

Metal bioaccumulation in plant leaves from an industrious area and the Botanical Garden in Beijing

LIU Yan-ju^{1,2,*}, DING Hui¹, ZHU Yong-guan²

(1. Beijing Centre for Physical and Chemical Analysis, Beijing 100089, China; 2. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: liuyanju@hotmail.com)

Abstract: The concentrations of Fe, Mn, Al, Zn, Pb, Ni, Cr, and As were measured in soils and leaves from 21 plant species growing on hills near the Beijing Steel Factory (BSF) and 17 plant species in the Beijing Botanical Garden (BBG). The results showed that soils from BSF were Zn contaminated according to the threshold of natural background of China. There was a metal contamination of the soils by Ni, and Cr in BSF comparing with those in BBG. The comparison between concentrations of metals in leaves from both sites indicated that, in general, accumulation of metals in the leaves of the same species was significantly different between the two sites. Even within the same locality each species accumulation of metals was significantly variable. The study aimed to screen landscape plants for the capacity to clean-up toxic metals in soils, and developed an overall metal accumulation index (MAI) for leaves and then categorized the MAI that can be applied broadly in the selection of species in polluted areas. To do this, the spectrum of MAI values were divided into four classes: strongly accumulated (SA or grade I), moderately accumulated (MA or grade II), intermediately accumulated (IA or grade III), and weakly accumulated (WA or grade IV). The results showed that elemental association between Fe, Al, Ni, and As was generally highly correlated with each other in the sampling sites. This may suggest their common biochemical characteristics. Generally, those species containing strong and moderate accumulation in both sites are considered including *Vitex negundo*, *Broussonetia papyrifera*, *Ulmus pumila*, and *Rubia cordifolia*. At BSF and other industrial sites with a similar ecosystem, strong and moderate accumulation species include *Sophora japonica*, *Ampelopsis aconitifolia* var. *glabra*, *Platycladus orientalis*, *Wikstroemia chamaedaphne*, *Cleistogenes squarrosa*, *Grewia biloba*, and in BBG, in addition *Setaria viridis*, *Cotinus coggygria*, *Lespedeza floribunda*, *Rhamnus parvifolia*, *Lespedeza tomentosa*.
Keywords: Fe; Mn; Al; Zn; Pb; Ni; As; metal accumulation index (MAI)

Introduction

Metals can be necessary or beneficial to plants at certain levels, but can also be toxic when exceeding specific thresholds (Williams, 2000; Facchinelli, 2001). Meanwhile, those non-essential heavy metals are highly toxic to plants and have become a problem of current interest as a result of environmental pollution on a global scale (Patra, 2000; Cervantes, 2001). The toxicity will lead to biosynthesis reduction and growth stagnation in plants (Vajpayee, 2000; MacFarlane, 2002). Deposition of particulate heavy metal in airborne pollutants has proved to result in stress on vegetation (Taylor, 1983). Increase in contaminant emissions may pose substantial implications on local soils as heavy metals may enter and accumulate in soils through atmospheric deposition or other ways (Haygarth, 1992; Chen, 1999). Soils provide another important polluted source harmful for plants and humans because they are subjected to a number of pollutants due to different anthropic activities such as industry, agriculture, transport, and so on (Facchinelli, 2001). Even worse, contaminated agricultural soils may be terrible source to do harm to humans who feed on their products (Wong, 2002). Therefore, the need to reduce soil contamination has become a universal problem.

Common woodland mosses are already known to

accumulate airborne metallic elements very efficiently (Goodman, 1971). Scientists have suggested that removal of defoliation might be a cheap strategy to clean heavy metals in soils (Dahmani-Muller, 2000). Bioaccumulation in leaves of plants was studied in variable metal-contaminated sites affected by atmospheric particulate deposition. The issue considered was that each biological species could accumulate particular kinds of metals (Samecka-Cymerman, 1999; Wenzel, 1999; Smith, 2000; Prasad, 2000; Campanella, 2001; Breulmann, 2002; Caliceti, 2002; Madejón, 2002; Cui, 2004; Tang, 2004; Zhu, 2004). The main object of this paper was to screen for plant species that can accumulate excess major and trace metals in the contaminated sites in Beijing.

Beijing Steel Factory (BSF) in the west of Beijing City, China was built 80 years ago. During the long period, BSF chiefly emitted metal-rich sulphurous smoke and dust containing excessive amounts of Fe, Mn, Al, Zn, Pb, Ni, Cr and As (data provided by Beijing Environmental Protection Bureau, Table 1). Beijing Botanical Garden (BBG) is in the northwest of Beijing City, 10 km away from and on the northeast of BSF. Comparison between the sulfur concentrations of the leaves of a species in BSF with that of the same species in BBG indicated that the former was generally higher than the latter but the latter was lightly polluted by sulfur (Liu, 2001). Soils and plants species near

BSF are potentially under the threat of heavy metal contamination. In this paper we aimed to address such questions by:

To test the concentrations of major and trace metals in soils from the hill near BSF and those in Beijing Botanical Garden (BBG) so as to investigate changes in metal concentrations in soils from hill near BSF and in BBG.

To compare leaf accumulation of the excessive metals in each species growing on the tested soils at BSF and BBG to investigate metal accumulation features for different species at

the same site and for same species at the different sites.

To develop the metals accumulation index (MAI) to compare overall metal accumulation in plant leaves quantitatively. Four accumulation classes were used to screen landscape plant for use in terms of the accumulation of toxic metals. Those tolerant or moderately accumulating plants will then be suggested as landscape plant genera on industrial and industrial neighboring sites with a similar ecosystem to prevent the localities from accumulating toxic metals.

Table 1 Heavy metal concentrations in air deposits for January in 1992($\mu\text{g}/\text{m}^3$)^{*}

Locality	Fe	Al	Mn	Zn	Pb	Ni	Cr	As
BSF	22.3	35.6	0.61	0.79	0.41	0.077	0.056	0.090
Downtown(Qianmen)	12.8	27.4	0.38	0.59	0.48	0.057	0.038	0.086
Control site(Miyun)	1.9	3.8	0.06	0.09	0.10	0.005	0.008	0.013
BSF/control site	11.8	9.4	10.9	8.6	4.1	14.8	6.8	6.9
BSF/downtown	1.7	1.3	1.6	1.3	0.8	1.3	1.5	1.0

Note: * Data kindly provided by Beijing Environmental Protection Bureau

1 Materials and methods

1.1 Sampling and sample preparation

Beijing City is located in the semi-humid warm temperature zone (39° 90' N, 116° 32' E) and affected by a continental monsoon climate. BSF belongs to Shijingshan District on the west of the city, with major prevailing winds from the northeast and southwest in both summer and autumn. With mountains on the west and north, the district is characterized by a valley circumfluence wind (southward in the daytime and northward at night). Vegetation on the hill near BSF is mainly composed of *Pinus tabulaeformis*, *Vitex negundo*, *Ziziphus jujuba* var. *spinosa* with thin soil. We chose one hill located on the northeast of the BSF as the contaminated sampling site that was affected by smoke dust over a long period. Leaves of 21 species were collected from the southward hillside on September 2, 2000. Four to eight individual plants were considered for each tree species and 10 to 20 for herbs, shrubs and vines. Leaves were collected from all sides of the plants exposed to sunlight and the samples were reached from the ground for trees. Leaf samples were washed in water, then deionized water, oven-dried at 70°C and crushed to pass through a 0.15 mm sieve. Soil samples, at 2–10 cm depth, were taken from each patch where the sampled plants were rooted. Soil samples were air-dried and crushed to pass through a 1 mm sieve. Leaves and soils were stored in glass bottles sealed with plastic tape.

We chose a hillside in the BBG as the controlled sampling site with a similar vegetation composition to that of BSF. The same species as those in BSF (17 in total, 4 unavailable) and the soils were sampled in BBG in October, 2000. The sample was prepared according to the method for samples in BSF.

1.2 Chemical analysis

Five sub-samples (1.0 g) were weighed to four decimal

places for each species. The samples were digested with a mixture of HNO_3 - HClO_4 (20/2, v/v) following the method of Zhao *et al.* (Zhao, 1994). Analyses of Fe, Mn, Zn, Pb, and Al were determined using Atomic Absorption Spectrophotometer equipped with a flame whose detection limits are 1×10^{-7} (0.1 ppm). Ni and Cr were analyzed using an Atomic Absorption Spectrophotometer equipped with a furnace whose detection limits are 1×10^{-9} (1 ppb). To analyze As, 0.5 g leaf powder was weighed and transferred into a 25 ml colorimetric tube, 10 ml concentrated HNO_3 added and left overnight. The solution was boiled for 1 h in a boiling water bath. After cooling down, the solution was diluted to 25 ml mark with deionized water, and then filtered. Reducing agents of ascorbic acid and urea were added before analysis by using an Atomic Fluorescence Spectrophotometer with the detection limit of 5×10^{-12} (5 ppt).

Five sub-samples for soils at each site were processed. To measure Fe, Mn and Al content, 1 g soil sample was weighed, mixed with 3 g lithium metaborate, and put in a platinum cup, dissolved completely at the 1000°C. After cooling, the solution was first diluted to 50 ml and then measured using an X-ray fluorescence instrument with the detection limit of 0.1 ppb. To measure Ni, Zn, Pb, Cr, As, the soil was digested following the method described by Tüzen (Tüzen, 2003) with concentrated $\text{HCl}:\text{HNO}_3$ (3:1) mixture (5 ml) and concentrated HClO_4 (5 ml). Analyses of Ni, Zn, Pb, Cr were performed using an Atomic Absorption Spectrophotometer. For As, the solution was filtered before adding reducing agents (ascorbic acid and urea), then measured by an Atomic Fluorescence Spectrophotometer.

The analysis results of soils were controlled with GBW07403 and GBW07404 provided by Ministry of Geology and Mineral, China and the results of leaves were controlled with GBW08501 and GBW08505 provided by China State

Bureau of Quality and Technical Supervision.

1.3 Statistical analysis

Mean metal concentrations were calculated, together with their standard deviations. As far as pooled samples were concerned, the standard deviations illustrated the variability within different replicates.

Both the existence of significant differences between metal concentrations in the leaves of different species at the same site and those in leaves of the same species at different sites were separately tested by a one-way analysis of variance using the Excel 97 program. Metal concentrations in the soils at the two sites were analyzed in the same way. In order to investigate element associations in leaves, Pearson correlation was separately performed for both BBG and BSF sampling sites using the Excel 97 program.

1.4 Development of metal accumulation index (MAI) for leaves

Plant leaves are able to accumulate different kinds of metals, but it is very difficult to compare one species' overall metal accumulation with others because each species has different characteristics in terms of their accumulation to different metals. Thus, the evaluation of the overall metal accumulation in leaves has become a complex process. Here we take advantage of a method for air quality indices provided by Sharma (Sharma, 1999) to develop an overall MAI for leaves using the equation:

$$MAI = (1/N) \sum_{j=1}^N I_j$$

Where N is the total number of tested metals, $I_j = x/\delta_x$ is the sub-index for variable j , obtained by dividing the mean value (x) of the variable metal by its standard deviation (δ_x).

Generally, the sub-indices are normalized as dividing the measured mean value by the prescribed standard (permissible) concentrations for any parameter. However, in China, the permissible standards for some parameters

measured here have not been prescribed. Instead, the standard deviations of the observed values of various parameters were used to calculate the sub-indices in this study.

1.5 Categorization of MAI

The goal of this study was to develop a categorization of MAI that can be applied broadly for the selection of species to grow in polluted areas. To do this, we divided the spectrum of MAI values into four classes by referring to the previous method (Liu, 1983): strongly accumulated (SA or grade I), moderately accumulated (MA or grade II), intermediately accumulated (IA or grade III), and weakly accumulated (WA or grade IV). The species were classified into above four grades separately based on the MAI value in their leaves. Strongly accumulated: $MAI > \text{mean } MAI + SD$; moderately accumulated: $\text{mean } MAI < MAI < \text{mean } MAI + SD$; intermediately accumulated: $\text{mean } MAI - SD < MAI < \text{mean } MAI$; weakly accumulated: $MAI < \text{mean } MAI - SD$.

2 Results

2.1 Metal concentrations in soils

Descriptive statistics of metal concentrations in soils from BSF and BBG are presented in Table 2. Compared with the Environmental Quality Standard for soils (National Environmental Protection Agency of China, 1995), mean Zn concentrations in BSF are higher than the corresponding threshold values of natural background (Table 2). The mean Pb, Ni, Cr and As concentrations in both sampling sites were below the threshold levels of the nationwide natural background. Overall, mean metal concentrations in soils of BSF were generally significantly higher than those of BBG including Fe, Mn, Zn, Ni, and Cr. The Al concentration in the soil of BBG is significantly higher than that in the soil of BSF. For Pb and As concentration, there were no significant differences between the two sites (Table 2).

Table 2 Concentrations of metals in soil sampled from hillsides near BSF and BBG

Sites	pH	Organism, %	Concentration, mg/g dry wt.			Concentration, $\mu\text{g/g}$ dry wt.				
			Fe	Al	Mn	Zn	Pb	Ni	Cr	As
BSF	7.35	4.44	40.12 \pm 0.11 **	67.87 \pm 0.52 **	693.66 \pm 5.45 **	185.15 \pm 7.05 **	18.58 \pm 1.19	18.29 \pm 1.25 *	43.35 \pm 2.93 *	7.26 \pm 0.33
BBG	6.29	3.64	32.71 \pm 0.77	77.17 \pm 0.37	529.61 \pm 6.23	114.41 \pm 7.68	18.33 \pm 0.91	16.74 \pm 0.49	38.53 \pm 1.70	6.67 \pm 0.54
Threshold of natural background in China	6.5—7.5	-	NA	NA	NA	\leq 100	\leq 35	\leq 40	\leq 90	\leq 15

Notes: Significantly different between metal content of soils from BSF and BBG ($p = 0.01$); NA, not available; Notes: significantly different between metal content of soils from BSF and BBG ($p = 0.05$).

2.2 Metal concentrations in leaves

Leaf metal concentrations of different species were significantly different at both sampling sites at $\alpha = 0.01$ (Table 3, Table 4).

2.2.1 BSF (Table 3)

For Fe, the highest concentrations were detected in *Sophora japonica* (630.68 \pm 3.88 $\mu\text{g/g}$ dry wt.) and the

lowest in *Lespedeza floribunda* (167.13 \pm 5.19 $\mu\text{g/g}$ dry wt.). Mn values ranged from 27.65 to 154.89 $\mu\text{g/g}$ dry wt.; the species with the highest value was *Robinia pseudoacacia*, which was approximately five times higher than in *Periploca sepium*. The concentrations of Al ranged from 67.90 $\mu\text{g/g}$ dry wt. in *Lespedeza floribunda* to 118.08 $\mu\text{g/g}$ dry wt. in *Platycladus orientalis*. For Zn, the mean

concentrations were three times higher in *Rubia cordifolia* (73.14 $\mu\text{g/g}$ dry wt.) than in *Grewia biloba* (23.61 $\mu\text{g/g}$ dry wt.). Compared with Pb concentration in *Platycladus orientalis* (0.10 $\mu\text{g/g}$ dry wt.), that in *Rubia cordifolia* was 10 times higher (1.03 $\mu\text{g/g}$ dry wt.). The Ni concentrations varied significantly from 3.58 $\mu\text{g/g}$ dry wt. in *Pinus*

tabulaeformis to 6.84 $\mu\text{g/g}$ dry wt. in *Rubia cordifolia*. The concentrations of Cr ranged from 0.59 $\mu\text{g/g}$ dry wt. in *Periploca sepium* to 0.87 $\mu\text{g/g}$ dry wt. in *Robinia pseudoacacia*. Concentrations of As ranged from 0.16 to 0.56 $\mu\text{g/g}$ dry wt., the highest was detected in *Rubia cordifolia*.

Table 3 Concentrations of metals in leaves of different plant species from the hillside near BSF

Species name	Species No.	Concentration of metals, $\mu\text{g/g}$ dry wt.							
		Fe	Mn	Al	Zn	Pb	Ni	Cr	As
<i>Robinia pseudoacacia</i>	1	251.72 \pm 9.07	154.89 \pm 4.94	93.12 \pm 3.79	32.97 \pm 1.03	0.77 \pm 0.03	4.00 \pm 0.22	0.87 \pm 0.03	0.27 \pm 0.04
<i>Vitex negundo</i>	2	353.04 \pm 15.70	33.77 \pm 0.78	85.69 \pm 2.07	65.49 \pm 0.88	0.76 \pm 0.03	4.58 \pm 0.19	0.85 \pm 0.03	0.30 \pm 0.03
<i>Ziziphus jujuba</i> var. <i>spinosa</i>	3	250.72 \pm 6.78	58.18 \pm 2.05	76.36 \pm 2.58	39.04 \pm 1.02	0.69 \pm 0.03	4.22 \pm 0.13	0.84 \pm 0.03	0.20 \pm 0.02
<i>Broussonetia papyrifera</i>	4	323.66 \pm 7.77	98.05 \pm 1.65	79.35 \pm 3.49	42.82 \pm 1.26	0.78 \pm 0.03	4.59 \pm 0.24	0.64 \pm 0.03	0.31 \pm 0.03
<i>Ailanthus altissima</i>	5	375.09 \pm 13.77	110.52 \pm 4.72	78.83 \pm 4.17	31.83 \pm 0.89	0.79 \pm 0.02	4.68 \pm 0.27	0.86 \pm 0.03	0.31 \pm 0.02
<i>Ulmus pumila</i>	6	530.46 \pm 7.72	58.52 \pm 1.86	102.88 \pm 2.14	39.09 \pm 1.27	0.83 \pm 0.02	4.73 \pm 0.30	0.76 \pm 0.06	0.22 \pm 0.03
<i>Sophora japonica</i>	7	630.68 \pm 3.88	57.64 \pm 2.14	109.70 \pm 6.87	35.69 \pm 1.35	0.96 \pm 0.03	4.94 \pm 0.20	0.66 \pm 0.05	0.45 \pm 0.04
<i>Grewia biloba</i>	8	411.50 \pm 8.23	87.75 \pm 2.89	88.39 \pm 3.06	23.61 \pm 1.09	0.87 \pm 0.02	4.03 \pm 0.12	0.78 \pm 0.04	0.21 \pm 0.02
<i>Artemisia gmelinii</i>	9	409.16 \pm 14.68	67.40 \pm 1.93	83.66 \pm 1.83	27.15 \pm 1.68	0.77 \pm 0.08	4.01 \pm 0.25	0.75 \pm 0.05	0.18 \pm 0.02
<i>Wikstroemia chamaedaphne</i>	10	391.80 \pm 7.99	83.07 \pm 2.03	86.08 \pm 1.24	26.71 \pm 3.16	0.91 \pm 0.05	4.35 \pm 0.08	0.81 \pm 0.04	0.22 \pm 0.01
<i>Ampelopsis aconitifolia</i> var. <i>glabra</i>	11	404.42 \pm 3.68	48.53 \pm 1.17	86.04 \pm 4.45	25.58 \pm 0.73	0.87 \pm 0.02	5.03 \pm 0.23	0.68 \pm 0.04	0.27 \pm 0.04
<i>Lespedeza floribunda</i>	12	167.13 \pm 5.19	46.45 \pm 1.84	67.90 \pm 4.60	32.25 \pm 1.35	0.69 \pm 0.03	4.11 \pm 0.33	0.62 \pm 0.04	0.20 \pm 0.02
<i>Lespedeza tomentosa</i>	13	263.42 \pm 8.92	58.77 \pm 1.98	77.76 \pm 3.45	32.45 \pm 1.43	0.73 \pm 0.03	4.29 \pm 0.11	0.86 \pm 0.02	0.25 \pm 0.02
<i>Rhamnus parvifolia</i>	14	537.35 \pm 9.98	71.59 \pm 1.61	110.77 \pm 5.11	25.85 \pm 1.06	0.89 \pm 0.03	6.05 \pm 0.17	0.86 \pm 0.05	0.22 \pm 0.02
<i>Setaria viridis</i> (L.) Beauv.	15	560.52 \pm 13.33	45.63 \pm 2.82	104.52 \pm 2.18	55.13 \pm 2.08	0.92 \pm 0.04	5.60 \pm 0.31	0.69 \pm 0.03	0.47 \pm 0.04
<i>Rubia cordifolia</i>	16	619.63 \pm 6.61	49.21 \pm 1.85	109.86 \pm 3.98	73.14 \pm 2.30	1.03 \pm 0.04	6.84 \pm 0.20	0.77 \pm 0.03	0.56 \pm 0.02
<i>Cleistogenes squarrosa</i>	17	338.29 \pm 7.69	28.72 \pm 0.99	97.98 \pm 1.32	36.67 \pm 1.60	0.82 \pm 0.03	4.30 \pm 0.12	0.75 \pm 0.04	0.19 \pm 0.02
<i>Cotinus coggygria</i>	18	277.66 \pm 7.06	31.77 \pm 1.66	70.94 \pm 2.97	34.02 \pm 1.14	0.80 \pm 0.03	4.37 \pm 0.16	0.72 \pm 0.05	0.20 \pm 0.01
<i>Periploca sepium</i>	19	268.36 \pm 7.04	27.65 \pm 1.55	83.27 \pm 2.88	34.57 \pm 1.25	0.72 \pm 0.02	3.83 \pm 0.19	0.59 \pm 0.05	0.16 \pm 0.01
<i>Platycladus orientalis</i>	20	616.14 \pm 5.00	34.75 \pm 1.61	118.08 \pm 6.92	27.72 \pm 1.05	0.10 \pm 0.03	4.88 \pm 0.22	0.86 \pm 0.02	0.37 \pm 0.04
<i>Pinus tabulaeformis</i>	21	286.76 \pm 8.98	48.26 \pm 1.18	83.14 \pm 2.11	32.65 \pm 1.01	0.66 \pm 0.03	3.58 \pm 0.15	0.78 \pm 0.05	0.30 \pm 0.02
		**	**	**	**	**	**	**	**

Notes: ** . significant difference between metal concentrations in species leaves from BSF ($p = 0.01$)

Table 4 Concentrations of metals in leaves of plant species from BBG

Species name	Species No.	Concentration of metals, $\mu\text{g/g}$ dry wt.							
		Fe	Mn	Al	Zn	Pb	Ni	Cr	As
<i>Robinia pseudoacacia</i>	1	160.97 \pm 10.95	91.08 \pm 1.88	67.51 \pm 3.61	27.30 \pm 1.50	0.76 \pm 0.03	3.80 \pm 0.18	0.86 \pm 0.03	0.07 \pm 0.01
<i>Vitex negundo</i>	2	203.08 \pm 7.21	48.19 \pm 1.43	68.37 \pm 3.99	83.21 \pm 1.92	0.78 \pm 0.03	4.22 \pm 0.07	0.92 \pm 0.03	0.25 \pm 0.02
<i>Ziziphus jujuba</i> var. <i>spinosa</i>	3	219.65 \pm 6.79	69.50 \pm 1.64	71.65 \pm 4.20	38.75 \pm 1.32	0.83 \pm 0.06	4.30 \pm 0.11	0.72 \pm 0.03	0.16 \pm 0.02
<i>Broussonetia papyrifera</i>	4	259.41 \pm 8.60	50.78 \pm 1.44	77.84 \pm 3.70	38.06 \pm 1.29	0.70 \pm 0.03	4.37 \pm 0.10	0.97 \pm 0.02	0.23 \pm 0.04
<i>Ailanthus altissima</i>	5	256.54 \pm 6.33	37.59 \pm 2.59	76.50 \pm 3.05	22.32 \pm 1.80	0.79 \pm 0.03	3.41 \pm 0.18	1.03 \pm 0.02	0.24 \pm 0.02
<i>Ulmus pumila</i>	6	262.37 \pm 6.33	40.60 \pm 2.37	89.75 \pm 1.86	58.88 \pm 1.72	0.82 \pm 0.05	4.16 \pm 0.22	0.92 \pm 0.04	0.08 \pm 0.01
<i>Sophora japonica</i>	7	357.73 \pm 10.89	54.40 \pm 2.47	104.51 \pm 4.62	32.08 \pm 1.78	0.82 \pm 0.04	4.68 \pm 0.33	0.55 \pm 0.04	0.61 \pm 0.06
<i>Wikstroemia chamaedaphne</i>	10	346.29 \pm 12.62	95.73 \pm 1.57	89.21 \pm 6.02	25.61 \pm 1.58	0.82 \pm 0.04	4.27 \pm 0.10	0.91 \pm 0.04	0.31 \pm 0.07
<i>Ampelopsis aconitifolia</i> var. <i>glabra</i>	11	187.92 \pm 4.29	52.98 \pm 1.13	76.48 \pm 2.75	24.96 \pm 2.17	0.73 \pm 0.07	4.44 \pm 0.15	0.62 \pm 0.05	0.20 \pm 0.02
<i>Lespedeza floribunda</i>	12	142.08 \pm 4.26	90.71 \pm 1.15	75.26 \pm 2.15	34.89 \pm 1.46	0.76 \pm 0.04	3.69 \pm 0.24	0.80 \pm 0.06	0.22 \pm 0.02
<i>Lespedeza tomentosa</i>	13	209.09 \pm 5.13	72.80 \pm 1.18	80.81 \pm 3.61	27.61 \pm 1.21	0.74 \pm 0.05	3.67 \pm 0.30	0.95 \pm 0.03	0.19 \pm 0.02
<i>Rhamnus parvifolia</i>	14	404.40 \pm 6.52	65.75 \pm 1.30	100.01 \pm 3.30	24.11 \pm 1.33	0.66 \pm 0.06	5.02 \pm 0.28	0.93 \pm 0.05	0.29 \pm 0.06
<i>Setaria viridis</i> (L.) Beauv.	15	323.02 \pm 5.97	46.84 \pm 1.42	101.63 \pm 2.35	54.56 \pm 1.12	0.71 \pm 0.03	4.34 \pm 0.23	0.80 \pm 0.04	0.29 \pm 0.03
<i>Rubia cordifolia</i>	16	402.26 \pm 7.59	34.16 \pm 1.39	92.72 \pm 3.76	48.08 \pm 1.88	0.82 \pm 0.03	4.33 \pm 0.07	0.85 \pm 0.04	0.24 \pm 0.02
<i>Cotinus coggygria</i>	18	156.91 \pm 5.65	25.04 \pm 1.18	63.47 \pm 2.86	30.15 \pm 0.94	0.62 \pm 0.01	3.90 \pm 0.11	0.88 \pm 0.05	0.08 \pm 0.01
<i>Platycladus orientalis</i>	20	248.77 \pm 7.60	45.66 \pm 2.22	73.19 \pm 4.51	30.47 \pm 1.63	0.70 \pm 0.03	4.00 \pm 0.17	0.87 \pm 0.03	0.24 \pm 0.04
<i>Pinus tabulaeformis</i>	21	203.63 \pm 8.16	79.05 \pm 1.39	64.76 \pm 2.66	29.57 \pm 1.97	0.60 \pm 0.03	3.49 \pm 0.25	0.75 \pm 0.03	0.32 \pm 0.04
		**	**	**	**	**	**	**	**

Notes: ** . significant difference between metal concentrations in plant leaves from BBG ($p = 0.01$)

2.2.2 BBG (Table 4)

Elements in leaves of 17 species investigated showed the significant difference in the concentrations. For example, *Rhamnus parvifolia* reached the highest Fe value (404.40 $\mu\text{g/g}$ dry wt.), which was 3.73 times more than that of *Lespedeza floribunda* (142.08 $\mu\text{g/g}$ dry wt.). Mn values ranged from 25.04 to 95.73 $\mu\text{g/g}$ dry wt.; the highest mean value was recorded in *Wikstroemia chamaedaphne*. Concentrations of Al were variable, from 64.76 in *Pinus tabulaeformis* to 104.51 $\mu\text{g/g}$ dry wt. in *Sophora japonica*. Zn concentrations in *Vitex negundo* (83.21 $\mu\text{g/g}$ dry wt.) were three times higher than in *Ailanthus altissima* (22.32 $\mu\text{g/g}$ dry wt.). The mean Pb concentrations were from 0.60 to 0.83 $\mu\text{g/g}$ dry wt. Ni value changed from 3.41 in *Ailanthus altissima* to 5.02 $\mu\text{g/g}$ dry wt. in *Rhamnus parvifolia*. Cr concentrations ranged between 0.55 $\mu\text{g/g}$ dry wt. in *Sophora japonica*, and 1.03 $\mu\text{g/g}$ dry wt. in *Ailanthus altissima*. As concentrations ranged from 0.07 $\mu\text{g/g}$ dry wt. in *Robinia pseudoacacia* to 0.61 $\mu\text{g/g}$ dry wt. in *Sophora japonica*.

Metal concentrations in leaves for the same species from BSF and BBG were compared and analyzed statistically (Table 5). Generally, metal concentrations in leaves were different for the same species at the different sampling sites. For example, the concentrations of Fe in all species from BSF were significantly higher than those in the same species in BBG (Table 5). This did not apply for all elements. Usually for one element, a species may have a higher value at one site in contrast to another species at another site. E.g., Mn value of *Robinia pseudoacacia* in BSF was 63.81 $\mu\text{g/g}$ dry wt. higher than that of the same species in BBG, while, Mn concentration in *Lespedeza floribunda* leaves from BSF was 44.26 $\mu\text{g/g}$ dry wt. less than that in the same species leaves from BBG (Table 5). The same species has different accumulation ability for different elements in the two sampling sites. For example, *Sophora japonica* had significantly higher concentrations of Fe, Zn, Pb and Cr in BSF and of As in BBG, while there were no significant differences between the concentration of Mn, Al and Ni between the two sites (Table 5).

Table 5 Comparison of metal concentrations in leaves between BSF and BBG

Species name	Species No.	Metal content difference in leaves from BSF and BBG, $\mu\text{g/g}$ dry wt.							
		Fe	Mn	Al	Zn	Pb	Ni	Cr	As
<i>Robinia pseudoacacia</i>	1	90.75 **	63.81 **	25.61 **	5.67 **	0.011	0.20	0.02	0.20 **
<i>Vitex negundo</i>	2	149.96 **	-14.42 **	17.32 **	-17.72 **	-0.02	0.36 **	-0.07 **	0.06 **
<i>Ziziphus jujuba</i> var. <i>spinosa</i>	3	31.07 **	-11.32 **	4.71	0.29	-0.13 **	-0.09	0.12 **	0.04 **
<i>Broussonetia papyrifera</i>	4	64.25 **	47.27 **	1.51	4.76 **	0.08 **	0.22	-0.33 **	0.08 **
<i>Ailanthus altissima</i>	5	118.55 **	72.93 **	2.33	9.51 **	0.00	1.27 **	-0.17 **	0.07 **
<i>Ulmus pumila</i>	6	268.09 **	17.92 **	13.13 **	-19.79 **	0.02	0.58 **	-0.16 **	0.14 **
<i>Sophora japonica</i>	7	272.95 **	3.24	5.19	3.61 **	0.14 **	0.27	0.10 **	-0.16 **
<i>Wikstroemia chamaedaphne</i>	10	65.21 **	-7.98 **	-0.82	-2.00 *	0.05 *	-0.24 **	-0.13 **	-0.10 *
<i>Ampelopsis aconitifolia</i> var. <i>glabra</i>	11	216.50 **	-4.45 **	9.56 **	0.62	0.14 **	0.58 **	0.07 *	0.07 **
<i>Lespedeza floribunda</i>	12	25.05 **	-44.26 **	-7.36 *	-2.64 *	-0.06 *	0.42 *	-0.19 **	-0.02
<i>Lespedeza tomentosa</i>	13	54.33 **	-14.03 **	-3.05	4.84 **	-0.01	0.62 **	-0.09 **	0.05 **
<i>Rhamnus parvifolia</i>	14	132.95 **	5.84 **	10.76 **	1.74 *	0.23 **	1.03 **	-0.06	-0.07 *
<i>Setaria viridis</i> (L.) Beauv.	15	237.50 **	-1.21	2.89	0.57	0.21 **	1.26 **	-0.11 **	0.18 **
<i>Rubia cordifolia</i>	16	217.37 **	15.05 **	17.14 **	25.06 **	0.21 **	2.51 **	-0.09 **	0.32 **
<i>Cotinus coggygria</i>	18	120.75 **	6.73 **	7.47 **	3.87 **	0.19 **	0.47 **	-0.15 **	0.12 **
<i>Platycladus orientalis</i>	20	367.37 **	-10.91 **	44.89 **	-2.75 **	0.30 **	0.87 **	-0.02	0.13 **
<i>Pinus tabulaeformis</i>	21	83.13 **	-30.79 **	18.38 **	3.08 *	0.05 *	0.11	0.04	-0.02

Notes: ** . significant difference ($p = 0.01$) of metal concentration of species between BSF and BBG; * . significant difference ($p = 0.05$) of metal concentration of species between BSF and BBG

2.3 Element associations

The Pearson correlation coefficient matrixes between some major elements and heavy metals in leaves are presented in Table 6. The two sampling sites showed different correlated situations. In BSF, Fe, Al, Ni, As, and Pb were significantly correlated with each other but not Zn, which only significantly correlated with Ni and As. Mn and Cr did not show any significant correlation with other elements. In BBG, Fe, Al, Ni and As were in general significantly correlated with each other. While Mn, Cr, Pb and Zn did not show any significant correlated relationship with other elements.

2.4 Metal accumulation indices

The MAI for species leaves in both sites were separately calculated using the method supplied in Section 1.4. The range of MAI for species in BSF was 18.77 to 34.83. The highest MAI occurred to *Sophora japonica*, which was almost twice higher than the lowest MAI value in *Lespedeza floribunda*. In BBG, MAI in species leaves ranged from 18.03 in *Sophora japonica* to 28.96 in *Rubia cordifolia* (Table 7). The MAI range in BBG was included in the range of MAI in BSF.

2.5 Categorization of MAI

The overall mean MAI for species leaves in BSF was 27.23 ± 4.62 ; the overall MAI mean for species leaves in BBG was 24.17 ± 3.15 (Table 7). The categorization of MAI

was calculated as described in Section 1.5. Some species showed a different metal accumulation class in the two sampling sites. E. g., *Sophora japonica* showed the strong accumulation ability in BSF while weak in BBG (Table 7). In both sampling sites, the species with strong and moderately accumulation ability included *Rubia cordifolia*, *Vitex negundo*, *Broussonetia papyrifera*, and *Ulmus pumila*. Species with a strong or moderately accumulated ability only

in BSF covered *Sophora japonica*, *Platycladus orientalis*, *Ampelopsis aconitifolia* var. *glabra*, *Wikstroemia chamaedaphne*, *Cleistogenes squarrosa*, and *Grewia biloba*. Species with a strong and moderately accumulated ability only in BBG included *Setaria viridis* (L.) Beauv., *Lespedeza floribunda*, *Lespedeza tomentosa*, *Rhamnus parvifolia*, and *Cotinus coggygia* (Table 7).

Table 6 Correlation between metal concentrations in leaves at (a) BSF ($n = 21$) and (b) BBG ($n = 17$)

	Fe	Mn	Al	Zn	Pb	Ni	Cr	As		Fe	Mn	Al	Zn	Pb	Ni	Cr	As
(a) Fe	1.00								(b) Fe	1.00							
Mn	-0.13	1.00							Mn	-0.18	1.00						
Al	0.89**	-0.08	1.00						Al	0.85**	-0.10	1.00					
Zn	0.24	-0.25	0.20	1.00					Zn	0.02	-0.33	0.06	1.00				
Pb	0.88**	-0.06	0.79**	0.20	1.00				Pb	0.25	0.07	0.33	0.28	1.00			
Ni	0.73**	-0.11	0.64**	0.52*	0.74**	1.00			Ni	0.65**	-0.15	0.66**	0.17	0.15	1.00		
Cr	0.08	0.36	0.18	-0.05	0.06	0.08	1.00		Cr	0.02	-0.12	-0.16	0.10	-0.06	-0.30	1.00	
As	0.67**	-0.03	0.58**	0.63**	0.64**	0.69**	-0.01	1.00	As	0.56*	0.07	0.57*	-0.07	0.12	0.37	-0.47	1.00

Notes: ** . significant difference ($\alpha = 0.01$) between metals at both sampling sites; * . significant difference ($\alpha = 0.05$) between metals at both sampling sites

Table 7 MAI in leaves of each species and the classification of the MAI

Species No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
BSF:																					
MAI	23.09	30.99	26.29	27.65	22.89	29.35	34.83	28.36	20.59	30.86	33.38	18.77	25.26	27.21	24.16	34.56	30.26	23.26	22.99	32.45	25.08
Sequence No.	16	5	12	10	18	8	1	9	20	6	3	21	13	11	15	2	7	17	19	4	14
Class of MAI	IA	MA	IA	MA ²	IA ³	MA	SA ¹	MA	WA ⁴	MA	SA	WA	IA	IA	IA	SA	MA	IA	IA	SA	IA
BBG:																					
MAI	21.01	27.54	23.47	27.44	21.15	24.92	18.03	23.91	-	-	22.08	25.91	24.67	24.91	28.55	28.96	-	26.58	-	20.36	21.38
Sequence No.	15	3	11	4	14	7	17	10	-	-	12	6	9	8	2	1	-	5	-	16	13
Class of MAI	WA	SA	IA	SA	IA	MA	WA	IA	-	-	IA	MA	MA	MA	SA	SA	-	MA	-	IA	IA

Notes: ¹. Strong accumulation; ². moderate accumulation; ³. intermediate accumulation; ⁴. weak accumulation

3 Discussion

3.1 Metal concentration comparison in soils from BSF and BBG

There were no significant differences between the concentrations of Pb, As in soils from BSF and those from BBG, and both metal concentrations were lower than the nationwide threshold values (Table 2). This suggested that soils in BSF and BBG are not contaminated by Pb and As. It is also agreed that air deposits in BSF was not polluted by Pb and As comparing to downtown (Table 1). The concentrations of Zn in soils from BSF exceeded the nationwide threshold values thus demonstrating that Zn contaminated the site. This might be resulted from high Zn content in air deposits from BSF (Table 1). Elevated concentrations of Ni, Cr in soils from BBG and BSF in this study suggested the potential metal contamination of the soils by these metals in BSF, although the mean concentrations of Ni, Cr from both sites were below the national threshold values. The threshold values were unavailable for Fe and Mn, while the concentrations of both elements were significantly higher in BSF than in BBG. The significant difference of metals in soils from BSF and from BBG also certified that airborne deposit is a main source of pollution affecting the area (Table 1). It agreed with the phenomenon that concentrations of metals in soil decline logarithmically with increasing distance from the origin of pollution (Taylor, 1983). The concentration of Al in soils

from BBG was significantly higher than that from BSF. The reason could be the soils in BBG had high Al background values.

3.2 Leaf metal concentrations of different species

As part of the plants' above ground organs, leaves accumulated different metals from atmospheric deposition as stated in previous studies (Angelova, 1999). By separately analyzing the samples from BBF and BBG, we found that the concentration of metals in leaves of different species were different for the same site as shown in Table 3 and Table 4, confirming Montagnini *et al.* (Montagnini, 1984). The comparison between concentrations of metals in the same species at both sites suggested that in general the ability of the leaves of the same species to accumulate the same element was also different when they grew in different sites (Table 5). Similar results have been reported for non-vascular plants (Montagnini, 1984). Sometimes higher accumulation for one element in a species might be led by higher content of this element in soil and air deposits, e.g. Fe. But this does not always happen, e.g. Mn (Table 1, Table 2, Table 5). For the investigated 21 species in this paper, each species enriches different elements in its leaves, consistent with Reimann *et al.* (Reimann, 2001). When one species strongly accumulated a metal, its ability to accumulate another element might be weak, e.g., *Rhamnus parvifolia* had higher concentrations of Fe, Mn, Al, Zn, Pb, Ni in BSF while higher concentration of As in BBG

(Table 5). Therefore, to overcome the complex evaluation of the overall metal accumulation data in leaves of different species, the MAI method was developed.

3.3 Element associations

The results of the Pearson correlation showed that the elemental association of Mn and Cr was generally weak in leaves of species from both sites indicating that the relationship between Mn, Cr and other metals was insignificant (Table 6). This also applied for Pb and Zn from BBG. In contrast, Fe, Al, Ni, As were generally highly correlated with each other in both sites. This may suggest their common biochemical characteristics. Zn and Pb were generally highly correlated with As and the metals Fe, Al, and Ni in BSF.

3.4 Metal accumulation indices

As stated in section 2.2, MAI of leaves was used to screen terrestrial plant species with an overall strong accumulation ability of metals in the sampling sites. One species may have a high MAI in one site and low MAI in another site. E.g., *Sophora japonica* was listed as the first in BSF but as the 17th in BBG (Table 7). This implies that the results in this paper could only be applied to those sites with similar contamination scenarios.

3.5 Categorization of MAI

The classes of MAI provided us with a more simple way to decide which plant species could be used as biomonitors. When biomonitoring BSF and similar places, those plants including *Sophora japonica*, *Rubia cordifolia*, *Ampelopsis aconitifolia* var. *glabra*, *Platyclusus orientalis* with a strong accumulation should be considered first. As a second choice plants with a moderate accumulation are also acceptable covering, e. g., *Vitex negundo*, *Wikstroemia chamaedaphne*, *Cleistogenes squarrosa*, *Ulmus pumila*, *Grewia biloba*, *Broussonetia papyrifera*. Plants suitable for BBG include those with strong accumulations, e. g. *Rubia cordifolia*, *Setaria viridis* (L.) Beauv., *Vitex negundo*, *Broussonetia papyrifera* and those with moderate accumulation, e. g., *Cotinus coggygria*, *Lespedeza floribunda*, *Ulmus pumila*, *Rhamnus parvifolia* and *Lespedeza tomentosa*. Generally, those species that showed the strong and moderate accumulation at both sites could be considered including *Vitex negundo*, *Broussonetia papyrifera*, *Ulmus pumila* and *Rubia cordifolia*.

Acknowledgements: The authors thanks to Xin-Jian Liu for her help with sampling collection and Professor Diane Edwards (Department of Geology, University of Wales) for her help with manuscript preparation.

References:

- Angelova V R, Braikov D M, Ivanov A S, 1999. Heavy metals (Pb, Cu, Zn and Cd) in the system soil-grapevine-grape [J]. *J Sci Food Agric*, 47(1): 1—26.
- Breulmann G, Markert B, Weckert V *et al.*, 2002. Heavy metals in emergent trees and pioneers from tropical forest with special reference to forest fires and local pollution sources in Sarawak, Malaysia [J]. *Sci Total Environ*, 285: 107—115.
- Caliceti M, Argese E, Sfriso A *et al.*, 2002. Heavy metal contamination in the seaweeds of the Venice Lagoon [J]. *Chemosphere*, 47: 443—454.
- Campanella L, Conti M E, Cubadda F *et al.*, 2001. Trace metals in seagrass, algae and molluscs from an uncontaminated area in the Mediterranean [J]. *Environ Pollut*, 111: 117—126.
- Cervantes C, Campos-García J, Devars S *et al.*, 2001. Interactions of chromium with microorganisms and plants [J]. *FEMS Microbiol Rev*, 25(3): 335—347.
- Chen H M, Zheng C R, Tu C *et al.*, 1999. Heavy metal pollution in soils in China: status and countermeasures [J]. *Ambio*, 28: 130—134.
- Cui Y J, Zhu Y G, Zhai R H *et al.*, 2004. Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China [J]. *Environ Intern*, 30: 785—791.
- Dahmani-Muller H, van Oort F, Gelie B *et al.*, 2000. Strategies of heavy metal uptake by three plant species growing near a metal smelter [J]. *Environ Pollut*, 109(2): 231—238.
- Facchinelli A, Sacchi E, Mallen L, 2001. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils [J]. *Environ Pollut*, 114: 313—324.
- Goodman G T, Roberts T M, 1971. Plants and soils as indicators of metals in the air [J]. *Nature*, 231(5301): 287—292.
- Haygarth P M, Jones K C, 1992. Atmospheric deposition of metals to agricultural surfaces [M]. In: *Biogeochemistry* (Adriano D. C., ed.). Boca Raton: Lewis Publishers. 249—276.
- Liu Y J, Ding H, Wang H, 2001. Comparisons of leaf sulfur content from trees near steel factory and Botanical Garden of Beijing [J]. *China Environ Sci*, 21(6): 498—502.
- Liu R K, Shen Y W, Liu X J, 1983. A study on physiological responses of plant to SO₂ [J]. *Plant Physiol Commun*, 4: 25—28.
- MacFarlane G R, Burchett M D, 2002. Toxicity, growth and accumulation relationships of copper, lead and zinc in the grey mangrove *Avicennia marina* (Forsk.) Vierh [J]. *Mar Environ Res*, 54(1): 65—84.
- Madejón P, Murillo J M, Marañón T *et al.*, 2002. Bioaccumulation of As, Cd, Cu, Fe and Pb in wild grasses affected by the Aznalcollar mine spill (SW Spain) [J]. *Sci Total Environ*, 290: 105—120.
- Montagnini F, Neufeld H S, Uhl C, 1984. Heavy metal concentrations in some non-vascular plants in an Amazonian rainforest [J]. *Water Air Soil Poll*, 21: 317—321.
- National Environmental Protection Agency of China, 1995. Environmental quality standard for soils [S]. (GB 15618—1995).
- Patra M, Sharma A, 2000. Mercury toxicity in plants [J]. *Bot Rev*, 66(3): 379.
- Prasad M N V, Freitas H, 2000. Removal of toxic metals from solution by leaf, stem and root phytomass of *Quercus ilex* L. (holly oak) [J]. *Environ Pollut*, 110(2): 277—283.
- Reimann C, Koller F, Kashulina G *et al.*, 2001. Influence of extreme pollution on the inorganic chemical composition of some plants [J]. *Environ Pollut*, 115(2): 239—252.
- Samecka-Cymerman A, Kempers A J, 1999. Bioindication of heavy metals in the town Wrocław (Poland) with evergreen plants [J]. *Atmos Environ*, 33(3): 419—430.
- Sharma V K, 1999. Development of air quality indices from Mumbai, India [J]. *Int J Environ Pollut*, 11(1): 141—146.
- Smith K E C, Jones K C, 2000. Particles and vegetation: implications for the transfer of particle-bound organic contaminants to vegetation [J]. *Sci Total Environ*, 246(2—3): 207—236.
- Tang X Y, Zhu Y G, Chen S B *et al.*, 2004. Assessment of the effectiveness of different phosphorus fertilizers to remediate Pb-contaminated soil using *in vitro* test [J]. *Environ Intern*, 30: 531—537.
- Taylor G J, Crowder A A, 1983. Accumulation of atmospherically deposited metals in wetland soils of Sudbury, Ontario [J]. *Water Air Soil Pollut*, 19: 29—42.
- Tützen M, 2003. Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry [J]. *Microchem J*, 74(3): 289—297.
- Vajpayee P, Tripathi R D, Rai U N *et al.*, 2000. Chromium(VI) accumulation reduces chlorophyll biosynthesis, nitrate reductase activity and protein content in *Nymphaea alba* L. [J]. *Chemosphere*, 41(7): 1075—1082.
- Wenzel W W, Jockwer F, 1999. Accumulation of heavy metals in plants grown on mineralized soils of the Austrian Alps [J]. *Environ Pollut*, 104(1): 145—155.
- Williams L E, Pittman J K, Hall J L, 2000. Emerging mechanisms for heavy metal transport in plants [J]. *Biochim Biophys Acta (BBA)-Biomembranes*, 1465(1—2): 104—126.
- Wong S C, Li X D, Zhang G *et al.*, 2002. Heavy metals in agricultural soils of the Pearl River Delta, South China [J]. *Environ Pollut*, 119: 33—44.
- Zhao F, McGrath S P, Crosland A R, 1994. Comparison of three wet digestion methods for the determination of plant sulphur by inductively coupled plasma atomic emission spectroscopy (ICP-AES) [J]. *Commun Soil Sci Plant Anal*, 25: 407—418.
- Zhu Y G, Chen S B, Yang J C, 2004. Effects of soil amendments on lead uptake by two vegetable crops from a lead-contaminated soil from Anhui, China [J]. *Environ Intern*, 30: 351—356.