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## Rehabilitation of a tailing dam at Shimen County, Hunan Province: Effectiveness assessment

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### ABSTRACT

This study was conducted to assess the effectiveness of phytoremediation on a tailing dam located in Shimen County, Hunan Province. Quadrat survey method was employed to investigate and sample the dominant plant species growing on the rehabilitated tailing dam. The fertilities of the soils were assessed, and concentrations of arsenic and other heavy metals in the plant and soil samples were measured. The results showed that no difference was found on the effect of soil capping with top and non-topsoils for rehabilitation of plants on the tailing dam. After rehabilitation, stable vegetation coverage types were established, 39 plant species were found to grow on the tailing dam, and the minimal area for plant communities was 30 m<sup>2</sup>. The dominant plant species were planted *Pteris vittata* and natural colonizing *Miscanthus sinensis*. The contents of organic matter, nitrogen and phosphorus in the soils were low, while the potassium content was at a middle level; however, plots where *Legumina* plants grew were found to have higher level of nitrogen and phosphorus in the growing soils. Arsenic (As) and Cadmium (Cd) concentrations in the soils were 8 and 7 times of the grade III value of the National Standard for Soil Quality (GB15618-1995), respectively; while in tailings these were 81 and 68 times. The available As concentration in the soils ranged as 3.7–29.5 mg kg<sup>-1</sup>, whereas the available As concentration in tailings was as high as 61.1 mg kg<sup>-1</sup>. Concentrations for most of the heavy metals were in the normal range of terrestrial higher plants, except As and Cd in *P. vittata* and *M. sinensis*, and As in the roots of *M. sinensis*. It is concluded that phytoremediation project has reduced the ecological and health risks caused by the tailing dam to the ambient environment. However, the plants growing on the tailing dam which contained high As and Cd should be kept from entering into food chain in order to protect the health of local residents.

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### 1. Introduction

Arsenic (As) is a toxic and carcinogenic element [1,2], it is usually present in coals or the ores with various sulfur-containing minerals. Anthropogenic activities such as mining, smelting and coal combustion have resulted in the release of As into land surface environment, causing serious As-contamination [3]. Approximate 70% of total As deposits are distributed in China, however, an average of 70% of the exploited As remain in tailings during the mineral processes under current technique level in China [4]. The open pit dumping of As-containing tailings has released large amounts of hazardous matters into soils and surface waters through wind and hydraulic erosion. Several As poisoning incidents that causing many people sick have been reported in Yunnan, Guangxi and Hunan Provinces, these were usually related with the leaching of heavy metals in tailings that had entered into the surface water and groundwater systems [3]. Arsenic can enter livestock and human

bodies via food chain, rendering detrimental effects to human health. Endemic epidemics of arsenicosis have occurred in 37 counties and eight provinces in China [5,6].

Currently, several technologies are available for remediation of arsenic contamination in tailings, including physical–chemical remediation and bioremediation (employing microorganisms or plants) approaches. Phytoremediation has the advantages in cost-effectiveness, effect-efficiency and no further contamination, it is also easy to be implemented [7,8]. Pilot experiments and surveys on the remediation of tailing dams have been conducted in Dexing copper mines in Jiangxi, Tongling copper mines in Anhui and Shao-guan lead–zinc mines in Guangdong [9–11]. These studies assessed the remediation effects only through the comparison of the values between detected target pollutants and those of the national soil environmental quality standards [12]. However, no information is available relating the rehabilitation processes with plant colonization and soil fertility improvement; in addition, the potential ecological and health risks due to the uptake and accumulation of various heavy metals by the plants are also left to be resolved. Therefore, the objectives of this study were: (1) to characterize

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the ecological and chemical processes of phytoremediation in tailing dam, by analysis the community structure of plants habitated in Shimen tailing dam, the changes of soil fertilities, and the concentrations and fractionations of As and other hazardous heavy metals in soils; (2) to estimate the effects of phytoremediation as well as the ecological and health risks associated with phytoremediation. It is expected to provide references for the choice of candidate plants and post-management in future practice of phytoremediation.

## 2. Materials and methods

### 2.1. Site descriptions

The tailing dam is located at Shimen Realgar Mine, Baiyun village, Shimen County, Hunan Province, with east longitude of 110°29′–110°33′ and north latitude of 29°16′–30°08′. The site has a monsoon climate condition as changing from mid-subtropical to subtropical zone. Annual precipitation and average temperature is 1560 mm and 16.7 °C, respectively.

The mine has the biggest reserves of realgar in Asia, and has been exploited for more than 1500 years. The discharge of waste gases and solid wastes has led to heavy contamination since 1958 [13]. Arsenic concentrations in three villages in the vicinity of mining area were previously recorded as 84.17–296.19 mg kg<sup>-1</sup> and 0.5–14.5 mg L<sup>-1</sup>, in the soils and river waters, respectively, far exceeding the values of the corresponding soil and water environmental quality standards [14]. During 1992–1994, tailings were open pit dumped, forming a dam with 3.5 m in height and 6200 m<sup>2</sup> in area. Arsenic concentration was as high as 5.24% in the tailings. The intensive wind and hydraulic erosion led to vegetation-less landscape on the tailing dam. One monitored arsenic level in the runoff waters of the tailing dam during a rainstorm was recorded as high as 5 mg L<sup>-1</sup>, the tailing dam thus had produced serious contamination to ambient farmland and water system.

The phytoremediation project was put in practice in July 2003. Surface of the tailing dam was evened, followed with construction of drainage ditches and cement barriers across the dam. The tailing dam was then capped with a cover of 35 cm soils dug from the nearby hillsides. The dam was divided into three separated plots, including plots I, II and III; among which, plots I and II were capped with non-topsoils while plot III was capped with topsoils (Fig. 1). *Pteris vittata* were planted with a spacing of 80 × 80 cm.

### 2.2. Plot survey and sampling

The survey and sampling were carried out in April 2008. Plot surveys were conducted in three different plots separated by dif-

ferent types of capping soils as non-topsoils and topsoils with different dominant plant communities. *P. vittata* and *Miscanthus sinensis* were the dominant plant species in plots I and II capped with non-topsoils, respectively; while *P. vittata* dominated in plot III capped with topsoils (Fig. 1). A total of 21 quadrats (10 × 10 m area) were applied in the tailing dam. The numbers and names of plants species colonizing in every quadrat were recorded, simultaneously the associated soil samples were collected.

Three to four dominant plant samples in each quadrat (perennial *P. vittata* or *M. sinensis*) were collected and mixed as one composite sample. Soils about 1 cm thick adhered to the roots of collected plants were sampled as the rhizosphere soils. In each quadrat, about 20 cm soils in depth where no plants colonized were sampled as non-rhizosphere soils. The height of each plant was recorded, and the vegetation coverage was estimated via eye-measurement.

### 2.3. Treatment and analysis of samples

Soil samples were air-dried and ground to pass through a 2 mm mesh sieve, then homogenized for measurement of pH (1:5 ratio of soil to water), texture and other physical-chemical properties. The content of organic matter was analyzed using the Walkley-Black method. The cation exchange capacity (CEC) assay was performed in accordance with barium chloride-magnesium sulfate method. Active iron (Fe) and aluminum (Al) were assessed by a buffer solution of oxalic acid-ammonium oxalate (pH 3.0), while available potassium (K) and phosphorus (P) by 1 mol L<sup>-1</sup> (pH 7.0) and 1 mol L<sup>-1</sup> (pH 4.8) ammonium acetate, respectively. Total nitrogen was assayed following the method of Kjeldahl Distillation [12]. The sequential extraction of various As forms in soils was performed according to the method of Wenzel et al. [15]. A portion of 10 g of each soil sample was ground to be less than 150 μm in particle size, and digested using mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> following the method of USEPA-3050B. Concentrations of P and heavy metals in soils were determined using ICP-OES (inductively coupled plasma atomic emission spectroscopy), arsenic in the digest was determined using a hydride generation atomic fluorescence spectrometer (HG-AFS) (AFS820, Beijing Titan Instruments Co., China). Standard reference material (GBW07401) was used to check the accuracy of the analysis.

Plant samples were rinsed thoroughly with tap water, followed with deionized water 2–3 times. After air-dried, the plant samples were oven dried at 55 °C, then separated into aboveground and roots portions, and pulverized using a high-speed electric miller. The plant tissues were digested using concentrated composite solution of HNO<sub>3</sub>-HClO<sub>4</sub>, As concentrations were determined using HG-AFS. The concentrations of phosphorus and other heavy metals were assayed using ICP-OES. The certified plant standards (poplar leaf, GBW07604) were also analyzed as a quality control procedure.

### 2.4. Data analysis

Data were analyzed and tested using SPSS and Origin8 software, with one-way ANOVA and multiple comparisons by Duncan's test at  $P < 0.05$ .

## 3. Results

### 3.1. Rehabilitation of plants in tailing dam and accumulation of elements

#### 3.1.1. Rehabilitation of plants in tailing dam

According to the species-area curve, the minimal area of plants in the tailing dam was determined as 30 m<sup>2</sup> based on relevé

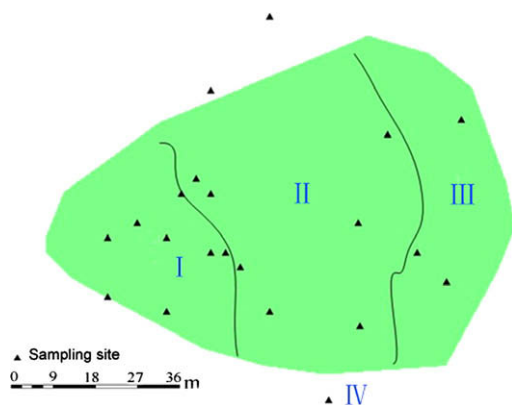


Fig. 1. The sketch map of the sampling sites on the tailing dams.

method [16]. Survey was then conducted on each quadrat of 10 × 10 m<sup>2</sup> in area. The results showed that plants habitated well on the capped soils, while only scarce of plants colonized on the un-capped tailings at the edge of the tailing dam. Plot II had the highest rehabilitation rates among the three survey plots. *P. vittata* was the dominant plant species in plot I with 15% coverage; while *M. sinensis*, *P. vittata* and *Astragalus sinicus* were the dominant plant species in plot II, with a coverage of 55%, 15% and 5%, respectively. In plot III, *P. vittata* and *M. sinensis* were the dominant plant species, having 35% and 15% coverages, respectively. No differences in coverage rates between plot II capped with non-topsoils and plot III capped with topsoils was found. Besides planted *P. vittata*, 38 plant species were found to have naturally colonized in the tailing dam, they belong to 24 different families. The top four families containing most of the plant species were *Compositae*, *Gramineae* or *Rosaceae*, *Leguminosae* and *Euphorbiaceae* (Table 1).

### 3.1.2. Concentrations of heavy metals in plants

*P. vittata* accumulated high concentrations of As and cadmium (Cd). The concentrations of As and Cd in the aboveground of *P. vittata* were higher than 800 mg As kg<sup>-1</sup> and 14 mg Cd kg<sup>-1</sup> (Table 2), being 800 and four times of the upper limit of the normal concentrations of As and Cd in the shoots of terrestrial higher plants, respectively [17]. *M. sinensis* took up certain As in its tissues, the average As concentration was recorded as 34.83 mg kg<sup>-1</sup>; however, most of the As (98%) was accumulated in roots, with mean As concentration in the shoots being only 0.45 mg kg<sup>-1</sup>. The concentrations of other tested elements in *P. vittata* and *M. sinensis* all fell into the corresponding ranges of normal concentrations in terrestrial higher plants (Table 2).

As compared with *M. sinensis*, *P. vittata* possessed more capabilities in accumulation and translocation of various heavy metal elements. Both in the aboveground parts and roots, the concentrations of As, Cd, chromium (Cr), copper (Cu), nickel (Ni) and lead (Pb) in *P. vittata* were obviously higher than those in *M.*

*sinensis* (Table 2). The translocation factors of As and Cd (TFs, defined as the ratios of aboveground parts-to-roots of As or Cd concentrations) in *P. vittata* both exceeded 1 (Table 3), with the highest TFs of Cd in *P. vittata* recorded as 9. In addition, both of the bioaccumulation factors of As and Cd (BFs, known as the ratios of plants to soils of As or Cd concentrations) were over 1, reaching up to 4.22 and 2.31, respectively. However, the BFs of other elements in *M. sinensis* and *P. vittata* were all lower than 1, showing relatively weak capability in accumulation of other elements in these two plants.

### 3.2. Variation of soil fertility and heavy metal concentrations

#### 3.2.1. Variation of soil fertility

The capped soils in the tailing dam were characterized as loam soils, with relatively low organic matter (<5 g kg<sup>-1</sup>) (Table 4). The concentrations of total phosphorus (P), available P and total nitrogen (N) in the soils fell into the ranges of 260–485 mg kg<sup>-1</sup>, 7.1–14.3 mg kg<sup>-1</sup> and 416–758 mg kg<sup>-1</sup>, respectively, which are all lower than the minimum criterions for cultivated lands [12]. The concentrations of total potassium (K) and available K of the capped soils were in the ranges of 9.3–14.3 g kg<sup>-1</sup> and 32–112 g kg<sup>-1</sup>, respectively, being a moderate level as compared to those of cultivated soils. The values of CEC and pH fell into the range of 7–12 cmol kg<sup>-1</sup> and 4.88–7.25, respectively, suggesting the capability of the capped soils to maintain the fertility to some extent. Compared to tailings, the physical–chemical properties of the capped soils had been remarkably improved, which benefited plant colonizing.

The fertilities of the soils in the plots capped with non-topsoils were obviously better than that capped with topsoils (Table 4). The concentrations of N, P and K, especially total K, available K and available P, in the capped non-topsoils of plots I (dominant species-*P. vittata*) and II (dominant species-*M. sinensis*), were all higher than those in the capped topsoils of plot III (dominant species-*P.*

**Table 1**  
List of plant species growing on the tailing dams.

Families	Number of species	Plant species
<i>Compositae</i>	10	<i>Artemisia eriopoda</i> , <i>Pterocypsela indica</i> , <i>Youngia japonica</i> , <i>Erigeron annuus</i> , <i>Conyzabonariensis</i> , <i>Artemisia argyi</i> , <i>Galinsoga parviflora</i> , <i>Artemisia velutina</i> , <i>Lxeris sonchifolia</i> , Japanese thistle herb
<i>Gramineae</i>	4	<i>Miscanthus sinensi</i> , <i>Cynodon dactylon</i> , <i>Poa annua</i> , <i>Bromus japonicus</i>
<i>Rosaceae</i>	4	<i>Pyracantha fortuneana</i> , <i>Rubus innominatus</i> , <i>Rosa laevigata</i>
<i>Leguminosae</i>	3	<i>Astragalus sinicus</i> , <i>Kummerowia</i>
<i>Euphorbiaceae</i>	2	<i>Sapium sebiferum</i> , <i>Euphorbia pekinensis</i>
Other families	1	<i>Pteridaceae</i> : <i>Pteris vittata</i> ; <i>Thelypteridaceae</i> : <i>Cyclosorus acuminatus</i> ; <i>Crassulaceae</i> : <i>Sedm sarmentosum</i> ; <i>Oxalidaceae</i> : <i>Oxalis corniculata</i> ; <i>Plantaginaceae</i> : <i>Plantago asiatica</i> ; <i>Convolvulaceae</i> : <i>Calystegin hederacea</i> ; <i>Umbelliferae</i> : <i>Torilis japonica</i> ; <i>Scrophulariaceae</i> : <i>Veronica didyma</i> ; <i>Polygonaceae</i> : <i>Rumex nepalensis</i> ; <i>Liliaceae</i> : <i>Hemerocallis citrina</i> ; <i>Urticaceae</i> : <i>Boehmeria nivea</i> ; <i>Labiatae</i> : <i>Prunella vulgaris</i> ; <i>Theaceae</i> : <i>Camellia sinensis</i> ; <i>Valerianaceae</i> : <i>Patrinia scabiosaefolia</i> ; <i>Simaroubaceae</i> : <i>Ailanthus altissima</i> ; <i>Pinaceae</i> : <i>Pinus</i> ; <i>Rubiaceae</i> : <i>Galium aparine</i> ; <i>Vitaceae</i> : <i>Ampelopsis delavayana</i> ; <i>Fabaceae</i> : <i>Dalbergia hupeana</i>

**Table 2**  
Heavy metal concentrations in the tissues of *Pteris vittata* and *Miscanthus sinensis* (mg kg<sup>-1</sup>).

Elements	Non-topsoil capping				Topsoil capping		The normal range for terrestrial higher plants in shoots
	Dominant species- <i>P. vittata</i>		Dominant species- <i>M. sinensis</i>		Dominant species- <i>P. vittata</i>		
	Shoots	Roots	Shoots	Roots	Shoots	Roots	
As	825 ± 188a	309 ± 128b	0.45 ± 1.01d	34.39 ± 40.14c	1359 ± 556a	252 ± 136b	0.01–1
Cd	14.34 ± 4.25a	2.97 ± 3.72b	ND	ND	9.84 ± 5.18a	1.69 ± 2.50b	0.1–1
Cr	3.27 ± 1.96bc	6.98 ± 6.57bc	9.86 ± 3.31ab	14.56 ± 6.89a	1.54 ± 1.00c	5.61 ± 7.28bc	0.006–18
Cu	16.48 ± 11.38a	12.73 ± 10.14a	0.25 ± 0.35c	8.39 ± 4.8b	3.93 ± 2.07c	4.64 ± 1.60c	3–20
Ni	5.53 ± 12.22a	5.25 ± 5.94a	1.85 ± 1.13a	ND	0.26 ± 0.58a	ND	0.05–5
Pb	3.64 ± 3.53b	6.63 ± 5.35ab	2.49 ± 5.08a	7.12 ± 6.05ab	2.86 ± 2.24b	10.48 ± 4.44ab	2–5

Note: Data are means and standard error of means, values followed by different letters in the same column indicate significant differences (*P* < 0.05); ND; not detected.

**Table 3**

The bio-concentration and translocation factors of heavy metals in the dominant plants species on the rehabilitated tailing dam.

		Cd		Cr		Cu		Ni		Pb		As	
		BF	TF	BF	TF	BF	TF	BF	TF	BF	TF	BF	TF
Non-topsoil capping	Dominant species- <i>P. vittata</i> (n = 11)	2.31	9.57	0.13	0.69	0.68	0.68	0.11	0.63	0.5	0.71	3.11	2.93
	Dominant species- <i>M. sinensis</i> (n = 5)	–	–	0.15	0.74	0.26	0.03	0.02	–	0.66	0.35	0.03	0.01
Topsoil capping	Dominant species- <i>P. vittata</i> (n = 5)	1.66	4.02	0.08	0.41	0.63	0.82	–	–	0.62	0.37	4.22	5.79

Note: TFs, defined as the ratios of aboveground parts-to-roots of As or Cd concentrations.

BFs: known as the ratios of plants to soils of As or Cd concentrations.

**Table 4**

The physical-chemical properties of the soils on the tailing dams.

	Non-topsoil capping				Topsoil capping	
	Dominant species- <i>P. vittata</i> (n = 11)		Dominant species- <i>M. sinensis</i> (n = 5)		Dominant species- <i>P. vittata</i> (n = 5)	
	Rhizosphere	Bulk	Rhizosphere	Bulk	Rhizosphere	Bulk
Organic matter (g kg <sup>-1</sup> )	2.62	3.08	2.75	3.22	3.47	3.59
CEC (cmol kg <sup>-1</sup> )	9.01	10.89	7.67	8.68	9.44	11.60
Texture (%)						
Sand	29.49	29.46	14.47	18.78	4.78	7.83
Silt	61.99	54.68	67.53	61.69	77.59	71.71
Clay	8.51	15.86	18.01	19.54	17.63	20.46
pH	5.44 ± 0.27b	5.99 ± 0.51ab	6.05 ± 0.10a	5.90 ± 0.35ab	5.25 ± 0.23b	5.61 ± 0.22ab
Active Fe (mg kg <sup>-1</sup> )	1693 ± 228b	2046 ± 598ab	2599 ± 640a	2536 ± 696a	2813 ± 309a	2652 ± 178a
Active Al (mg kg <sup>-1</sup> )	1022 ± 182b	1090 ± 77b	1174 ± 337ab	1307 ± 345a	1530 ± 129a	1521 ± 91a
Total P (mg kg <sup>-1</sup> )	421.8 ± 65.1ab	352.2 ± 93.9ab	484.6 ± 68.8a	329.7 ± 146.6b	284.1 ± 35.2b	260.3 ± 36.5b
Available P (mg kg <sup>-1</sup> )	10.1 ± 1bc	11.1 ± 1.5ab	13.6 ± 3.4ab	14.3 ± 5.1a	7.1 ± 1.0d	8.4 ± 0.9cd
Total K (g kg <sup>-1</sup> )	27.3 ± 1.6a	19.5 ± 4.1b	22.6 ± 4.4ab	13.9 ± 5.4c	11.8 ± 0.8c	9.3 ± 1.4c
Available K (mg kg <sup>-1</sup> )	59.3 ± 6.73b	112.6 ± 16.1a	56.8 ± 15.4b	105.9 ± 16.6a	32.2 ± 3.8c	108.8 ± 27.2a
Total N (mg kg <sup>-1</sup> )	464 ± 47b	647 ± 88a	634 ± 152a	758 ± 135a	416 ± 57b	636 ± 36a

Note: Data are means and standard error of means, values followed by different letters in the same column indicate significant differences ( $P < 0.05$ ).

*vittata*). In the same plot, concentrations of available K, available P and total N in the rhizosphere soils were lower than those in the non-rhizosphere soils, especially in plots II or III. The concentrations of available K and total N between rhizosphere and non-rhizosphere soils were significantly different ( $P < 0.05$ ). Differences in the fertilities among the plots in which different dominant species grew were also observed. For example, the concentration of total K in plot I was slightly higher, but the concentrations of the total N and available P significantly lower, than those in plot II; however, no significant differences in the concentrations of available K and total P was observed.

### 3.2.2. Concentrations of heavy metals in soils

Except for As and Cd, concentrations of other heavy metal elements in the capped soils were all lower than the corresponding values of the National Standard for Soil Quality. In addition, the concentrations of zinc (Zn), Ni and Cr were lower than the grade II values of the national standard; while the copper (Cu) and lead (Pb) concentrations were below the grade I value (Table 5).

No significant differences were observed in the concentrations of As, Pb and Cd in the capped soils among different survey plots; however, the concentrations of Cr, Cu, Zn and Ni in plots I and II capped with non-topsoils were evidently higher than those in plot III capped with topsoils ( $P < 0.05$ ). At the same time, the concentrations of Cr, Zn and Ni in plot I (dominant species-*P. vittata*) were all significantly higher than those in plot II (dominant species-*M. sinensis*) ( $P < 0.05$ ). Furthermore, Cu concentration in plot I was also slightly higher than that in plot II.

Significant differences were also found in the element concentrations between rhizosphere and non-rhizosphere soils (Table 3). For instance, in all survey plots, the concentrations of Cr, Zn and Ni in the rhizosphere soils appeared to be higher than those in non-rhizosphere soils; The same variation trend was also found in plot II (dominant species-*M. sinensis*) for Pb and As, however, reverse trends were observed for Pb in plots I and III (dominant species-*P. vittata*).

The concentrations of As and Cd of the capped soils were more than eight and six times higher than their corresponding grade III

**Table 5**

Heavy metal concentrations in the soils of the tailing dam (mg kg<sup>-1</sup>).

Elements	Non-topsoil capping				Topsoil capping		Value in National Standard Quality (GB15618-1995)
	Dominant species- <i>P. vittata</i> (n = 11)		Dominant species- <i>M. sinensis</i> (n = 5)		Dominant species- <i>P. vittata</i> (n = 5)		
	Rhizosphere	Bulk	Rhizosphere	Bulk	Rhizosphere	Bulk	
As	344.9 ± 189.0a	344.8 ± 376.7a	418.7 ± 301.1a	214.1 ± 135.4a	213.4 ± 44.6a	200.2 ± 44.8a	30 Class III
Cd	7.89 ± 1.56a	6.12 ± 0.97a	8.01 ± 1.58a	7.64 ± 1.07a	6.97 ± 1.35a	6.54 ± 0.78a	1.0 Class III
Cr	95.2 ± 11.9a	70.6 ± 10.8bc	85.1 ± 10.5ab	45.5 ± 29d	62.7 ± 4.4 cd	46.9 ± 15.4d	150 Class II
Cu	21.7 ± 3.2a	19.0 ± 6.0a	15.6 ± 5.0a	14.1 ± 9.5ab	7.5 ± 1.4b	7.6 ± 1.4b	35 Class I
Zn	136.2 ± 22.2a	116.4 ± 14.0ab	92.5 ± 23.6bc	71.4 ± 23.4 cd	61.8 ± 3.2d	57.5 ± 6.0d	200 Class II
Pb	11.6 ± 4.8a	17.4 ± 6.0a	15.1 ± 2.5a	10.1 ± 8.2a	8.9 ± 1.4a	13.2 ± 6.2a	35 Class I
Ni	52.1 ± 6.0a	47.3 ± 3.8ab	43.5 ± 7.6bc	38.4 ± 6.4 cd	37.0 ± 1.6 cd	33.2 ± 0.5d	50 Class II

Note: Data are means and standard error of means, values followed by different letters in the same column indicate significant differences ( $P < 0.05$ ).



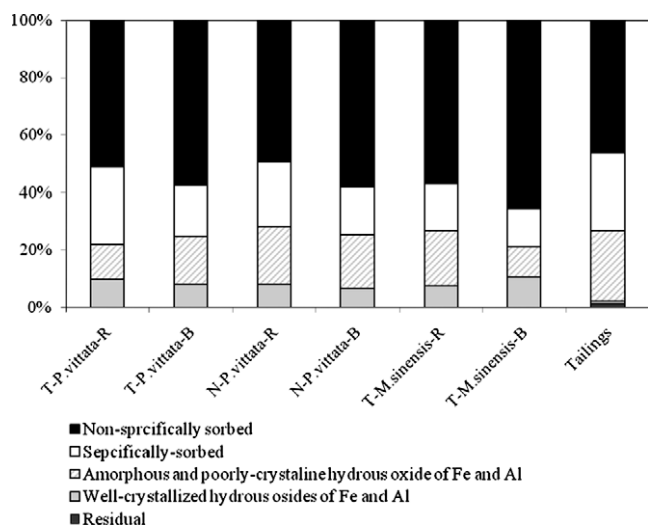


Fig. 2. The sequential extracted As forms in the soils of top and non-topsoil capping plots of the tailing dam. Note: T and N represent the top and non-topsoil capping, respectively; R and B indicate the rhizosphere and bulk soils of the plants, respectively.

values of the national standard, respectively (Table 5). On average, the concentration of As of the tailings was  $2883 \text{ mg kg}^{-1}$ , being 10 folds of that of the capped soils and 95-folds of the grade III value of the national standard. Cd concentration of the tailings reached up to  $68.35 \text{ mg kg}^{-1}$ , being 67 times of the grade III value in national standard. Concentrations of the other elements in the tailings were low, e.g., for Cr, Cu, Zn and Pb these were all lower than the grade I value in national standard. Thus soil capping has greatly reduced the stress of As and Cd to plants, which benefited plants growing normally.

Although the concentration of total As in the capped soils was high, the phyto-available As concentration in soils, including non-specific-adsorptive and exchangeable As forms, was generally low as in the range of  $3.7\text{--}29.5 \text{ mg kg}^{-1}$ . The sequential extraction analysis results showed that, in the capped soils, As appeared mainly as residual (45–66%), followed in decreasing order as well-crystallized hydrous oxides of Fe and Al (13–27%), amorphous and poorly-crystalline hydrous oxide of Fe and Al (11–24%), exchangeable (1–10%) and non-specific-adsorptive (0.01–0.1%), forms of As (Fig. 2). In tailings, As also existed as residual (46%), however, only 2% of the total As appeared as non-specific-adsorptive and exchangeable, with the highest concentration recorded as  $61.1 \text{ mg kg}^{-1}$ . The concentrations of active iron, active aluminum and clay in capped soils were far greater than those in tailings (Table 1), suggesting a stronger fixing but a lower releasing effects to As in capped soils than in tailings [18].

#### 4. Discussion

The results of the present study indicate that vegetation on the dam has been well established after soil capping. The dominant plant species in different plots of the tailing dam were influenced by anthropogenic factors, in the planted plants *P. vittata* became one of the dominant species in the tailing dam. Plants inhabited infrequently on the tailings uncapped with soils at the edge of the dam, whereas re-vegetation of tailings capped with soils was well established, indicating soil capping benefits vegetation development, and it was necessary to grow tolerant plants as well. The phytoremediation project had dramatically reduced the wind-borne dust of the tailing dam, which is in agreement with the results of Ward et al. [19]. In addition, seed banks in the capped soils

can be efficiently utilized to establish stable ecosystem with potential plant communities [20].

Soil capping improved the physical–chemical properties and fertilities of the tailing dam. The fertility of the plots capped with non-topsoils was slightly better than the plots capped with topsoils; however, there was no remarkable difference in the vegetation coverage between them. Concentrations of heavy metals in the plots capped with topsoils were lower than those in the plots capped with non-topsoils, however, except for As and Cd, concentrations of other heavy metals in capped non-topsoils were all lower than the corresponding grade II values of the national standard. Therefore, the non-topsoils can be used as capping materials on the tailing dam for sake of farmland protection and economical considerations.

It was worthy to note that the structure of plant community in plot II was distinctly different from those in the other plots. For example, in plot II, the vegetation coverages of dominant plant species—*M. sinensis*, *P. vittata* and *Leguminosae A. sinicus* L. reached up to 55%, 15% and 5%, respectively. Nevertheless, the frequency and abundance of *Leguminosae* in other two plots were much less than those in plot II. The results showed that the concentrations of N and P in the soils of plots II were obviously higher than those in plots I and III. Similar results were also reported by Hong et al. [21] and Tian et al. [22], who found that the concentration of total N was higher in soils with than without *Leguminosae* plants growing during the rehabilitation process of derelict land in mining area. Harris et al. [23] also claimed that annual/perennial *Leguminosae* plants can supply lots of organic matters through their dead-wood and defoliation. Since the organic matters have a low ratio of carbon to N, their decomposition can increase the accumulation of N in soils. However, the efficiency of N fixation of *Leguminosae* plants is affected by the extent of P abundance or deficiency in soils, when plants store N for maintaining the activities of N fixing enzymes, more P will be required [24]. In this study, the P level in the soils of plot II was gently higher than those in the other two plots, which favored the survival of *Leguminosae* plants in plot II and the fixing of N. Reports also have shown that *Leguminosae* plants exert no obvious effects on the accumulation of N in the soils of some derelict lands in the mining area where severe P deficiency exists [23].

The concentration of As in the capped soils of Shimen tailing dam is still over the values of the National Standard Soil Quality. However, the concentrations of bio-available As, including non-specific-adsorptive and exchangeable forms of As, in the soils of three survey plots are in the range of  $3.7\text{--}29.5 \text{ mg kg}^{-1}$ , only accounting for less than 10% of the total As in all soils, and is far below the average concentration of bio-available As in uncapped tailings ( $61.1 \text{ mg kg}^{-1}$ ). According to the monitoring results provided by the local environment protection department, the level of As in the runoff of tailing dam rapidly decreased from 5 to  $0.1 \text{ mg L}^{-1}$  after the phytoremediation project had been successfully implemented. Dust pollution derived from wind erosion of the tailing dam disappeared completely after the establishment of a stable ecosystem with flourishing vegetation, which helped to greatly reduce the environment pollution generated from the tailing dam and the threat to human health of local residents as well.

In this survey, *P. vittata* accumulated As and Cd to some extent, which might probably be a threat to the health of local residents via the entrance of these two heavy metals into food chain. However, *P. vittata* containing high level of As can resist the prey of herbivores according to the current reports. Rathinasabapathi et al. [25] and Mathews et al. [26] have studied the potential of *P. vittata* in withstanding the prey by herbivores, including grasshopper and scale-insect, under hydroponic condition and natural growth condition, respectively. They found that when *P. vittata* exposed to

high level As (1 mM treatment concentration under hydroponic condition; the concentration of As in aboveground of *P. vittata* was in the range of 5.40–812 mg kg<sup>-1</sup>) could efficiently resist the prey by herbivores; but when it was exposed to low level As, no significant resisting effect was observed. Similar results were obtained in a hydroponic experiment employed with lettuce [25]. Consequently, high As level may suggest the existing of an obvious elemental defense action in plants [27], thus can reduce the threat of As to human health via the food chain. In this study, the concentrations of As in aboveground *P. vittata* growing in the soils of tailing dam ranged in 504–2148 mg kg<sup>-1</sup>, far exceeding the reported threshold value which can trigger the elemental defense action in plants. Furthermore, *P. vittata* is not used conventionally as forage, thus avoiding its ingestion by livestock. It can be then concluded that planting *P. vittata* for rehabilitation of the tailing dam does not lead to risks to human health via food chain.

Except for As, the concentrations of other heavy metals in *M. sinensis* were all in the normal ranges of common terrestrial higher plants. The concentration of As in aboveground *M. sinensis* that was possibly ingested by animals was lower than 4.77 mg kg<sup>-1</sup>, but this concentration still exceeded the maximum permitted value of 2.0 mg kg<sup>-1</sup> as the National Hygienic Standard for Forage (GB 13078-2001). In this survey, 14% of the *M. sinensis* samples had As concentrations greater than this reference value. However, in a survey on As concentrations in forage at 183 farms in England and Wales, Nicholson et al. [28] found that As concentration in forage as 5 mg kg<sup>-1</sup> was a safe level. The concentration of As in the aboveground of *M. sinensis* growing in the capped soils of this tailing dam was within the range of this limit. However, other reports also showed that concentrations of As in the aboveground of *M. sinensis* growing in soils with high As levels (ranged in 212–1307 mg kg<sup>-1</sup>) were recorded as much as 13–706 mg kg<sup>-1</sup> [29]. These might suggest potential health risks due to animal ingestion of *M. sinensis* containing high levels of As in its aboveground parts. Therefore, more attention should be paid for post-management of the rehabilitated tailing dam in prohibiting the grazing around the tailing dam for avoidance of As into food chain through ingestion of *M. sinensis* by livestock.

## 5. Conclusions

The results of this study suggest that soil capping can reduce the stress of heavy metals on plants and phytoremediation has greatly enhanced the ability of plant colonizing on the tailing dam. Vegetation composed of planting, natural colonizing in soil seed banks, and local pioneer species of plants developed rapidly, the health and environmental risks caused by the tailings were reduced to be negligible. Although concentrations of As and Cd in the capped soils exceeded the corresponding values of the National Standard for Soil Quality, they were still far lower than those in the tailings. The capped soils had a low level of fertility; however they could maintain the normal growth of the plants in the tailing dam.

The planting species of *P. vittata* plants could accumulate As and Cd, but this had not brought health risks via the food chain. Nevertheless, health risks would probably present when *M. sinensis* containing high levels of As was ingested by livestock. Therefore, post-management of the tailing dam after phytoremediation should be involved.

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