54.1
Extracted Cr (mg/kg)	0.33 ± 0.02a (0.17%)	0.46 ± 0.17a (0.18%)	0.42 ± 0.06a (0.17%)	0.53 ± 0.02a (0.23%)		
Total Cd (mg/kg)	4.29 ± 0.77a	7.55 ± 0.81a	6.48 ± 0.79a	6.13 ± 0.24a	0.0786	0.07
Extracted Cd (mg/kg)	0.19 ± 0.03a (4.43%)	0.31 ± 0.07a (4.11%)	0.25 ± 0.05a (3.86%)	0.11 ± 0.01a (1.79%)		

[a] Source from Guangxi Environmental Science Institute, 1991.

[b] Different letters in the same row indicate significant difference at $p < 0.05$ according to the least significant difference test.

Table 2. The pollution (Pi) and geo-accumulation (I-geo) indices of minesoils and their pollution grading.

Metal		**Site**			
		MA[a]	**FTD**	**RTD**	**RA**
Pb	Pi	0.68	0.96	0.70	0.63
	Grade	Unpolluted	Unpolluted	Unpolluted	Unpolluted
	I-geo	2.49	2.97	2.53	2.38
	Grade	SMC[b]	SMC	SMC	SMC
Zn	Pi	0.68	0.99	0.72	0.81
	Grade	Unpolluted	Unpolluted	Unpolluted	Unpolluted
	I-geo	0.55	1.08	0.63	0.79
	Grade	SMC	MC	SMC	SMC
Cu	Pi	0.27	0.57	0.34	0.30
	Grade	Unpolluted	Unpolluted	Unpolluted	Unpolluted
	I-geo	0.09	1.17	0.41	0.25
	Grade	SMC	MC	SMC	SMC
Cr	Pi	1.31	1.71	1.69	1.57
	Grade	Slight	Slight	Slight	Slight
	I-geo	1.02	1.41	1.39	1.28
	Grade	MC	MC	MC	MC
Cd	Pi	14.29	25.18	21.60	20.44
	Grade	Heavy	Heavy	Heavy	Heavy
	I-geo	5.18	6.00	5.78	5.70
	Grade	EC	EC	EC	EC
Mn	I-geo	4.98	5.75	3.81	2.66
	Grade	SEC	EC	SC	MSC

[a] See Table 1 for the complete site name.
[b] Pollution grades for I-geo: SMC: Slightly moderately contaminated; MC: Moderately contaminated; MSC: Moderately severely contaminated; SC: Severely contaminated; SEC: Severely extremely contaminated; EC: Extremely contaminated.

As for Mn, there was no stipulated value in China soil quality standard, but the calculated I-geos were 4.98, 5.75, 3.81 and 2.66 respectively for the mining area, fresh tailings dam, reclaimed tailings dam and restored area. These results reflected moderately severe to extreme contamination existed. Also, a reported appropriate Mn range in soil was 170–1,200 mg/kg (Wang, 1995), but Mn levels in this mineland were about 1.8–14.9 times of the upper limit, supporting that the minesoil was contaminated with Mn, especially in the active mining area and fresh tailings dam.

Phytoaccumulation and transfer of heavy metals

Heavy metal contents in the dominant plants were showed in Table 3. Different plants and different tissues of the same species varied greatly in heavy metal concentrations with Mn ranging from 1.3–9975.6 (average at 1341.5) mg/kg, Pb $<$ limit of detection-51.5 (26.4) mg/kg, Zn 1.6–121.4 (46.3) mg/kg, Cd 0.01–11.39 (3.82) mg/kg, Cr 1.0–100.3 (41.1) mg/kg, and Cu 0.3–55.6 (11.8) mg/kg. In general, the normal heavy metal contents of terrestrial plants growing in uncontaminated soil were in the range of 0.1–41.7 mg/kg for Pb, 1–160 mg/kg for Zn, 0.2–0.8 mg/kg for Cd, 0.2–8.4 mg/kg for Cr, 0.4–45.8 mg/kg for Cu (Cao and Chi, 2001) and 1–700 mg/kg for Mn (Gerber et al. 2002). Thus, for these mineland plants, all Cu and Zn contents fell within the normal range, and some Mn and a few Pb levels above the range while all Cd and almost all Cr levels greatly exceeded the upper limit of the normal range, showing they accumulated higher Cd and Cr from

Table 3. Heavy metal concentrations of the plant tissues for the dominant species in Pingle mineland.

Localization	Species	Tissue	Mn (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Cd (mg/kg)
Mining area	*Schima superba*	Leaf	9975.61	10.57	32.90	3.89	74.34	2.66
		Shoot	1665.88	43.74	39.51	8.10	22.62	0.87
		Root	739.04	32.06	86.98	4.36	29.51	1.19
	Pinus massoniana	Leaf	1670.33	18.43	46.78	1.19	8.49	2.99
		Shoot	1218.37	23.44	43.77	5.75	4.41	3.50
		Root	1193.57	16.10	71.62	6.70	64.01	3.24
	Imperata cylindrical	Leaf	250.07	3.81	78.01	2.96	69.16	1.44
		Root	136.06	6.89	44.35	2.49	77.84	2.02
Fresh tailings dam	*Phytolacca acinosa*	Leaf	5300.98	24.09	49.02	28.23	95.09	3.69
		Shoot	405.00	7.50	22.77	9.04	84.74	2.99
		Root	237.66	30.46	36.86	6.99	7.33	3.05
	Solanum nigrum	Leaf	325.30	19.18	71.26	28.35	93.37	2.66
		Shoot	89.55	33.92	57.24	22.14	79.55	6.13
		Root	60.94	27.16	61.53	39.82	93.37	4.46
	Amaranthus tricolor	Leaf	313.59	30.85	67.83	55.62	100.27	4.14
		Shoot	77.48	32.69	51.69	11.85	89.92	3.24
		Root	85.47	23.47	32.03	14.66	98.53	3.63
Reclaimed tailings dam	*Prunus persica*	Fruit	13.62	7.01	16.47	3.41	10.12	0.15
		Leaf	242.83	24.95	19.95	5.28	15.79	2.54
		Shoot	99.44	35.47	30.64	8.41	12.29	2.79
		Root	226.83	30.46	21.18	6.89	10.54	2.02
	Castanea mollissima	Nut	139.44	6.99	18.31	10.58	6.86	1.96
		Leaf	1674.87	37.97	45.66	6.03	19.58	0.87
		Shoot	1032.19	49.50	32.61	6.60	18.12	3.24
		Root	489.54	11.91	23.58	6.23	17.83	1.96
	Erigeron acer	Leaf	734.30	32.96	78.40	26.37	19.87	11.39
		Shoot	430.69	33.47	60.61	13.45	28.33	11.32
		Root	488.60	29.96	39.29	32.83	21.92	7.67
	Panicum repens	Leaf + Shoot	271.97	41.98	22.65	6.22	18.70	1.89
		Root	134.99	51.51	33.85	7.84	21.04	2.02
Restored area	*Prunus persica*	Leaf	346.42	47.00	27.86	7.27	22.21	2.66
		Shoot	137.02	28.45	35.51	7.08	19.58	2.73
		Root	55.25	41.49	26.67	5.09	18.41	2.54
	Phytolacca acinosa	Leaf	7122.42	12.42	53.85	10.69	26.29	9.01
		Shoot	881.56	43.98	24.92	7.55	24.54	4.72
		Root	583.12	36.47	23.42	9.07	22.20	4.07
	Imperata cylindrical	Leaf	302.12	2.23	41.10	1.35	23.40	3.54
		Root	142.24	ND[a]	13.23	3.75	27.16	2.21
	Hedyotis auricularia	Leaf	1586.73	31.24	121.41	7.09	28.26	6.77
		Root	942.62	13.65	118.68	14.74	22.06	6.57

[a] ND, not detectable.

substrate even though the bioavailability is low in relation to the total Cr.

Table 4 presented the Bioaccumulation Factor (BAF) and Biological Transfer Factor (BTF) of the dominant plants. Almost all BAFs were less than 1.0 except the Mn hyperaccumulator *P. acinosa* in the restored area for Mn and *E. acer*, *P. acinosa* and *H. auricularia* for Cd. On average, plants tended to have a relatively higher BAF for Cd (0.66) but lower BAF for Pb (0.13). However, all plants showed high Mn transfer rate (BTF = 5.6) while Pb and Cu were few transported to the above-ground parts. In addition, *S. superba* and *P. acinosa* demonstrated unusually high Mn relocation ability and high Cd transfer feature as well.

Discussion

Soil pollution and phytotoxicity

In general, minesoil is characterized by the elevated heavy metal concentrations, deficiency of major nutrients, poor physical structure, extreme acidity and/or salinity, drought, and other stressful factors (Li, 2006; Shu et al. 2005; Wong and Luo, 2003; Yang et al. 2003). Heavy metal pollution of minesoil is a widely documented problem (Liu et al. 2004; Lei et al. 2005; Xie et al. 2005) but has been largely overlooked in China because they are usually remote to the densely populated urban areas. For example, in the five Pb/Zn mineland in south China, very high Pb, Zn, Cu and Cd concentrations were found in the substrates with plant communities (Shu et al. 2005); Investigations on the six tailings dams (mainly Sn and Sb mines) in northwest Guangxi showed very high levels of Pb, Zn, As, Cd, Cu, Sb and Sn in tailings substrate (Zhou et al. 2003). In a slag wasteland of Xiangtan Mn mine in the neighboring Hunan Province, minesoil was contaminated with Mn (7990.2 mg/kg), Pb (401.15 mg/kg), Zn (640.32 mg/kg), Cd (13.15 mg/kg) and Ni (91.33 mg/kg), especially most severely with Cd and Mn (Fang et al. 2006).

The pollution index (Pi) was extensively used for soil pollution assessment in China (Chen et al. 2005; Fang et al. 2006; Li et al. 2005; Zheng et al. 2006) and proved to be simple and effective because it related directly to a certain quality criterion. I-geo was also employed for evaluation of heavy metal contamination (Yang et al. 2004a; Li et al. 2006; Chen et al. 2006) of sediment when its natural background value was available. In this study, I-geo assessment indicated a severer pollution of minesoil than Pi, the similar scenario also reported by Hu (2003) who used a modified correction factor (1.0 instead of 1.5). The difference of the two

Table 4. Bioaccumulation Factor (BAF) and Biological Transfer Factor (BTF) of the dominant plants in Pingle mineland.

Species (site)	**Mn**		**Pb**		**Zn**		**Cu**		**Cr**		**Cd**	
	BAF	**BTF**	**BAF**	**BTF**	**BAF**	**BTF**	**BAF**	**BTF**	**BAF**	**BTF**	**BAF**	**BTF**
S. superba (MA)	0.96	13.50	0.06	0.33	0.24	0.38	0.10	0.89	0.38	2.52	0.62	2.24
P. massoniana (MA)	0.16	1.40	0.11	1.14	0.34	0.65	0.03	0.18	0.04	0.13	0.70	0.92
I. cylindrical (MA)	0.02	1.84	0.02	0.55	0.57	1.76	0.07	1.19	0.35	0.89	0.34	0.71
P. acinosa (FTD)	0.30	22.31	0.10	0.79	0.25	1.33	0.33	4.04	0.37	12.98	0.49	1.21
S. nigrum (FTD)	0.02	5.34	0.08	0.71	0.36	1.16	0.33	0.71	0.36	1.00	0.35	0.60
A. tricolor (FTD)	0.02	3.67	0.13	1.31	0.34	2.12	0.65	3.79	0.39	1.02	0.55	1.14
P. persica (RTD)	0.05	1.07	0.14	0.82	0.14	0.94	0.10	0.77	0.06	1.50	0.39	1.25
C. mollissima (RTD)	0.36	3.42	0.22	3.19	0.32	1.94	0.12	0.97	0.08	1.10	0.13	0.44
E. acer (RTD)	0.16	1.50	0.19	1.10	0.54	2.00	0.52	0.80	0.08	0.91	1.76	1.49
P. repens (RTD)	0.06	2.01	0.24	0.81	0.16	0.67	0.12	0.79	0.07	0.89	0.29	0.94
P. persica (RA)	0.17	6.27	0.30	1.13	0.17	1.04	0.16	1.43	0.16	1.21	0.43	1.05
P. acinosa (RA)	3.40	12.21	0.08	0.34	0.33	2.30	0.24	1.18	0.19	1.18	1.47	2.21
I. cylindrical (RA)	0.14	2.12	0.01	NA[a]	0.26	3.11	0.03	0.36	0.17	0.86	0.58	1.60
H. auricularia (RA)	0.76	1.68	0.20	2.29	0.75	1.02	0.16	0.48	0.21	1.28	1.10	1.03

[a] NA, not available because the Pb content in the root was not determined.

assessments lies in that I-geo linked theoretically all "pollution contribution" to the single soil background value only, not discriminating the natural lithogenic effect from anthropogenic contribution within the mineland context. The high metal levels of minesoil may be caused by a combination of naturally elevated background value owing to the parent rock weathering with the extra released metals through mining (pollution). The index of geoaccumulation considered them all as pollution contribution, thus overestimated the real pollution effect. To make the I-geo assessment results comparable for minelands, the real background value of minesoil (usually higher than the local natural soil) must be reinvestigated or the correction factor be properly modified.

Phytotoxicities have generally been associated with 3–8 mg/kg total Cd in soil, 60–125 mg/kg Cu, 1500–3000 mg/kg Mn (Ross, 1994), 500–1000 mg/kg Pb (Chaney, 1993), or 300 mg/kg Zn (Lepp, 1981). In this mineland, soil Mn, especially in the tailings dam and mining zone, is potentially phytotoxic and may constrain initial colonization by pioneers (Ye et al. 2002). However, it is widely accepted that the total metal concentration in soil overestimates the risk of phytotoxity, but in the present study, despite the low relative extractability of the metals, the bioavailable concentration of some metal is marginally high and surpass the thresholds of phytotoxity. In addition, several studies have shown a poor correlation between plant uptake and total metal levels in soil (Kabata-Pendias, 1993; Remon et al. 2005) mainly due to the various chemical association forms with different bioavailability (Maiz et al. 1997, 2000). Moreover, even the bioavailable metals are poorly correlated to the metals absorbed by plants (Wang et al. 2003), as the latter can modify the soil conditions in the rhizosphere, and may develop specific physiological strategies for excluding and accumulating metals. Using the same soil extraction scheme (0.1 M HCl) for Lipu Mn mineland (about 35 km away from Pingle), the mean mobilizable fractions were 1.2% for Pb, 2.8% for Cu, 2.4% for Cd, 1.6% for Zn and 3.1% for Mn (Li et al. 2007), the results agreeing well with those from this study.

Phytoremediation and restoration of mineland

Phytoremediation is defined as the use of plants to remove pollutants from soils or to render them harmless (Salt et al. 1998). Within the mineland context, phytoremediation technologies basically include phytoextraction in which hyperaccumulator plants remove metals from the abandoned substrates and concentrate them in the harvestable parts of plants (Kumar et al. 1995), and phytostabilisation where plants reduce the mobility and bioavailability of metals in the sediments either by immobilization or by prevention of migration (Smith and Bradshaw, 1972; Vangronsveld et al. 1995). Among the studied plants in this mineland, *P. acinosa* (a perennial herb) is a reported Mn hyperaccumulator and its maximum Mn content in leaves reached 19,300 mg/kg (Xue et al. 2004). However, the leaf Mn content was only 7122.4 mg/kg in this mineland, the difference may be caused by the great variation of soil Mn concentrations (52,359–114,013 mg/kg in Xiangtan vs. 2,095.6–17,839.7 in Pingle). Another plant of interest is *S. superba*, a wide distributed tree species commonly used for forest firebreak, contained 9975.6 mg/kg Mn in leaves. This result was very close to the suggested hyperaccumulator threshold by Baker and Brooks (1989). Furthermore, its BAF and BTF for Mn were 0.96 and 13.5, showing this woody plant could be a prospective Mn hyperaccumulator. A further pot growth experiment confirmed this species is a Mn hyperaccumulator (Yang et al. 2008).

While phytoextraction seems only promising for cleanup of slight to moderate polluted soil (Wong, 2003), phytostabilization is more realistic for remediation of minesites usually with higher heavy metal levels. A desired species for revegetating mine wasteland should best grow well on poor and harsh soils and develop vegetation cover in a relatively short time and accumulate biomass rapidly. In addition, native species with metals stored in roots (low BTF) are most beneficial to minimize dispersal. Shen et al. (2004) listed a wide range of plant species used for phytostabilization of minesites and evaluated their growth performances in different parts of China. In an almost barren slag wasteland of Xiangtan Mn mine, the initial natural herbaceous colonizers were *Imperata cylindrical*, *Erigeron annuns*, *Cynodon dactylon*, *Paspalum ethunbergii*, *Arthraxon hispidus*, *Juncus effuses*, and *P. acinosa* (Yan et al. 2006). In the less harsh minesoil of Lipu Mn mine, Guangxi, 36 species (26 herbs and 10 woody) were found colonizing (Li et al. 2007), of which *Digitaria sanguinalis, Erigeron canadensis, Urena lobara, Imperata cylindrica* var. *major, P. acinosa, Pteridium* *aquilinum* var. *latiusculum* and *Pteris multifida* were dominant. These floras give some insights to the restoration design of Mn mine wasteland in Guangxi: firstly, the local pioneer species *D. sanguinalis, C. dactylon, I. cyclindrica* var. *major,* and *E. canadensis* could be employed to colonize and ameliorate the wasteland, and then an association with fast growing species *C. henryi, P. massoniana* and *Eucalyptus spp*. might restore some functional uses.

The aim of restoration of mine wastelands is to remediate ecological destruction and reduce pollution dispersion. If rehabilitation of mine spoils causes another serious pollution to human being, the loss outweighs the gain. A general tendency of mineland rehabilitation in China is the utilitarian reclamation for agriculture. From our investigation on the six major Mn minelands in Guangxi, more than 50 edible plants were found planting on the mine wasteland including Chinese chestnut, sugarcane, peanut, beans, potato and tubes, mandarin, orange, peach, Taiwan green Jujube, and tea trees. This conduct is more common in Guangxi than other areas of China probably owing to the poverty and severer shortage of cultivated land and to some extent is encouraged by the local government (Li et al. 2007). Worries arose because there were usually no protective treatments in place before planting and no monitoring of residual toxic metals was exercised before they enter the food chain. In the present study, both the peach fruit (*P. persica*) and Chinese chestnut (*C. mollissima*) greatly exceeded the Food Safety Standards of China in terms of the maximum allowable Cd, Cr and Pb levels (Table 3). Thus simple reclamation for agriculture use is of high risk unless sufficient treatments, e.g. separation layer, cover of guest soil over 50-cm deep (Wong and Luo, 2003), or substantial substrate amendments (Li, 2006), are in place before planting.

Other diverse restoration goals can also be considered. In Bayi Mn mineland of Guangxi, large areas were reclaimed with the fast-growing Eucalyptus forest for pulpwood while in Lipu Mine (Guangxi), some wastelands were reused as osmanthus (a local favorite gardening tree) nursery. This restoration mode has lower environmental risk and is more adaptive to different minelands. Furthermore, to leap out of the utilitarianism-oriented reclamation, biodiversity conservation, providing habitat to wildlife, checking soil and wind erosion and mitigating pollution dispersal, recreation and tourism, or beautifying the damaged landscape alone can become the aims of ecological restoration.

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Disclosure

The authors report no conflicts of interest.

References

Andrews-Speed, P., Yang, M.Y., Shen, L. and Cao, S. 2003. The regulation of China's township and village coal mines: a study of complexity and ineffectiveness. *J. Clean. Prod.*, 11:185–96.

Baker, AJM. and Brooks, R.R. 1989. Terrestrial higher plants which hyperaccumulate metallic elements—a review of their distribution, ecology and phytochemistry. *Biorecovery*, 1:81–126.

Cao, J.L. and Chi, B.L. 2001. Urban ecological corridor. Meteorological Press. Beijing.

Chaney, R.L. 1993. Zinc phytotoxicity. In: Robson, A.D., editor. Zinc in soils and plants. Kluwer Academic Publishers. *Dordrecht.*, p. 135–150.

Chen, T.B., Zheng, Y.M., Lei, M., Huang, Z.C., Wu, H.T., Chen, H., Fan, K.K., Yu, K., Wu, X. and Tian, Q.Z. 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere*, 60:542–51.

Chen, X.Y., Huang, H. and Sang, H.Q. 2006. The application of the index of Geoaccumulation to evaluate heavy metal pollution in sediments in the Huainan section of the Huaihe River. *J. Anhui Sci. Technol. Univ.*, 20(2):35–8[in Chinese with English abstract].

Erikson, K.M. and Aschner, M. 2003. Manganese neurotoxicity and glutamate_GABA interaction. *Neurochem. Int.*, 43:475–80.

Fang, X., Tian, D.L. and Xie, R.X. 2006. Soil physical and chemical properties of the wasteland in Xiangtan manganese mine. *Acta. Ecol. Sin.*, 26(5):1494–501[in Chinese with English abstract].

Gerber, G.B., Leonard, A. and Hantson, P. 2002. Carcinogenicity, mutagenicity and teratogenicity of manganese compounds. *Crit. Rev. Oncol./Hematol.*, 42:25–34.

Guangxi Environmental Science Institute. 1991. Study on the soil background values of Guangxi. Guangxi Science and Technology Press, Nanning. p. 156–67.

Hu, N.J. 2003. Study on environmental geochemistry of heavy metal and assessment in sewage-irrigated paddy soil in Guixi region. Master's degree thesis, Chengdu University of Science and Technology, China.

Kabata-Pendias, A. 1993. Behavioral properties of trace metals in soils. *Appl. Geochem.*, 2:3–9.

Kumar, PBAN, Dushenkov, V., Motto, H. and Raskin, I. 1995. Phytoextraction: the use of plants to remove heavy metals from soils. *Environ. Sci. Technol.*, 29:1232–8.

Lei, M., Yue, Q.L., Chen, T.B., Huang, Z.C., Liao, X.Y., Liu, Y.R., Zheng, G.D. and Chang, Q.R. 2005. Heavy metal concentrations in soils and plants around Shizhuyuan mining area of Hunan Province. *Acta. Ecol. Sin*, 25(5):1146–151[in Chinese with English abstract].

Lepp, N.W. 1981. Effect of heavy metal pollution on plants. Volume 1. Effects of trace metals on plant function. Applied Science Publishers, London.

Li, J.T., Qiu, J.W., Wang, X.W., Zhong, Y., Lan, C.Y. and Shu, W.S. 2006a. Cadmium contamination in orchard soils and fruit trees and its potential health risk in Guangzhou, China. *Environ. Pollut.*, 143(1):159–65.

Li, J., Xie, Z.M., Zhu, Y.G. and Naidu, R. 2005. Risk assessment of heavy metal contaminated soil in the vicinity of a lead/zinc mine. *J. Environ. Sci.*, 17(6):881–5.

Li, M.S. 2006. Ecological restoration of mineland with particular reference to the metalliferous mine wasteland in China: A review of research and practice. *Sci. Total Environ.*, 357:38–53.

Li, M.S., Luo, Y.P. and Su, Z.Y. 2007. Heavy metal concentrations in soils and plant accumulation in a restored manganese mineland in Guangxi, South China. *Environ. Pollut.*, 147:168–75.

Liu, H.X., Wang, X.Y. and Han, B.P. 2004. Soil pollution evaluation with heavy metals in Baodian Coal field of Yanzhou Mineral Industry Group. *Energy Environ. Protect.*, 18(2):56–8[in Chinese with English abstract].

Liu, Y.L. and Jiang, X.Y. 2004. Evaluation of heavy metal pollution of soil and crops in Baima village, Zhuzhou City. *Soils*, 36(5):551–6[in Chinese with English abstract].

Maiz, I., Arambarri, I., Garcia, R. and Millán, E. 2000. Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. *Environ. Pollut.*, 110:3–9.

Maiz, I., Esnaola, M.V. and Millán, E. 1997. Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure. *Sci. Total Environ.*, 206:107–15.

Müller, G. 1969. Index of geoaccumulation in sediments of the Rhine River. *Geo. J.*, 2:109–18.

Pugh, R.E., Dick, D.G. and Fredeen, A.L. 2002. Heavy metal (Pb, Zn, Cd, Fe, and Cu) contents of Plant Foliage near the Anvil Range Lead/Zinc Mine, Faro, Yukon Territory. *Ecotox. Environ. Saf.*, 52:273–9.

Raven, P.H. 2002. Science, sustainability, and the human prospect. *Science*, 297:954–8.

Remon, E., Bouchardon, J.L., Cornier, B., Guy, B., Leclerc, J.C. and Faure, O. 2005. Soil characteristics, heavy metal availability and vegetation recovery at a former metallurgical landfill: Implications in risk assessment and site restoration. *Environ. Pollut.*, 137:316–23.

Ross, S.M. 1994. Toxic metals in soil-plant systems. John Wiley and Sons, Chichester.

Salt, D.E., Smith, R.D. and Raskin, I. 1998. Phytoremediation. *Ann. Rev. Plant. Physiol.*, 49:643–468.

Shen, W.S., Cao, X.Z. and Jin, Y. 2004. Ecological Destruction and Reconstruction of Minelands. China Environmental Science Press, Beijing. [in Chinese].

Shu, W.S., Ye, Z.H., Lan, C.Y., Zhang, Z.Q. and Wong, M.H. 2001. Acidification of lead/zinc mine tailings and its effect on heavy metal mobility. *Environ. Int.*, 26:389–94.

Shu, W.S., Ye, Z.H., Zhang, Z.Q., Lan, C.Y. and Wong, M.H. 2005. Natural colonization of plants on five Lead/Zinc mine tailings in Southern China. *Restor. Ecol.*, 13(1):49–60.

Smith, RAH. and Bradshaw, A.D. 1972. Stabilisation of toxic mine wastes by the use of tolerant plant populations. *Trans. Inst. Min. Metall. Sect. A.*, 81:230–7.

Vangronsveld, J., van Assche, F. and Clijsters, H. 1995. Reclamation of a bare industrial area contaminated by non-ferrous metals: in situ metal immobilization and revegetation. *Environ. Pollut.*, 87:51–9.

Vartanian, J.P., Sata, M., Henry, M., Hobson, S.W. and Meyerhans, A. 1999. Manganese cations increase the mutation rate of human immune deficiency virus type 1 ex vivo. *J. Gen. Virol.*, 80:1983–6.

Wang, J.G. 1995. Soil chemistry of plant nutrients. China Agricultural University Press, Beijing.

Wang, W.S., Shan, X.Q., Wen, B. and Zhang, S.Z. 2003. Relationship between the extractable metals from soils and metals taken up by maize roots and shoots. *Chemosphere*, 53:523–30.

Wong, M.H. 2003. Ecological restoration of mine degraded soils, with emphasis on mental contaminated soils. *Chemosphere*, 50:775–80.

Wong, M.H. and Luo, Y.M. 2003. Land remediation and ecological restoration of mined land. *Acta. Pedol. Sin.*, 40(2):161–9[in Chinese with English abstract].

Xie, R.X., Tian, D.L. and Fang, X. 2005. Assessment of pollution of heavy metals on the slag wasteland of Xiangtan manganese mine. *J. Central South For. Uni.*, 25(2):38–41[in Chinese with English abstract].

Xue, S.G., Chen, Y.X., Reeves, R.D., Baker, A.J.M., Lin, Q. and Fernando, D.R. 2004. Manganese uptake and accumulation by the hyperaccumulator plant *Phytolacca acinosa* Roxb. (Phytolaccaceae). *Environ. Pollut.*, 131:393–9.

Yan, W.D., Xiang, J.L. and Tian, D.L. 2006. Study on characteristics of soil in mining abandoned lands in Xiangtan, Hunan Province. *Scientia Silvae Sinicae.*, 42(4):12–8[in Chinese with English abstract].

Yang, B., Shu, W.S., Ye, Z.H., Lan, C.Y. and Wong, M.H. 2003. Growth and metal accumulation in vetiver and two Sesbania species on lead/zinc mine tailings. *Chemosphere.*, 52:1593–600.

Yang, Q.W., Shu, W.S., Qiu, J.W., Wang, H.B. and Lan, C.Y. 2004a. Lead in paddy soils and rice plants and its potential health risk around Lechang Lead/Zinc Mine, Guangdong, China. *Environ. Int.*, 30:883–9.

Yang, S.Y., Xie, J.C. and Liu, D.Y. 2004b. Reclamation and plant colonization in Copper mine tailings in Tongling, Anhui Province. *Res. Environ. Yangtze Basin.*, 13(5):488–93 [in Chinese with English abstract].

Yang, S.X., Deng, H. and Li, M.S. 2008. Manganese uptake and accumulation in a woody hyperaccumulator, *Schima. superba*. *Plant. Soil Environ.*, 54(10):441–6.

Ye, Z.H., Shu, W.S., Zhang, Z.Q., Lan, C.Y. and Wong, M.H. 2002. Evaluation of major constraints to revegetation of lead/zinc mine tailings using bioassay techniques. *Chemosphere*, 47:1103–11.

Zhejiang Agricultural University, 1991. Plant nutrition and fertilizer. Agricultural Press, Beijing [in Chinese].

Zheng, G.Z., Yue, L.P., Li, Z.P. and Chen, C. 2006. Assessment on heavy metals pollution of agricultural soil in Guanzhong District. *J. Geograph. Sci.*, 16(1):105–13.

Zhou, X., Song, S.Q. and Wu, H. 2003. An investigation of plants on the tailings of abandoned nonferrous mines in the Diaojiang basin of Guangxi. *Trop. Geography*, 23(3):226–30 [in Chinese with English abstract].

Zhu, C.C., Zhang, B.Y., Ye, F.L., Zhu, G.X. and Yang, J.Q. 1999. Effects of manganese exposure on male sexual hormone. *Chin. Public Health*, 15:63–4 [in Chinese].

Zu, Y.Q., Li, Y., Chen, J.J., Chen, H.Y. and Schvartz, C. 2005. Hyperaccumulation of Pb, Zn and Cd in herbaceous grown on lead-zinc mining area in Yunnan, China. *Environ. Int.*, 31:755–62.