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Accumulation of Pb, Cd, Cu and Zn in plants and hyperaccumulator choice in Lanping lead–zinc mine area, China

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Abstract

A field survey of higher terrestrial plants growing on Lanping lead–zinc mine, China were conducted to identify species accumulating exceptionally large concentrations of Pb, Cd, Cu and Zn of 20 samples of 17 plant species. Concentrations of Pb and Zn in soil and in plant were higher than that of Cu and Cd. Significant difference was observed among the average concentrations of four heavy metals in plants (except Cd and Cu) and in soil (except Pb and Zn) ($P < 0.05$). For the enrichment coefficient of the four heavy metals in plant, the order of average was Pb < Cu < Cd < Zn. Between four heavy metals, only significant difference was observed between the enrichment coefficient average of Cd and Cu ($P < 0.05$). The enrichment coefficients were higher than 1 in *Llex plyneura* and *Rhododendron annae* in Paomaping for Pb, *Salix cathayana*, *L. plyneura* and *R. annae* in Paomaping for Cd, and *R. annae* in Paomaping for Zn, respectively. Concentrations and enrichment coefficient of Pb, Cd and Zn of *Rhododendron* were higher than that of *Gramimeae*. Enrichment coefficient of Pb, Cd and Zn were bush > tree>herbaceous, and herbaceous grew in soil with the highest concentrations of four heavy metals. In different areas, the concentrations of Pb, Cd, Cu and Zn in plants and soils and enrichment coefficient were different. Plants in Paomaping had more accumulating ability to Pb, Cd and Zn, and plants in Jinfeng River had more accumulating ability to Cu. Six plant species, i.e. *S. cathayana*, *Lithocarpus dealbatus*, *L. plyneura*, *Fargesia dura*, *Arundinella yunnanensis* and *R. annae* in Paomaping, had high accumulation capacity. *R. annae* in Paomaping had hyperaccumulating capacity to Pb, Cd and Zn, *L. plyneura* to Pb and Cd, and *S. cathayana* to Cd, respectively.

Keywords: Pb–Zn mine; Heavy metal; Plant; Concentration; Enrichment coefficient; Hyperaccumulator

1. Introduction

Human activity has continuously increasing the level of heavy metals circulating in the environment. Heavy metal pollution of the biosphere has accelerated rapidly since the onset of the industrial revolution and heavy metal toxicity poses major environmental problems (Gisbert et al., 2003). Mining activities generate a large amount of waste rocks and tailing which deposited at the surface. The land surface is damaged and the waste rocks and tailings are often very unstable and will become sources of pollution. The direct effects will be loss of cultivated land, forest or grazing land, and the overall loss of production. The indirect effects will include air and water pollution and siltation of rivers. These will eventually lead to the loss of biodiversity, amenity and economic wealth (Bradshaw, 1993). So, it is very important for restoration of a vegetation cover in mining area and removing heavy metal from cultivated land by plants (Wong, 2003).

Phytoremediation is a relatively new approach to removing contaminants from the environment. It may be defined as the use of plants to remove, destroy or sequester hazardous substances from environment. It has become a topical research field in the last decades as it is safe and potentially cheap compared to traditional remediation techniques (Salt et al., 1998; Mitch, 2002; Glick, 2003; Pulford and Watson, 2003). The basic idea that plants can be used for environmental remediation is very old, and cannot be

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traced to any particular source. However, a series of fascinating scientific discoveries combined with an interdisciplinary research approach have allowed the development of this idea into a promising, cost-effective, and environmentally friendly technology (Baker et al., 1991). Phytoremediation can be applied to both organic and inorganic pollutants, present in soil substrates (e.g. soil), liquid substrates (e.g. water), and the air (Salt et al., 1998; Adler et al., 1994). Phytoremediation is currently divided into many types: phytoextraction (hyperaccumutalor), phytodegradation, rhizofiltration, phytostabilization and phytovolatilization (Salt et al., 1998). Although phytoremediation has received considerable attention recently, and there are an increasing number of reports suggesting that it should become the technology of choice for the clean up of various types of environment contamination, this technology is still in its infancy (Glick, 2003).

Most of reviews focus on the phytoremediation of the metallic pollutants in soil, particularly the area of metal hyperaccumulator, which is the area of major scientific and technological progress in the past years (Brown et al., 1995; Cunningham et al., 1995; Cunningham and Ow, 1996). There were many reports of hyperaccumulating plant (Berti and Cunningham, 1993; Brown et al., 1995; Shen and Liu, 1998; Ozturk et al., 2003). A hyperaccumulator has been defined as a plant that can accumulate cadmium>100 mg/kg, copper, lead>1000 mg/kg, zinc>10,000 mg/kg in their shoot dry matter, and in accumulator plants, the metal concentrations in shoots are invariably greater than that in roots, showing a special ability of the plant to absorb and transport metals and store them in their above-ground part (Baker and Brooks, 1989; Baker et al., 1994; Brown et al., 1994; Wei et al., 2002). Meanwhile, a hyperaccumulator is regarded as plant which the concentrations of heavy metal in its above ground part is 10–500 times more than that in usual plant (Shen and Liu, 1998). To some extent, it will be useful to find some plants that have accumulating ability to heavy metals. The hyperaccumulator was characterized at first was members of the *Brassicaceae* and *Fabaceae* families (Salt et al., 1998). At present, at least 45 families are known to contain metal-accumulating species. To date, more than 400 plant species of metal hyperaccumulator plants have been reported in the literature (Salt et al., 1998). Some research works have also been done with cultivated crops and green plant (Ernst, 1996; Ebbs et al., 1997; Desouza et al., 2000; Cunningham and Ow, 1996). As more of the metal-enriched environments are investigated, new hyperaccumulators will be identified.

It is clear that the utilization of the remarkable potential of green plant to accumulate elements and compounds from the environment and to perform biochemical transformation is becoming a new frontier of plant biology. However, the distribution, ecology, and phytochemistry of the wild plants in metal mines in China are poorly understood. Only a hyperaccumulator of Arsenic, *Pteris vittata* L. (Chinese brake fern) was discovered (Wei et al., 2002).

There are very abundant metal resources in Yunnan Province, China. These metal resources include Pb, Zn, Cd and Cu. Pb–Zn mine is of dominating mines in Yunnan Province. The total reserves of Pb–Zn mines are 26.053 million tons in Yunnan Province (Bai et al., 1985). On the other hand, plant species was diverse in metal mining area, including tree, bush and herbaceous. Because of interspecific difference in accumulating capacity of plant to metal, hyperaccumulator choice was possible from metal mining area.

In this study, we investigated the concentrations and enrichment coefficient of Pb, Cd, Cu and Zn of 20 samples of 17 plant species in Lanping lead–zinc mine with the objective to (1) get better knowledge of the accumulating capacity of 20 samples of 17 plant species to Pb, Cd, Cu and Zn in such a environment condition, and (2) choose hyperaccumulator that would be used for the remediation of agricultural field polluted by heavy metals and metal mine area soils. We hypothesized that the differences in the concentrations and enrichment capacity to Pb, Cd, Cu and Zn of 20 samples of 17 plant species in Lanping lead–zinc mine exist. The choice of hyperaccumulator is available, and the hyperaccumulator will be used for phytoremediation.

2. Materials and methods

2.1. Site description

In Lanping County, the reserves of Pb–Zn mine are 15.476 million tons. It is the largest Pb–Zn mine in China and the secondary in Aisa. The average grade is 2.5 times more than mean. About the site of Lanping Pb–Zn mine, East longitude is 96°58′–99°38′, North latitude is 26°0′–27°05′, the altitude is 2430–2790 m, annual average temperature is 11.2 °C, annual rainfall is 1008.1 mm, and the areas is 5 km^2. It is belongs to sedimentary-heating mineral bed and exists in cretaceous dolomite, braccia, marlite, quartzy sandstone. The main metal minerals are pyrite, sphalerite, galena exploited easily. It was exploited by shelling out in the top of mountain and by digging mine in the bottom of mountain (Bai et al., 1985). Vegetation is subtropical alpine forest, including broad-leaved trees, needle-leaved tree, bush and herbaceous.

2.2. Sampling

Samples of plant and soil were collected from three zones: Jinding (East longitude is 99°25′, North latitude is 26°25′, mountain top, soil properties: burozem, pH 5.7, organic matter 5.3%, CEC 18.5 me/100 g soil.), Paomaping (East longitude is 99°26′, North latitude is 26°24′, mountain middle, soil properties: burozem, pH 5.5, organic matter 5.7%, CEC 19.1 me/100 g soil.) and Jinfeng River (East longitude is 99°25′, North latitude is 26°25′, mountain lower, soil properties: burozem, pH 5.8, organic matter 4.8%, CEC 17.9 me/100 g soil.) of Lanping Pb–Zn mine in April, 2002 (Table 1). These plant species grow very well and were dominant in mine areas. Plant samples included leaves for tree and bush, and shoots for herbaceous. At least six individual plants of each plant species were randomly collected within the sampling area, then were mixed to give a composite whole plant sample.

The soils in which the plants were growing were representative of the surface horizon, maximum sampling depth was about 20 cm. Soil samples were composite mixtures of soils from the rhizosphere of each plant.

2.3. Plant analysis

The plant samples were carefully washed with deionized water and oven-dried at 105 °C for 30 min and 60 °C for 24 h, then ground into fine powder, sieved through 1 mm nylon sieve.

Table 1
Plant species together with their sites, elevation, type and part in Lanping lead–zinc mine

Sample no.	Species	Sites	Elevation (m)	Types	Plant part
1	*Salix cathayana*	Jinding	2790	Tree	Leaves
2	*Populus yunnanensis*	Jinding	2790	Tree	Leaves
3	*Rhododendron decorum*	Jinding	2790	Bush	Leaves
4	*Rhododendron annae*	Jinding	2785	Bush	Leaves
5	*Carpinus wangii*	Jinding	2785	Tree	Leaves
6	*Pinus yunnanensis* Tranch	Jinding	2780	Tree	Leaves
7	*Achnatherum chingii*	Jinding	2775	Herbaceous	Shoots
8	*Juncus effusus*	Jinding	2770	Herbaceous	Shoots
9	*Arundinella yunnanensis*	Jinding	2760	Herbaceous	Shoots
10	*Polystichum disjurctam*	Paomaping	2640	Herbaceous	Shoots
11	*Lithocarpus dealbatus*	Paomaping	2640	Tree	Leaves
12	*Llex plyneura*	Paomaping	2540	Tree	Leaves
13	*Adiantun capillus-veneris* L.	Paomaping	2540	Herbaceous	Shoots
14	*Fargesia dura*	Paomaping	2535	Herbaceous	Shoots
15	*Artemisia lancangensis*	Paomaping	2530	Herbaceous	Shoots
16	*Rhododendron decorum*	Paomaping	2500	Bush	Leaves
17	*Rhododendron annae*	Paomaping	2500	Bush	Leaves
18	*Sambucus chinensis*	Jinfeng River	2420	Tree	Leaves
19	*Arundinella yunnanensis*	Jinfeng River	2420	Herbaceous	Shoots
20	*Trifdium repensl*	Jinfeng River	2420	Herbaceous	Shoots

The concentrations of Pb, Cd, Cu and Zn in plants were determined in Key Laboratory of Subtropcial Resources and Environment, Ministry of Agriculture, Huazhong Agricultural University, Wuhan, P.R. China. One-gram plant samples were digested by HNO_3:$HClO_4$ (3:1). The concentrations of Pb, Cd, Cu and Zn were determined by an Inductively Coupled Plasma Emission Spectroscopy (ICP-AEC). Standard materials were included for assurance control. Standard materials were $Pb(NO_3)_2$, $CdCl_2$, $Cu(NO_3)_2$, and $ZnCl_2$. Means of Pb, Cd, Cu and Zn were calculated from triplicate.

2.4. Soil analysis

The soil samples were air-dried at room temperature for 6 days, then ground into fine powder and sieves through 0.25 mm nylon sieve.

The concentrations of Pb, Cd, Cu and Zn in soils were determined in Key Laboratory of Subtropcial Resources and Environment, Ministry of Agriculture, Huazhong Agricultural University, Wuhan, P.R. China. 0.5 g soil samples were digested by HNO_3:HCI:$HClO_4$ (1:2:2) to obtain a total extraction of heavy metal. The total concentrations of Pb, Cd, Cu and Zn were determined by Inductively Coupled Plasma Emission Spectroscopy (ICP-AEC). Standard materials were included for assurance control. Standard materials were $Pb(NO_3)_2$, $CdCl_2$, $Cu(NO_3)_2$, and $ZnCl_2$. Means of Pb, Cd, Cu and Zn were calculated from triplicate.

2.5. Enrichment coefficient equator

Enrichment coefficient was described as the heavy metal element concentration (DM) in plant above ground part divided by this heavy metal element concentration (DM) in soil, which can be used to evaluate accumulating capacity of plant to heavy metal.

2.6. Statistical analysis

Statistical differences between the concentrations of Pb, Cd, Cu and Zn in plants and soils were determined by Duncan's Multiple Range Test at $P < 0.05$ level, and regression analysis was undertaken for assess the relationship between concentrations of Pb, Cd, Cu and Zn in plants and soils, and between enrichment coefficient of Pb, Cd, Cu and Zn at $P < 0.05$ or $P < 0.01$ level.

3. Results

3.1. Concentrations of Pb, Cd, Cu and Zn in plants

The concentrations of Pb, Cd, Cu and Zn were different in the same plant species (Table 2). For average concentrations, Cd was the lowest (6.96 ± 7.67 mg/kg), followed

Table 2
Concentrations of Pb, Cd, Cu and Zn of 20 plants and soils in Lanping lead–zinc mine (mg/kg DM)

Sample no.	Species	Pb		Cd		Cu		Zn	
		Plants	Soils	Plants	Soils	Plants	Soils	Plants	Soils
1	*Salix cathayana*	95.92	407.74	11.26	6.18	34.49	16.63	483.44	407.74
2	*Populus yunnanensis*	2.54	694.91	3.19	8.61	8.41	15.94	131.54	538.86
3	*Rhododendron decorum*	2.28	555.33	0.59	27.74	5.07	17.65	61.67	1426.40
4	*Rhododendron annae*	353.82	763.38	23.87	61.24	29.81	20.33	1140.99	6348.55
5	*Carpinus wangii*	75.37	507.53	4.56	9.79	20.60	14.81	321.54	883.12
6	*Pinus yunnanensis* Tranch	13.01	780.04	1.81	9.19	7.76	15.86	130.68	601.08
7	*Achnatherum chingii*	29.97	12139.50	2.75	428.3	5.93	104.47	234.34	16579.94
8	*Juncus effusus*	12.78	702.23	10.36	84.31	7.49	25.09	427.78	5946.73
9	*Arundinella yunnanensis*	208.04	702.22	5.22	84.30	16.56	25.08	356.17	5946.73
10	*Polystichum disjurctam*	117.34	1914.62	4.64	10.73	12.19	22.09	294.17	383.41
11	*Lithocarpus dealbatus*	136.67	929.66	3.76	9.36	10.99	24.01	258.16	235.07
12	*Llex plyneura*	304.39	229.62	25.18	4.13	7.61	31.22	406.73	143.32
13	*Adiantun capillus-veneris* L.	286.61	5211.32	0.35	20.58	9.76	27.98	78.76	1133.05
14	*Fargesia dura*	209.53	803.50	8.53	6.05	14.83	26.25	516.94	148.38
15	*Artemisia lancangensis*	12.833	1717.50	1.65	19.81	16.40	20.07	114.68	834.61
16	*Rhododendron decorum*	146.09	1244.56	0.14	6.44	7.78	19.56	35.27	153.55
17	*Rhododendron annae*	369.49	100.51	20.46	3.40	20.86	31.85	1115.09	107.36
18	*Sambucus chinensis*	89.84	267.54	1.69	9.06	15.37	18.59	273.18	359.59
19	*Arundinella yunnanensis*	121.56	1391.57	5.93	9.14	61.68	22.13	373.26	967.69
20	*Trifdium repensl*	82.87	1581.49	3.36	11.59	14.09	14.30	269.78	974.19
Average		133.55 ± 118.44a	1632.24 ± 2703.60A	6.96 ± 7.67b	41.50 ± 94.44B	16.65 ± 13.18b	25.70 ± 19.26C	351.21 ± 300.14c	2205.97 ± 3950.41A
Minimum		2.28	100.51	0.14	3.40	5.07	14.30	35.27	107.36
Maximum		369.49	12139.50	25.18	428.30	61.68	104.47	1140.99	16579.94

Averages of the concentrations of Pb, Cd, Cu and Zn in plants or soils followed by the same letter are not significantly different at $P < 0.05$ level, according to Duncan's Multiple Range Test, $n = 20$.

by Cu (16.38 ± 13.18 mg/kg), Pb (133.52 ± 118.44 mg/kg), and Zn (351.21 ± 300.14 mg/kg). There were significant differences ($P<0.05$) among the average concentrations of four heavy metals, except for Cd and Cu. For different plant species, the concentrations of Pb, Cd, Cu or Zn in plants were different, respectively, such as Cd concentrations, maximum was 25.18 mg/kg in *Llex plyneura*, minimum was 0.144 mg/kg in *Rhododendron decorum* in Paomaping.

3.2. Concentrations of Pb, Cd, Cu and Zn in soils

Of all the heavy metals examined in the soil from Lanping mining area, the average concentration of Cu (25.70 ± 19.26 mg/kg) was the lowest, followed by Cd (41.50 ± 94.44 mg/kg), Pb (1632.24 ± 2703.60 mg/kg), and Zn (2205.92 ± 3950.41 mg/kg) (Table 2). Significant difference was observed between the concentrations of four heavy metals, except for Pb and Zn ($P<0.05$) (Table 2). For different plant species, the concentrations of Pb, Cd, Cu or Zn in soils were different, such as Zn concentrations, maximum was 16579.94 mg/kg in the soil of *Achnatherum chingii*, minimum was 107.36 mg/kg in the soil of *Rhododendron annae* in Paomaping (Table 2).

3.3. Enrichment coefficient of Pb, Cd, Cu and Zn in plants

For the enrichment coefficient of the four heavy metals in plants, the average of Pb was the lowest (0.56 ± 1.49), followed by Cu (0.77 ± 0.67), Cd (0.96 ± 1.81), and Zn (1.14 ± 2.37) (Table 3). Between four heavy metals, only there was significant different between the enrichment coefficient average of Cd and Cu ($P<0.05$). For different plant species, the enrichment coefficient of Pb, Cd, Cu or Zn were different, respectively, such as the enrichment coefficient of Pb, maximum was 6.6761 of *R. annae* in Paomaping, minimum was 0.0025 of *A. chingii* (Table 3). The enrichment coefficients were higher than 1 in *L. plyneura* and *R. annae* in Paomaping for Pb, *Salix cathayana*, *L. plyneura* and *R. annae* in Paomaping for Cd, and *R. annae* in Paomaping for Zn, respectively.

3.4. Concentrations and enrichment coefficient in different plant types

Concentrations of Pb, Cd and Zn of *Rhododendron* were higher than that of *Gramimeae*, on the other hand, concentrations of Pb, Cd and Zn of soils of *Gramimeae* were above 2 times higher than that of *Rhododendron*. So, enrichment coefficient of Pb, Cd and Zn of *Rhododendron* were above 2 times higher than that of *Gramimeae*, but only enrichment coefficient of Pb was observed significant difference between *Rhododendron* and *Gramimeae* ($P<0.05$) (Table 4).

Concentrations of the four heavy metals in herbaceous and tree were approach ($P>0.05$) (Table 4). Only there was significant ($P<0.05$) difference of concentration of Zn

Table 3
Enrichment coefficients of Pb, Cd, Cu and Zn of plants in Lanping lead–zinc mine

Sample no.	Species	Pb	Cd	Cu	Zn
1	*Salix cathayana*	0.2354	1.8219	2.0700	1.1860
2	*Populus yunnanensis*	0.0037	0.3703	0.5276	0.2440
3	*Rhododendron decorum*	0.0041	0.0213	0.2870	0.0420
4	*Rhododendron annae*	0.4634	0.3897	1.4660	0.1797
5	*Carpinus wangii*	0.1485	0.4617	1.3900	0.3640
6	*Pinus yunnanensis* Tranch	0.0167	0.1966	0.4260	0.2170
7	*Achnatherum chingii*	0.0025	0.0064	0.0570	0.0141
8	*Juncus effusus*	0.0182	0.1229	0.2980	0.0720
9	*Arundinella yunnanensis*	0.2963	0.0620	0.6608	0.0599
10	*Polystichum disjurctam*	0.0613	0.4323	0.5520	0.7670
11	*Lithocarpus dealbatus*	0.1470	0.4497	0.4580	1.0980
12	*Llex plyneura*	1.3256	6.0953	0.2430	2.8380
13	*Adiantun capillus-veneris* L.	0.0550	0.0163	0.3490	0.0695
14	*Fargesia dura*	0.2608	1.4093	0.5649	3.4840
15	*Artemisia lancangensis*	0.0075	0.0834	0.8173	0.1370
16	*Rhododendron decorum*	0.1174	0.0224	0.3979	0.2297
17	*Rhododendron annae*	6.6761	6.0161	0.6550	10.386
18	*Sambucus chinensis*	0.3351	0.1866	0.8270	0.7597
19	*Arundinella yunnanensis*	0.0874	0.6488	2.7864	0.3900
20	*Trifdium repensl*	0.0524	0.2897	0.9850	0.2770
Average		0.56 ± 1.49ab	0.96 ± 1.81a	0.77 ± 0.67b	1.14 ± 2.37ab
Minimum		0.0025	0.0064	0.0167	0.0141
Maximum		6.6761	6.0953	2.7864	10.386

Averages of the enrichment coefficients of Pb, Cd, Cu and Zn followed by the same letter are not significantly different at $P<0.05$ level, according to Duncan's Multiple Range Test, $n=20$.

Table 4
Concentrations (mg/kg DM) of Pb, Cd, Cu, and Zn in plants and soils of different plant types and enrichment coefficient of Pb, Cd, Cu and Zn

Plant types	Heavy metal	Average concentration (range) in plant	Average concentration (range) in soil	Enrichment coefficient (range)
Gramimeae	Pb	142.28 ± 85.84 (3.42 – 209.53)a	3759.20 ± 5595.12 (702.22 – 12139.50)a	0.16 ± 0.14 (0.0025 – 0.2963)a
	Cd	5.61 ± 2.38 (1.30 – 10.36)a	131.95 ± 200.85 (6.05 – 428.30)a	0.53 ± 0.65 (0.0064 – 1.4093)a
	Cu	24.74 ± 25.06 (5.93 – 61.68)a	44.48 ± 40.03 (20.33 – 104.47)a	1.02 ± 1.21 (0.0570 – 2.7864)a
	Zn	370.18 ± 115.75 (80.77 – 516.94)a	5910.69 ± 7560.24 (148.38 – 16579.94)a	0.99 ± 1.67 (0.0141 – 3.484)a
Herbaceous	Pb	120.17 ± 97.47 (12.78 – 286.61)a	2907.11 ± 3727.42 (702.22 – 12139.50)a	0.09 ± 0.11 (0.0025 – 0.2963)a
	Cd	4.78 ± 3.20 (0.33 – 10.36)a	74.98 ± 136.13 (6.05 – 428.30)a	0.34 ± 0.46 (0.0064 – 1.4093)a
	Cu	17.66 ± 16.94 (5.93 – 61.68)a	31.94 ± 27.50 (14.30 – 104.47)a	0.79 ± 0.80 (0.057 – 2.7864)a
	Zn	296.21 ± 141.57 (78.76 – 516.94)a	3657.19 ± 5353.51 (148.38 – 16579.94)a	0.59 ± 1.11 (0.0141 – 3.484)a
Bush (*Rhododendron*)	Pb	217.79 ± 176.17 (2.28 – 369.49)b	665.95 ± 474.78 (100.51 – 1244.56)b	1.82 ± 3.25 (0.0041 – 3.6761)b
	Cd	11.27 ± 12.66 (0.14 – 23.87)a	24.71 ± 26.66 (3.40 – 61.24)a	1.61 ± 2.94 (0.0213 – 6.0161)b
	Cu	15.88 ± 11.57 (5.07 – 29.81)a	22.35 ± 6.43 (17.65 – 31.85)a	0.70 ± 0.53 (0.229 – 2.07)a
	Zn	588.26 ± 623.47 (35.27 – 1115.09)b	2008.97 ± 2956.92 (107.36 – 6348.55)a	2.71 ± 5.12 (0.042 – 10.386)b
Tree	Pb	102.25 ± 100.81 (2.54 – 304.39)ab	545.29 ± 265.52 (229.62 – 929.66)b	0.46 ± 0.56 (0.0037 – 1.3256)c
	Cd	7.35 ± 8.50 (1.81 – 25.18)a	8.05 ± 2.09 (4.13 – 9.79)b	1.37 ± 2.16 (0.1470 – 1.8219)b
	Cu	20.19 ± 17.73 (7.61 – 34.49)a	20.60 ± 5.66 (14.81 – 31.22)a	0.86 ± 0.65 (0.0167 – 2.07)a
	Zn	286.47 ± 131.49 (130.68 – 483.44)a	452.68 ± 247.81 (143.32 – 883.12)b	0.96 ± 0.92 (0.217 – 2.838)a

Gramimeae included *Achnatherum chingii*, *Arundinella yunnanensis* in Jinding, and *Fargesia dura* and *Arundinella yunnanensis* in paomaping.
Means in each column for each element in different plant types followed by the same letter are not significantly different at $P < 0.05$ level, according to Duncan's Multiple Range Test, $n = 20$.

between bush and herbaceous, tree, respectively, of Pb had between bush and herbaceous. On the contrast, concentrations of Pb, Cd and Zn in soil were significant ($P < 0.05$) different between tree soil and herbaceous soil, bush soil, except Pb between tree and bush ($P > 0.05$).

Enrichment coefficient of Pb was significant ($P < 0.05$) different among herbaceous, bush and tree, and enrichment coefficient of Zn was significant ($P < 0.05$) different between bush and tree, herbaceous, respectively, and enrichment coefficient of Cd was significant ($P < 0.05$) different between herbaceous and tree, bush, respectively (Table 4).

3.5. Concentrations and enrichment coefficient in different sites

The concentrations of Pb, Cd and Zn in plant were highest in Paomaping, respectively, and Cu in Jinfeng River. However, only there was significant ($P < 0.05$) difference of Cu among Jinding, Paomaping and Jinfeng River (Table 5).

The concentrations of four heavy metals in soil were not significant different among Jinding, Paomaping and Jinfeng River, except concentrations of Cd and Cu in soil had significantly ($P < 0.05$) difference between Jinding and Paomaping. But it still can be find the concentrations of Pb, Cd, Cu and Zn in soils were Jinding>Paomaping>Jinfeng River.

The enrichment coefficients of Pb, Cd, Zn in Paomaping were 3–5 times than that in Jinding and Jinfeng River, and for Cu, the highest in Jinfeng River. Enrichment coefficients of Cd, Cu and Zn were significant different ($P < 0.05$) between Jinding and Paomaping (Table 5). Enrichment coefficients of Cu was significant different ($P < 0.05$) between Paomaping and Jinfeng River.

Enrichment coefficient of Pb and Cd were Paomaping> Jinding>Jinfeng River, respectively, of Zn was Paomaping> Jinfeng River>Jinding, and of Cu was Jinfeng River>Jinding ≧ Paomaping, respectively. It can be concluded that plants in Paomaping had more accumulating ability to Pb, Cd and Zn, and plants in Jinfeng River area had more accumulating ability to Cu.

Table 5
Concentrations (mg/kg DM) of Pb, Cd, Cu, Zn in plants and soil in different sites and enrichment coefficient of Pb, Cd, Cu, and Zn

Sites	Heavy metal	Average concentration (range) in plant	Average concentration (range) in soil	Enrichment coefficient (range)
Jinding	Pb	81.77 ± 125.14 (2.28–353.82)a	2264.06 ± 4356.83 (407.74–12139.50)a	0.27 ± 0.44 (0.0025–0.4634)a
	Cd	6.86 ± 8.26 (0.59–23.86)a	78.72 ± 155.39 (6.18–428.30)a	0.47 ± 0.62 (0.0064–1.8219)a
	Cu	16.01 ± 12.25 (4.76–34.49)a	29.38 ± 33.16 (14.81–104.47)a	0.83 ± 0.81 (0.057–2.07)a
	Zn	357.74 ± 373.32 (61.67–1140.99)a	3826.38 ± 6004.71 (407.74–16579.94)a	0.32 ± 0.40 (0.0141–1.1860)a
Paomaping	Pb	180.38 ± 118.91 (12.83–369.49)a	1355.57 ± 142.17 (100.51–5211.32)a	0.90 ± 2.07 (0.0075–3.6761)a
	Cd	8.03 ± 8.52 (0.1441–25.18)a	24.91 ± 31.86 (3.40–84.30)b	1.47 ± 2.45 (0.0163–6.0161)b
	Cu	12.45 ± 4.57 (7.14–20.86)b	25.32 ± 4.20 (19.56–31.22)b	0.50 ± 0.18 (0.229–0.8173)b
	Zn	360.38 ± 309.30 (29.09–1115.09)a	1503.22 ± 2366.22 (107.36–5946.73)a	1.92 ± 3.22 (0.0163–10.386)b
Jinfen River	Pb	98.09 ± 20.62 (3.42–121.56)a	1080.20 ± 710.16 (267.54–1581.49)a	0.16 ± 0.15 (0.0025–0.3350)a
	Cd	3.66 ± 2.14 (1.31–5.93)a	9.93 ± 1.44 (9.06–11.59)ab	0.38 ± 0.24 (0.1428–0.6488)ab
	Cu	30.38 ± 27.11 (8.24–61.68)c	18.34 ± 3.92 (14.30–22.13)ab	1.54 ± 1.09 (0.3723–2.7864)a
	Zn	305.41 ± 58.79 (80.77–373.27)a	767.38 ± 352.98 (359.59–974.19)a	0.48 ± 0.25 (0.083–0.7597)ab

Means in each column for each element in different areas followed by the same letter are not significantly different at $P<0.05$ level, according to Duncan's Multiple Range Test, $n=20$.

3.6. Hyperaccumulator choice

The concentrations of four heavy metals in many samples were higher than that in usual plant (Table 6). Ninety percent samples was Pb concentration higher than usual plant, 85% Cd, 63% Cu and 85% Zn, respectively (Table 2). Comparing the highest concentrations of these plants with that in usual plants, the concentrations were 74, 25, 6.2, 11.4 times higher for Pb, Cd Cu and Zn, respectively. According to a hyperaccumulator being regarded as plant which the concentrations of heavy metal in its above-ground part is 10–500 times more than that in usual plan, Pb concentrations of 13 samples were satisfied for this standard value, Cd concentrations of four samples and Zn concentrations of 2 samples, respectively (Table 6). Meanwhile, the concentrations of Pb, Cd and Zn in *R. annae* in Jinding and Paomaping were 10 times more than usual plant.

Table 6
Concentrations (mg/kg DM) in plant 10 times more than that in usual plant[a]

Heavy metal	Sample no.	Species	Times	Enrichment coefficient
Pb	1	*Salix cathayana*	18	0.2354
	4	*Rhododendron annae*	71	0.4634
	5	*Carpinus wangii*	15	0.1485
	10	*Polystichum disjurctam*	24	0.0613
	11	*Lithocarpus dealbatus*	27	0.1470
	12	*Llex plyneura*	61	1.3256
	13	*Adiantun capillus-veneris* L.	57	0.0550
	14	*Fargesia dura*	42	0.2608
	16	*Rhododendron decorum*	29	0.1174
	17	*Rhododendron annae*	74	3.6761
	18	*Sambucus chinensis*	18	0.3351
	19	*Arundinella yunnanensis*	24	0.0874
	20	*Trifdium repensl*	16	0.0524
Cd	1	*Salix cathayana*	11	1.8219
	4	*Rhododendron annae*	23	0.3897
	12	*Llex plyneura*	25	6.0953
	17	*Rhododendron annae*	20	6.0161
Zn	4	*Rhododendron annae*	12	0.1797
	17	*Rhododendron annae*	11	10.386

[a] Concentration of usual plant: Pb 5 mg/kg DM, Cd 1 mg/kg DM, Cu 10 mg/kg DM, Zn 100 mg/kg DM.

Considering the enrichment coefficients, overall, *L. plyneura*, *R. annae* in Paomaping had high accumulating capacity to Pb and Cd, and *R. annae* in Paomaping had high accumulating capacity to Zn. *S. cathayana* had high accumulating capacity to Cd, respectively (Table 6).

But comparing with the absolute concentrations of hyperaccumulator (Cd>100 mg/kg, Cu, Pb>1000 mg/kg, Zn>10000 mg/kg in shoot dry matter), no sample could be regarded as hyperaccumulator.

Six plant species, i.e. *S. cathayana*, *Lithocarpus dealbatus*, *L. plyneura*, *Fargesia dura*, *Arundinella yunnanensis* and *R. annae* in Paomaping, had high accumulating capacity to four heavy metals. *R. annae* in Paomaping had hyperaccumulating capacity to Pb, Cd and Zn, *L. plyneura* to Pb and Cd, and *S. cathayana* to Cd, respectively.

4. Discussion

This is the first report about the concentrations and enrichment capacity of Pb, Cd, Cu and Zn of 20 plants species and hyperaccumulator choice in Lanping lead–zinc mine area, China. The discussion will be concentrated on uptake and accumulation of Pb, Cd, Cu and Zn, and the choice of hyperaccumulator and pioneer plant.

4.1. Uptake and accumulation

Comparing to previous results concerning soil heavy metal background value in this area (Pb 55.89 mg/kg, Cd 1.80 mg/kg, Cu 20.10 mg/kg, and Zn 67.02 mg/kg, respectively) (Yan, 1998), indicated heavy metal concentrations in soils were greatly increased. The average value of Pb, Cd, Cu and Zn in soils was 30, 23, 3, 33 times higher than the background value, respectively. This may be because Pb, Cd and Zn exist accompanying in Pb–Zn mine. In soil sample of *A. chingii*, Pb, Cd, Cu and Zn concentrations were very high (Table 2). The reason is not clear.

The order of concentrations of four heavy metals in soils were the similar as in plants, this result meant the concentrations of heavy metal in soils should have effect on the concentrations in plants. Only the concentrations in plant and the enrichment coefficients had significant relationship ($P<0.01$) between Pb and Cd, Pb and Zn, and Cd and Zn, although the concentrations of Pb, Cd, Cu and Zn in soil had significant relationship ($P<0.01$) each other (Table 7). The reason maybe due to the fact that total concentrations of four heavy metals in soils were affected by many factors, and influenced the concentrations in plant indirectly. Selecting different extract solution to get different part concentrations of heavy metals is necessary, which could find direct factor that affect the concentration of plant (Ramos et al., 1994; Calvet et al., 1990).

Table 7
Relationship between concentrations (mg/kg DM) of Pb, Cd, Cu and Zn in plants and soils, and between enrichment coefficient of Pb, Cd, Cu and Zn

X	*Y*	Equation	R^2	*F* value
Plants				
Pb	Cd	$Y=0.98+0.045X$	0.480**	16.64
Pb	Cu	$Y=13.50+0.022X$	0.038	0.70
Pb	Zn	$Y=120.79+1.73X$	0.464**	15.60
Cd	Cu	$Y=13.58+0.402X$	0.055	1.04
Cd	Zn	$Y=123.79+32.65X$	0.696**	41.12
Cu	Zn	$Y=204.62+8.95X$	0.154	3.29
Soils				
Pb	Cd	$Y=-8.62+0.031X$	0.773**	61.16
Pb	Cu	$Y=15.27+0.0064X$	0.804**	73.74
Pb	Zn	$Y=368.53+1.13X$	0.594**	26.28
Cd	Cu	$Y=17.76+0.19X$	0.880**	131.76
Cd	Zn	$Y=541.83+40.10X$	0.919**	204.18
Cu	Zn	$Y=-2201.9+171.54X$	0.699**	41.82
Enrichment coefficients				
Pb	Cd	$Y=0.409+0.976X$	0.632**	30.94
Pb	Cu	$Y=0.788+0.0054X$	0.000	0.0026
Pb	Zn	$Y=0.288+1.509X$	0.897**	156.57
Cd	Cu	$Y=0.803-0.013X$	0.001	0.02
Cd	Zn	$Y=0.111+1.079X$	0.677**	37.69
Cu	Zn	$Y=1.318-0.224X$	0.004	0.07

** Significant at $P<0.01$ ($R_{0.01}=0.561$, $F_{0.01}=8.29$), $n=20$.

Considering different plant type, the concentrations of Pb, Cd, Cu and Zn in soil which those three type plants grew in were herbaceous>bush>tree. In general, concentrations of Pb, Cd and Zn in tree soil were 3–10 times significantly lower than that in bush soil and herbaceous soil, but concentrations in tree still were close to herbaceous and bush; this may be because the tree was perennial plant and can absorb heavy metals from soil continuously and accumulate in tissue (Landberg and Greger, 1996). In other word, the tolerant ability of plant to heavy metals was herbaceous>bush>tree, and accumulating ability of plant to heavy metals was bush>tree>herbaceous (Landberg and Greger, 1996).

The concentrations in plants and soils, and enrichment coefficient of four heavy metals were different in different sites. This was identical with the grade of lead–zinc mine and the way of exploitation. The way of exploitation was shelling out on the surface in Jinding, digging wells in Paomaping, and Jinfen River have some distance from the main mine area. According to enrichment coefficient of heavy metals in three sites, plants in Paomaping had much stronger accumulating ability to Pb, Cd and Zn, and plants in Jinfeng River had much stronger accumulating ability to Cu.

4.2. Hyperaccumulator

Six plant species, i.e. *S. cathayana*, *L. dealbatus*, *L. plyneura*, *F. dura*, *A. yunnanensis* and *R. annae* in Paomaping, showed higher concentrations and enrichment coefficient of heavy metals, indicating its higher accumulating ability. There are many reports about *Salix* and *Maidenhair*, which been described as heavy metal hyperaccumulator in roots and shoots (Landberg and Greger, 1996; Hammer and Keller, 2002). A very important fact was that out of six plant species, three were trees, i.e. *S. cathayana*, *L. dealbatus* and *L. plyneura*, and one was bush, i.e. *R. annae* in Paomaping. Enrichment coefficient in bush and tree were higher than that in herbaceous, this showed the bush and tree can absorb heavy metal gradually as perennial plants. Considering the enrichment coefficient, to use 1 or 2 as standard, *L. plyneura* and *R. annae* were thought to have hyperaccumulating ability. The use of trees and bushes for the phytoremediation of land contaminated by heavy metal does seem to have considerable potential (Pulford and Watson, 2003). These plants respond to heavy metals by employing the strategy of accumulation and sequestration of metals. Plants have an extremely high capacity to take up metals by roots and translocate and store them in the shoot (Baker et al., 2000; McGrath et al., 2001; Ozturk et al., 2003). Hyperaccumulation may be associated with depressed translocation of K from roots to shoots (Wenzel and Jockwer, 1999). Because *L. plyneura* and *R. annae* were perennial plant, there were still some problems that must be noticed in further research, for example, the sampling time, the sampling organ, age of sample. In stems and leaves of *Salix* species growing on mine spoil, metal concentrations were generally higher in the early vegetative growth stage, due to a relatively high nutrient uptake compared to growth rate. This was followed by a period of vigorous growth, which diluted the concentrations until the flowering stage, in which the minimum values for almost all elements were obtained (Dinelli and Lombini, 1996). Under natural conditions, metals accumulated in shoots are annually recycled to the soils (Wenzel and Jockwer, 1999).

The standard for hyperaccumulator have not been defined scientifically still. In the present, the standard is described as three rules, i.e. the concentrations of heavy metal in its above-ground part is 10–500 times more than that in usual plant (Shen and Liu, 1998), the concentrations of heavy metal reach hyperaccumulating level (Baker et al., 1994; Brown et al., 1994; Wei et al., 2002), and enrichment coefficient >1. It is difficult to judge whether a plant species is hyperaccumulator or not if the plant species do not accord with above three rules simultaneously. So, define and use of a scientific standard for hyperaccumulator will be very necessary for hyperaccumulator choice and phytoremediation of soil polluted by heavy metal.

4.3. Pioneer plant

A. chingii had the lowest enrichment coefficient growing in soil with highest concentrations of heavy metal. This showed its strong tolerance to four heavy metals. It can be considered as a pioneer plant in the restoration of a vegetation cover in mining area. It was reported that grass was suitable for the rehabilitation of Pb, Cd, Cu, and Zn contaminated soils, in terms of highly tolerant to heavy metal, biomass production and coverage (Wong, 2003). These plants respond to heavy metals by employing the exclusion strategy. Plants maintain metals at relatively low concentrations within plants by avoiding excessive metal uptake and transport (McGrath et al., 2001; Ozturk et al., 2003). The mechanisms include chelation, compartmentalization, biotransformation, and cellular repair mechanisms (Salt et al., 1998; Hammer and Keller, 2002).

In conclusion, the differences in the concentrations and accumulating capacity to Pb, Cd, Cu and Zn of 20 sampling of 17 plant species in Lanping lead–zinc mine exist. The hyperaccumulator chosen primarily, if confirmed and optimized, could have impact on practical phytoremediation approaches, and decrease ultimately the risk of heavy metals to human health (Mattina et al., 2003). This is an important work for phytoremediation of soil polluted by heavy metal. However, this work is complex and interdisciplinary studies on soil characteristic, the mechanism of plants in accumulating heavy metals, interaction between plant and soil and hyperaccumulator plant breeding are necessary; further research will be undertaken (Lindegaard and Barker, 1997).

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