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RESEARCH ARTICLE

Evaluation of heavy metal and polycyclic aromatic hydrocarbons accumulation in plants from typical industrial sites: potential candidate in phytoremediation for co-contamination

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Abstract The heavy metal and polycyclic aromatic hydrocarbons (PAHs) contents were evaluated in surface soil and plant samples of 18 wild species collected from 3 typical industrial sites in South Central China. The accumulative characteristics of the plant species for both heavy metal and PAHs were discussed. The simultaneous accumulation of heavy metal and PAHs in plant and soil was observed at all the investigated sites, although disparities in spatial distributions among sites occurred. Both plant and soil samples were characterized by high accumulation for heavy metal at smelting site, moderate enrichment at coke power and coal mining sites, whereas high level of PAHs (16 priority pollutants according to US Environmental Protection Agency) at coke power site, followed sequentially by coal mining and smelting sites. Based on the differences of heavy metal and PAH accumulation behaviors of the studied plant species, heavy metal and PAH accumulation strategies were suggested: *Pteris vittata* L. and *Pteris cretica* L. for As and PAHs, *Boehmeria nivea* (L.) Gaud for Pb, As, and PAHs, and *Miscanthus floridulu* (Labnll.) Warb for Cu and PAHs. These native plant species could be proposed as promising materials for heavy metal and PAHs combined pollution remediation.

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Introduction

Industrial contamination has long been recognized as priority environmental concern in the process of industrialization and urbanization. The European environmental protection agency in 2006 identified 3,000,000 potential industrial contaminated sites in Europe, 83 % of which would pose health threat to human beings (EEA 2007). In the USA, 1,536 industrial contaminated sites were classified as priority remediation sites during 1982–2005 (US EPA 2004). It is reported that Pb, As, Cr, Cd, Zn, polycyclic aromatic hydrocarbons (PAHs), etc. ranked the top 12 contaminants of concern at 568 Superfund sites in the USA (US EPA 2002). The simultaneous accumulation of heavy metals and PAHs have gained considerable attention since soils contaminated with PAHs were frequently reported to contain high amounts of heavy metal (Achten and Hofmann 2009; Wang et al. 2009; Sun et al. 2013). Several studies have demonstrated that the combination of these two types of contaminants could potentiate great environmental risk to vegetation, soil microbial, and human health (Maier et al. 2002).

Phytoremediation has been proposed as promising technology to treat a wide range of contaminants and applied well in many contaminated sites (US EPA 2005). Generally, collection of plant species with genetic ability to survive, reproduce in barren site, and tolerate excessive toxic substance plays a critical role in the success of phytotechnology application (Parizanganeha et al. 2010). So far, a number of metal-tolerant plant species have been identified to be efficient in heavy metal accumulation. Some plants have also been demonstrated for the phytoremediative potentials of PAHs (Sojinua et al. 2010). Recently, several researches have paid attention to screening effective plant species to remediate heavy metal and PAH combined pollution, most of which were based on the pot culture study. For a few field trials, the test subject was often the introduced plant species rather than the native or naturalized species (Vervaeke et al. 2003; Sébastien et al. 2005; Sun et al. 2011). Whether native plant species is of great significance in phytoremediation for heavy metal and PAH combined pollution was seldom reported. In fact, it is increasingly believed that plant species endemic to contaminated site would have excellent potential for phytoremediation with its adaptation to growth conditions (Parizanganeha et al. 2010). Thus, identifying and collecting plant species spontaneously grown in industrial areas, which are resistant to metals and PAHs co-exposure, and can accumulate considerable amounts of them, would facilitate the phytoremediation technology development.

China is one of the world's largest coal and metallic mineral producer and consumer. Because of the rapid industrial growth in China over the past decades, the number of industry enterprises has reached 375,000 in 2008, and the pillar industry including coke power, coal mining, and metal smelting accounted for 12.5 % of the total (NBS 2010). The industries of coke power, coal mining, and metal smelting are generally recognized as the main heavy metal and PAH pollution sources (Cheng 2003; Achten and Hofmann 2009; Wang et al. 2009). However, limited information is available on the characterization of heavy metal and PAH pollution at these sites in China. In this study, heavy metal and PAHs of soil and plant samples collected from coke power, metal smelting, and coal mining sites were investigated. The main objectives were (1) to identify and characterize heavy metal and PAHs distribution and potential sources of three industrial sites and (2) to evaluate the phytoremediation potential of endurant plant species for heavy metal and PAH combined pollution.

Materials and methods

Site description and sampling

This study was conducted in industrial region in Chenzhou city, Hunan province in South Central China, which has long been recognized as the base of nonferrous metals and energy. The climate of the study area is typically subtropical with a mean annual rainfall around 1,500 mm and temperature of 17.4 °C. The mean altitude above the sea level is 400 m. Two large coke power stations, three smelting factories, and two coal mining workings are located (Fig. 1). The coke power plants are important producers of electricity and coal tar in Chenzhou. The main products of the smeltery are Pb, Zn, Cu, Au, and Ag. The surface coal mining is on the basis of Bituminous coal. Two areas in the proximity of the coke battery for coke power site, three areas nearby the smelting furnace of smelting site, and two areas in the vicinity of coal washing poor and coal picker for coal mining site, each of about 25×25 m^2, were selected for soil and plant sampling. Soil samples of references were collected from an unaffected area far from the influence of the anthropogenic activities. Forty-nine surface (0–20 cm) soil samples were collected, and each soil sample was gathered and mixed properly by five subsamples collected randomly from the surroundings following different directions. Among 49 soil samples, 12 were collected from coke power site, 18 from smelting site, 13 from coal mining site, and 6 from reference area.

Plant species sampling was performed in the vicinity of soil sampling points where the plants were grown. At least three or five individual plants of each plant species were collected randomly within the sampling area, and then they were mixed to give a composite plant sample for each species. The corresponding soil samples were also a mixture of single samples taken from three to five locations where the plants were sampled. The identification of species was realized with the help from the Institute of Botany, Chinese Academy of Sciences. Plant samples were cleaned with tap water and distilled water and then prepared for heavy metal and PAH analysis. Soil was dried and sieved through a 2-mm screen for analysis.

Chemical analysis

For heavy metal analysis, the dried and ground plant samples were digested with HNO_3–$HClO_4$, while soil samples were digested with HNO_3–H_2O_2 (EPA 3050B). The elements of Cu, Pb, Zn, and Cd were determined by inductively coupled plasma optical emission spectrometry (5300DV, PerkinElmer U. S.). As was determined using atomic fluorescence spectroscopy (9130, Beijing Titan Instruments Co., China). Accuracy of the elemental analysis was verified by standard reference material. The results showed a recovery of Cu, Pb, Zn, Cd, and As in the range of 90.6–103.3 %, 93.4–106.8 %, 89.2–98.5 %, 95.7–112.4 %, and 95.6–109.6 %.

For PAH analysis, certain amounts of freeze-dried soil or plant fragment were extracted by ultrasonication with dichloromethane or acetone–dichloromethane mixture. The extracts were concentrated and then transferred to silica gel column for cleanup by washing with hexane and dichloromethane mixture. The eluate was concentrated and analyzed by Agilent GC-MS [Agilent 7890A gas chromatography (GC) coupled with a 5975C mass spectroscopy (MS) system]. A mixture of PAH containing 16 compounds were determined: naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene.

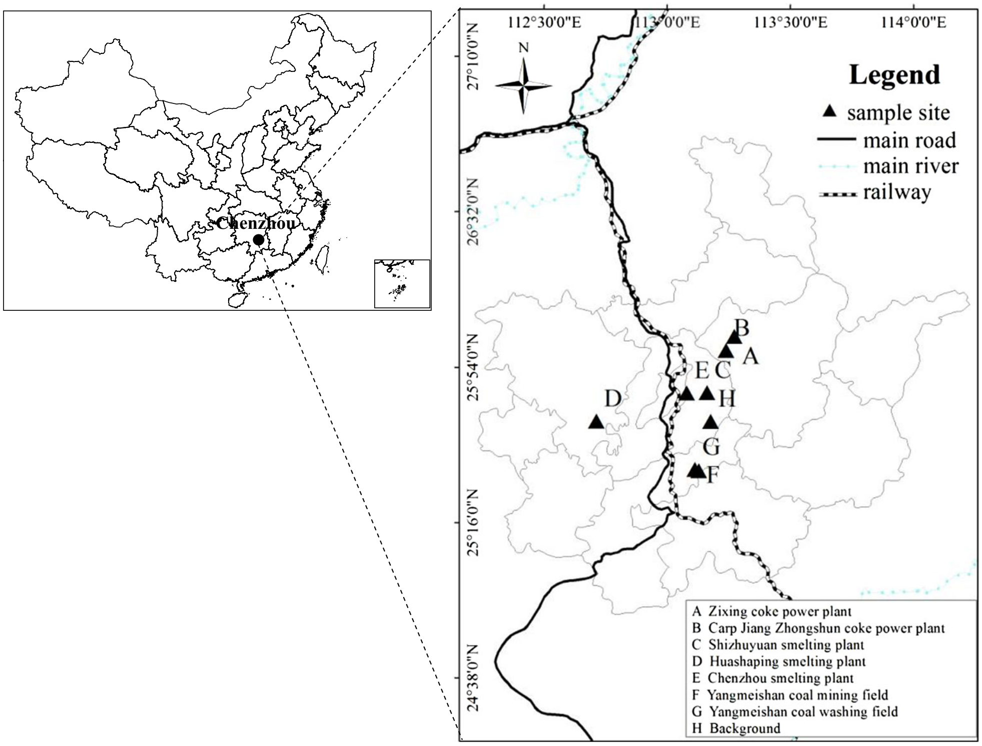


Fig. 1 Map showing the location of sampling sites

Data analysis

Statistical analysis was performed using SPSS 13.0. The difference of heavy metal and ∑16 PAHs concentrations in soil and plant samples among different sampling sites was determined by the Kruskal–Wallis test. Spearman's correlation was conducted to examine the relationships among heavy metal and PAHs in soil and plant samples. A probability of 0.05 or lower was considered as significant. Principal component analysis (PCA) was performed to investigate the relationship between plant species and contaminant concentrations.

Results and discussion

The concentrations of As, Cd, Cu, Pb, Zn, and ∑16 PAHs in soil samples are listed in Table 1. According to the heavy metal contents determined in the reference area, which were in line with the corresponding natural background values in Hunan province (As, Cd, Cu, Pb, and Zn at the levels of 13.6, 0.079, 25.4, 27.3, and 88.6 mg/kg, respectively) (MEP 1990), the total metal concentrations in the soil samples of industrial sites were higher than the background values by approximately 1 to several hundred times based on the mean concentration. Compared with ∑16 PAHs levels determined in the reference area, which were below the documented standard in Dutch (1 mg/kg), the contents of ∑16 PAHs in the soil samples of industrial sites exceeded the background level by approximately 78 times at coke power site, about 32.5 times at coal mining site, and more than 20 times at smelting site. The concentrations of heavy metals and ∑16 PAHs in soils of the study area were among the high level compared to the reported values for other contaminated soils at industrial sites in the literature, which clearly highlighted the strong anthropogenic input from industrial processing activities on these spots.

Variation of industrial pollution feature was observed at three types of sites. In general, the soil heavy metal concentrations were found to decrease in the order smelting site>coal mining site>coke power site; while in contrast, ∑16 PAHs concentrations were highest at coke power site, and followed sequentially by coal mining and smelting sites. The polymetallic pollution was observed due to As, Cd, Cu, Zn, and Pb at smelting site with the concentration median values of 251, 34.9, 851, 2,315, and 4,610 mg/kg, amounting several orders of magnitude higher than those at coal mining and coke power sites ($P<0.01$). The primary metal-bearing minerals for smelting in the study area are galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and arsenopyrite (FeAsS). The high concentrations of As, Cd, Cu, Zn, and Pb in the soil are probably due to airborne emissions, transportation, and deposition of volatile particles and aerosols from stack emission or the fugitive emissions. High As level was recorded at coal mining site, with the highest concentration of 127 mg/kg. He et al. (2002) reported that coal mines undergone mineralization could result in enrichment of toxic trace elements, e.g., arsenic and fluorine. It was speculated that the local coal as

Table 1 Concentrations of heavy metal (mg/kg) and PAHs (μg/kg) in soil in the vicinities of industrial activities

Location	As	Zn	Cu	Cd	Pb	∑PAHs	Reference
Backgroud area (n=6)	14.3 (7.1–25.9)[a]	61.8 (33.9–113)	23.4 (10.6–37.1)	ND	31.5 (13.2–57.1)	55.0 (10–123) (∑16 PAHs)	This study
Coke power site (n=12)	21.1 (3.03–28.1)	115.0 (3.9–229)	33.6 (5.2–73.3)	ND	55.5 (5.0–126)	4,296 (882–32,474) (∑16 PAHs)	This study
Smelting site (n=18)	251 (50.6–880)	2,315 (164–10,240)	851 (35.3–6,367)	34.9 (1.8–249)	4,610 (126–40,600)	1,194 (215–2,612) (∑16 PAHs)	This study
Coal mining site (n=13)	50.4 (11.9–127)	111 (24.5–283)	33.8 (10.3–198)	ND	35.4 (5.2–96.8)	1,790 (751–2,789) (∑16 PAHs)	This study
E-waste processing centers	–	144–661	77.9–1,641	0.6–12.5	81.3–2,374	372–1,231 (∑16 PAHs)	Tang et al. 2010
Industry complex	–	1,136	–	–	2,430	118–5,913(∑31 PAHs)	Shukurov et al. 2009; Musa et al. 2010
Chemical and petrochemical industries	5.50	–	–	0.21	36.3	1,002 (∑16 PAHs)	Nadal et al. 2004a, b
Lignite-fired power plants	–	19.5–119	8.13–46.7	–	7.3–52	50–500 (∑16 PAHs)	Stalikas et al. 1997
Railway junction	–	84–1,244	24–115	<0.5–5.2	55–506	641–846 (∑16 PAHs)	Malawska and Wiłkomirski 2001
Iron–steel plant	9	531	61	2	109	4,192±6309 (∑5 PAHs)	Odabasi et al. 2010

ND not detected

[a] The concentrations of heavy metals and PAHs are given as means, minimum, and maximum in brackets

potential pollution source would result in emission of unburnt coal particles containing As in the process of coal mining, storage, and transportation. The heavy metal concentrations were relatively lower at coke power site; however, compared to the background, the enrichment of Pb was obvious ($P<0.05$).The enrichment of heavy metal in soil was also observed at several coal-based electricity production sites where heavy metals are released into the atmosphere during the combustion of fossil fuels, as well as from high temperature industrial processes and ultimately accumulate in the surface soil (Cheng 2003; Petaloti et al. 2006; Shukurov et al. 2009). Therefore, the combustion for power generation can be interpreted as main heavy metal source at coke power site.

The ∑16 PAHs concentrations at industrial sites ranged from 215 μg/kg (smelting site) to 32,474 μg/kg (coke power site). Soils collected from the coke power and coal mining sites showed higher ∑16 PAHs concentrations than those from smelting site ($P<0.05$). This is in accordance with previous findings that coal combustion for power generation and coal mining activities are likely the main sources of PAHs (Musa et al. 2010). The contribution of the two- and three-ring PAHs to ∑16 PAHs were <50 % (9.6–46.2 %) at coke power site, whereas they were >50 % at smelting (50.8–86.9 %) and coal mining sites (50.8–79.8 %) (Fig. 2). The mixtures of ∑16 PAHs in soil were dominated by fluoranthene (13.8–23.2 %) and pyrene (9.3–16.8 %) at coke power site. The predominant PAH species were naphthalene (12.1–28.1 %), acenaphthene (8.0–26.7 %), and phenanthrene (7.8–18.8 %) at smelting site, and phenanthrene (12.5–36.5 %) and acenaphthene (9.2–38.2 %) at coal mining site. It is suggested that higher molecular weight PAHs are deposited near coal combustion emission sources for power generation as a consequence of lower vapor pressure (Bakker et al. 2000). The local Bituminous coal dust with distinct low molecular weight aromatic

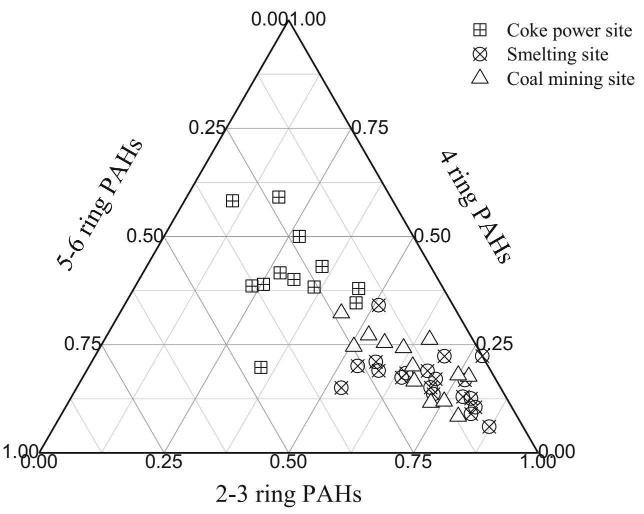


Fig. 2 Comparison of PAH compositions in soil samples from three industrial sites

compounds emanating from the coal mining activities would contribute to higher contents of two- and three-ring PAHs in coal mining site.

Heavy metal in plant

Eighteen plant species from 16 families were found in the studied area (Table 2). These plant species are perennials belonging to herb, shrub, and tree. The ferns of *Pteris vitatta*, *Pteris cretica*, and *Cyclosorus parasiticus*, and the grass of *Boehmeria nivea* dominate the sampling areas at three industrial sites. Non-endemic tree species of *Cunninghamia lanceolata*, and *Broussonetia papyrifera* are able to grow on coke power and coal mining sites. However, they all show a leafy crown and thick trunks with clear signs of poor growth.

Heavy metal contents in aerial part of plant samples showed significant differences among industrial sites except As ($P<0.01$) (Table 2). Chaney (1989) reported that heavy metal concentrations in plant growing on uncontaminated sites were generally in the range of 0.01–1.0 mg/kg for As, 0.05–0.2 mg/kg for Cd, 0.1–10 mg/kg for Pb, 27–150 mg/kg for Zn, and 5.0–30 mg/kg for Cu, respectively. A comparison of these known background values with determined metal levels in plant samples of industrial sites indicates that plant samples collected from the coke power and coal mining sites had the normal concentrations for Cd, Cu, Pb, and Zn, while As (0.89–381 mg/kg) was relatively higher in current study. Plants collected from the smelting site were characterized by high levels of As, Cd, Cu, Pb, and Zn with the maximum concentrations reaching 1,276, 34.8, 1,187, 4,430, and 6,565 mg/kg, respectively. Analytical results for comparing heavy metal composition of both plant and corresponding soil samples of three industrial sites are given in Fig. 3. It was shown that the order of metal concentration in plant samples followed a similar pattern to that in soil samples, reflecting the accumulative indication potential of these wild plants, which was also reported in the corresponding studies (Guo et al. 2009; Franco-Hernández et al. 2010). However, no significant correlation between plant and soil heavy metal content was found ($P>0.05$).

Plant As content varied between species, but independently of the soil As concentration, the species *P. vitatta* had the highest capacity to accumulate As with the maximum content of 1,276 mg/kg in shoots. Furthermore, high As accumulation levels were also measured in *P. cretica*, *B. nivea*, and *Selaginella davidii*, with their shoots As concentrations up to 216, 360, and 169 mg/kg, respectively. Regarding the plant accumulation of Cd, *Equisetum hyemale* and *P. vitatta* had significantly higher concentrations with the values of 34.8 and 14.0 mg/kg, respectively. Efficient accumulation of Cu was found in *Miscanthus floridulu* (1,187 mg/kg), *E. hyemale* (265 mg/kg), *Polygonum pubescens* (113 mg/kg), and *P. vitatta* (107 mg/kg). Specially, it is worth noting that Cu concentration in aerial part of *M. floridulu* reached the criterion for considering a hyperaccumulator plant (1,000 mg/kg) (Brooks et al. 1998). Considerable amounts of Zn and Pb were accumulated in more species, exactly in plant species from the smelting industrial site, where maximum of Pb (4,430 mg/kg) and Zn (6,565 mg/kg) were found concurrently in *E. hyemale*. The calculated bioconcentration factor (BCFs), defined as the concentration ratio of heavy metal in plant aerial part to that in soil, demonstrated that most of the collected plants behaved as endurant excluder with low BCFs (≤1), except that *P. vitatta* (1.61–6.53), *P. cretica* (1.27–4.60), and *B. nivea* (1.99–4.59) had relatively high BCFs for As, and *B. nivea* had high BCFs for Pb (2.07–3.10).

The excellent As-accumulating ability of *P. vitatta*, *P. cretica*, and *B. nivea*, and Pb-accumulating ability of *B. nivea* have been well recognized (Wei and Chen 2002; Zhao et al. 2002; Yang et al. 2010), which was also demonstrated in the present study. Although soil with high level of combined pollution would restrict the plant accumulation ability, it seemed that several plant species possess a certain degree of constitutional metal tolerance and accumulating potential for various heavy metals. For instance, *P. vitatta* was able to accumulate considerable amounts of heavy metals such as As, Cd, Cu, Pb, and Zn. *B. nivea* was efficient in accumulating As, Pb, and Zn; *P. cretica* for As and Pb; and *M. floridulu* for Cu, Pb, and Zn.

PAHs in plant

It is generally believed that the uptake of PAHs by plant is primarily from atmosphere through gas and particle-bound depositions (Slaski et al. 2000).

Thus, ∑16 PAHs concentrations in plant aerial part samples are shown in Table 2. The aerial part of wild plants showed similar PAHs spacial distribution pattern to soil, recurring in high ∑16 PAHs amount in plant samples of the coke power and coal mining sites relative to those of smelting site. Furthermore, there was a significant variation of PAHs profiles in plant samples of three sites (Fig. 4). The levels of four-, five-, and six-ring PAHs in plant samples were much higher at coke power site (50.4–72.0 %), whereas two- and three-ring PAHs were much higher at smelting (50.4–97.0 %) and coal mining (68.6–89.1 %) sites, which was consistent with PAHs distribution in soil samples. However, no significant correlation between plant and soil ∑16 PAHs content was found ($P>0.05$). Furthermore, the PAH profiles were not much similar for the plant and soil samples. The concentrations of two- and three-ring PAHs were relatively higher, and four- and six-ring PAHs were lower in plant samples than those of soils. The phenomenon has also previously been described by Bakker et al. (2000) and Sojinua et al. (2010), who proposed that this could be attributed to wind drift and wash-off of the high molecular compounds from the leaves or the low absorptivity of these classes of compounds.

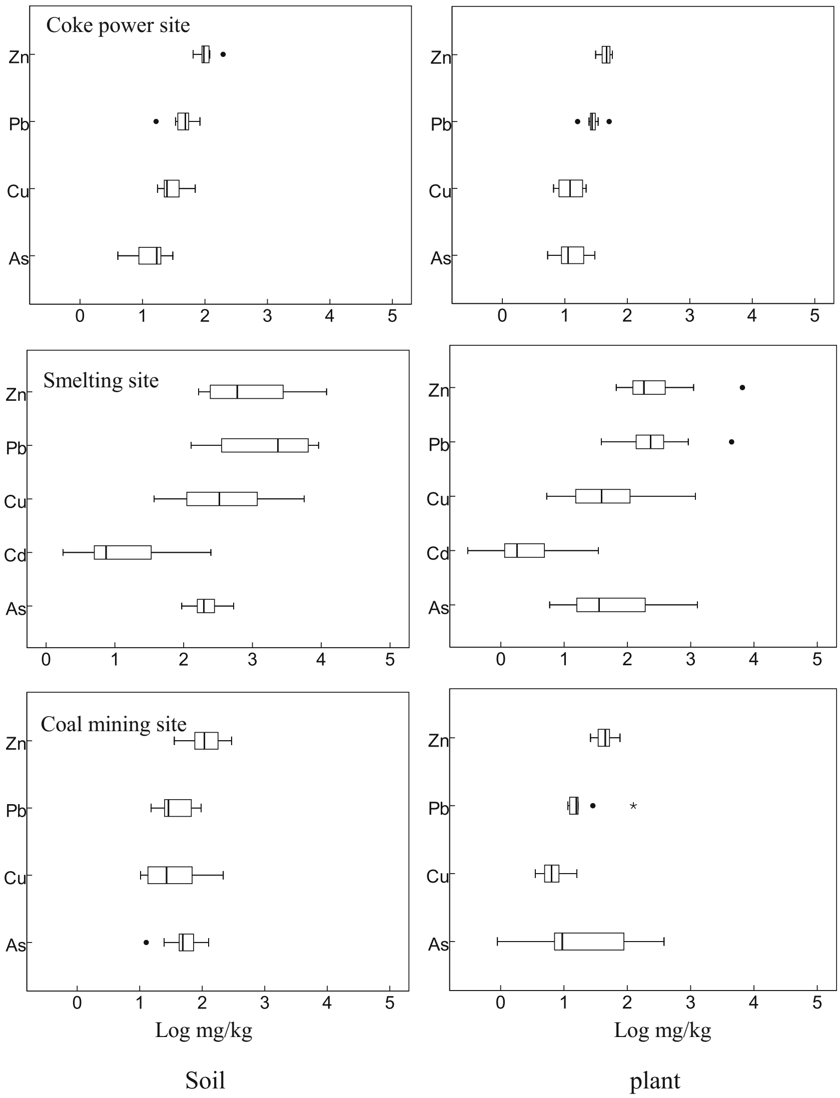
Table 2 Concentrations of heavy metal (mg/kg) and ∑16 PAHs (μg/kg) in plant and corresponding soil samples of three industrial sites

Family/taxa	Site[a]	As		Cd		Cu		Pb		Zn		∑16 PAHs	
		Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil
Pteridaceae													
Pteris vittata L.	1	30.3	10.8	ND	ND	7.3	17.4	34.1	33.8	54.8	64.5	1,488	1,269
	2	1,276	195.4	14	43.8	107	713.3	914	9,140	1,112	3,177	706	1,052
	3	381	126.6	ND	ND	5.5	68.9	16.7	66.8	29.4	294	1,223	1,120
Pteris cretica L.	1	21.7	7.1	ND	ND	6.6	20.6	27.1	54.2	50.7	90.5	1,216	1,097
	2	216	104.3	6.6	3	11.9	37.2	241	227.4	96.2	218.6	915	486
	3	113	24.6	ND	ND	7.4	24.8	16.5	25	46.5	98.9	1,065	849
Urticaceae													
Boehmeria nivea (L.) Gaud	1	18.5	4	ND	ND	21.9	70	51.2	16.5	57.6	112.9	2,136	871
	2	360	169	1.1	4.8	72.2	144.4	259	128.2	262	164.8	687	872
	3	88.4	44.4	ND	ND	16	76.2	125	60.4	76.9	178.8	1,149	1,630
Thelypteridaceae													
Cyclosorus parasiticus (L.) Farwell	1	5.3	19.6	ND	ND	8.9	24.7	24.4	55.5	42.2	95.9	444	1,330
	2	44.1	93.8	1.2	1.8	36.8	85.6	46.9	360.8	66.5	302.3	180	751
	3	7.1	64.4	ND	ND	4.3	217	13.8	76.7	26.3	202.3	414	1,035
Gramineae													
Stipa bungeana Trin.	1	11	30.6	ND	ND	20.1	37.9	27.6	48.4	46.6	119.5	651	1,094
	2	44	531.6	2.1	6.6	31.7	288.2	226	594.7	167	265.1	980	447
Miscanthus floridulu (Labnll.) Warb	2	18	225	1.3	26	1,187	1,935	538	5,978	553	3,456	795	1,163
Taxodiaceae													
Cunninghamia lanceolata (Lamb.) Hook	1	7.1	19.7	ND	ND	12.1	24.2	16.0	40	31.1	88.9	608	2,083
Blechnaceae													
Brainia insignis (Hook.) J. Sm	1	11.3	16.9	ND	ND	18.4	39.1	27.4	83	37.1	195.3	556	5,634
Valerianaceae													
Patrinia villosa (Thunb.) Juss.	2	29	370.6	3.6	21.2	13.1	145.6	221	3,157	155	1,192	356	631
Polygonaceae													
Polygonum pubescens Blume	2	9.7	194	1.9	5.3	113	5,650	89.9	4,495	283	2,021	664	967
Selaginellaceae													
Selaginella davidii Franch.	2	169	211.3	1.7	7.4	41.4	376.4	244	1,743	193	224.4	226	686
Moraceae													
Broussonetia papyrifera (L.) Vent	2	5.9	196.7	0.3	7.5	5.3	75.7	38.7	351.8	67.6	270.4	307	477
	3	0.9	12.7	ND	ND	6.4	13.3	12.3	15.2	34.7	35.8	435	692
Equisetaceae													
Equisetum hyemale L.	2	25.1	147.6	34.8	248.6	265	3,786	4,430	7,383	6,565	11,936	285	845
Oleaceae													
Forsythia viridissima L.	2	14	350	0.9	45	17.8	445	210	7,100	172	2,457	554	876
Compositae													
Folium artemisise Argyi	3	9.3	48.7	ND	ND	8.3	26.9	28.6	28.9	60.8	108.6	983	884
Phytolaccaceae													
Phytolacca acinosa Roxb.	3	1	102	ND	ND	10.5	10.3	11.7	16.5	52.4	63.1	653	982
Plantaginaceae													
Plantago asiatica L.	3	21.8	72.7	ND	ND	5.0	38.1	11.5	95.8	45	118.4	1,205	1,432
Athyriaceae													
Athyrium dissitifolium (Bak.) C. Chr.	3	9.4	42.8	ND	ND	3.5	13.5	15.7	27.5	41.1	76.1	541	790

ND not detected

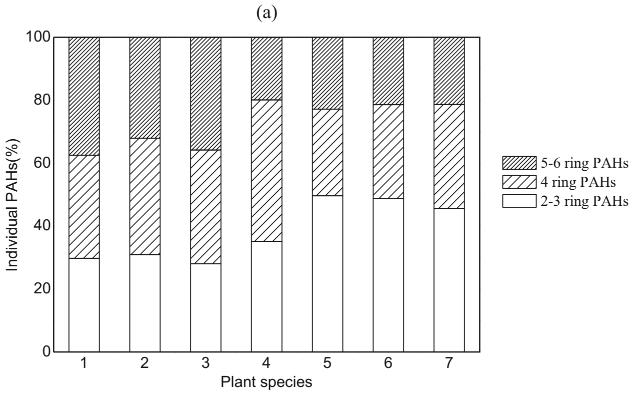
[a] Industrial sites: 1, coke power site; 2, smelting site; 3, coal mining site

Fig. 3 Box plot of log transformation value of heavy metal in plant and corresponding soil samples at three industrial sites. The *whiskers from the upper and lower edge of the box* define the range of all the data; the *central line inside the box* represents the median; data outliers are marked by *circles* (N1.5×hinge spread) and extreme outliers by stars (N3×hinge spread)

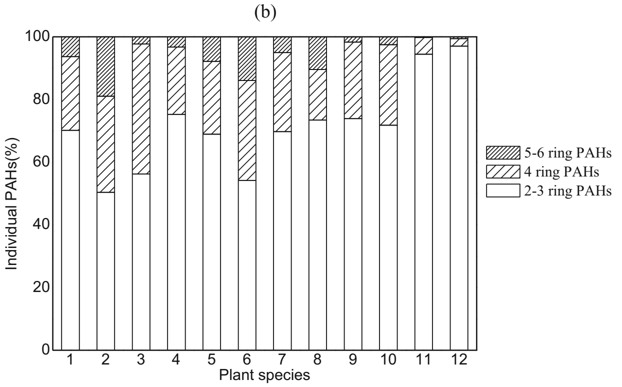


The species *B. nivea*, *P. vitatta*, and *P. cretica* with rough or hairy leaf surfaces, larger exposed foliage surface area, or the presence of trichome were more efficient in accumulating and retaining high-molecular PAHs. *S. bungeana* and *M. floridulu* with the characteristics of thin layer of cutile or smooth and sharp leaf were observed to have higher concentrations of low-molecular PAHs (Table 2). *B. nivea* showed the strongest accumulation of PAHs with the value of 2,136 μg/kg at coke power site, especially four-, five-, and six-ring PAHs (71.9 %). Researchers defined that plants with hairy foliage would be more efficient in accumulating PAHs especially the high molecular weight PAHs than the hairless foliage (Howsam et al. 2000; Mikefryer and Agrosso 2006). Consequently, the rough leaf surface and the large leaf area might contribute to the high PAHs accumulation in *B. nivea*. Brighigna et al. (2002) and Pereira et al. (2007) demonstrated that the trichomes, which increase the plant–air interfaces, play an important role in retaining the particles such as the particle-bound PAHs. It is well known that *P. vitatta* and *P. cretica* are abundant of trichomes (Xie et al. 2009), which could be one reason for the excellent capacity of the two ferns in accumulating PAHs. Mclachlan et al. (1995) and Sojinua et al. (2010) considered that the plant species belonging to Gramineae with the characteristics of succulent, porous stems or smooth and sharp leaf were potential accumulating material for low molecular PAHs, which was also observed in the current study that the concentrations of PAHs were relatively higher in *S. bungeana* (980 μg/kg) and *M. floridulu* (795 μg/kg) at smelting site.

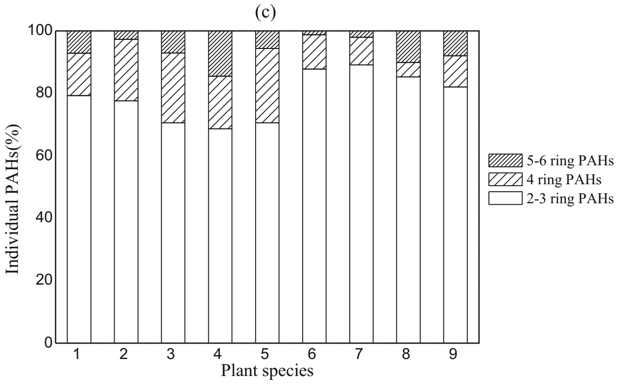
Plants can reduce the amount of PAHs by gaseous diffusion and intercepting particles on their leaf and bark surfaces. Simonich and Hites (1995) remarked that, on average, 40 % of emitted PAHs were removed by plants with higher PAH burdens in areas adjacent to local sources. Sojinua et al. (2010) also demonstrated the bioconcentration potentials of plant aerial parts for PAHs at polluted sites. In the present study, ∑16 PAHs concentrations in the species *B. nivea*, *P. vitatta*,



1 *P. vittata*; 2 *P. cretica*; 3 *B. nivea*; 4 *C. parasiticus*; 5 *S. bungeana*; 6 *C. lanceolata*; 7 *B. insignis*



1 *P. vittata*; 2 *P. cretica*; 3 *B. nivea*; 4 *C. parasiticus*; 5 *S. bungeana; 6 P. pubescens*; 7 *M. floridulu*; 8 *P. villosa*; 9 *S. davidii*; 10 *B. papyrifera*; 11 *E. hyemale*; 12 *F. viridissima*



1 *P. vittata*; 2 *P. cretica*; 3 *B. nivea*; 4 *C. parasiticus*; 5 *B. papyrifera*; 6 *F. artemisise*; 7 *P. acinosa*; 8 *P. asiatica*; 9 *A. dissitifolium*

Fig. 4 PAH profiles in plant samples collected from **a** coke power site, **b** smelting site, and **c** coal mining site

P. cretica, and *S. bungeana* were relatively higher than the values determined in the soils from the same location, indicating the bioaccumulation and phytoremediation potentials of these species under investigation.

Heavy metal and PAH combined accumulation

Table 3 Correlation coefficients between heavy metal elements and ∑16 PAHs of soil and plant at three industrial sites

Industrial sites		Soil ∑PAHs	Plant ∑PAHs
Coke power	As	0.535*	0.700*
	Cu	0.305	0.151
	Pb	0.718**	0.767*
	Zn	0.569*	0.750*
Coal mining	As	0.444	0.817*
	Cu	0.279	0.267
	Pb	0.760*	0.300
	Zn	0.623	0.317
Smelting	As	−0.126	0.210
	Cd	0.357	0.238
	Cu	0.692*	0.042
	Pb	0.608*	0.287
	Zn	0.608*	0.189

*$p<0.05$, **$p<0.01$

Correlation analysis was applied to investigate the relationship among heavy metal and ∑16 PAHs in soil and plant samples (Table 3). Generally, there was significant positive correlation between Pb and ∑16 PAHs concentrations ($P<0.05$) in soil samples regardless of industrial sites. In addition, ∑16 PAHs was positively correlated with As and Zn ($P<0.05$) at coke power site, while positively correlated with Cu and Zn ($P<0.05$) at smelting site. The significant positive correlations between ∑16 PAHs and various heavy metals produced from industrial emissions indicate the common source of PAHs and these metals in soil (Musa et al. 2010; Fabietti et al. 2010). Significant positive correlations among As, Pb, Zn, and ∑16 PAHs ($P<0.05$) in plant samples were evident at coke power site, which was in accordance with those in soil. At coal mining site, ∑16 PAHs closely positively related to the element of As. No significant correlation between ∑16 PAHs and heavy metals was observed for plants at smelting site.

PCA based on heavy metal and ∑16 PAH concentrations in plant samples was employed for the plant accumulation characteristics evaluation. For coke power and coal mining sites, two factors explaining 92.5 and 87.4 % of the total variance were extracted, respectively. Three components were extracted covering 90.9 % of the data variance for smelting site. The results obtained further showed a positive association among the contents of As, Pb, Zn, and ∑16 PAHs in plants samples at coke power site. The contents of ∑16 PAHs in plants were associated with Cu at smelting site while they were positively correlated with As at coal mining site (Table 4).

The scatter plot of the component scores of plant species is depicted in Fig. 5. At coke power site, the PC1-positive loadings for *P. vitatta*, *P. cretica*, and *B. nivea* indicated main accumulation of As, Pb, Zn, and ∑16 PAHs, with average contents of As, Pb, Zn, and ∑16 PAHs relatively higher than other species. At coal mining site, the distribution in PC2 showed that *P. vitatta*, *P. cretica*, *B. nivea*, and *P. asiatica*

Table 4 Principal component analysis factors and loadings for heavy metal and ∑16 PAHs contents in plant samples at three industrial sites

Variables	Coke power		Smelting			Coal mining	
	PC1	PC2	PC1	PC2	PC3	PC1	PC2
As	0.85			0.92			0.94
Cu		0.98			0.89	0.94	
Pb	0.86		0.99			0.90	
Zn	0.95		0.99			0.96	
Cd			0.98				
PAHs	0.95				0.62		0.83
Eigenvalues	3.3	1.3	3.0	1.3	1.1	1.9	1.5
%Var.acum.	66.1	92.5	50.6	71.9	90.9	57.5	87.4

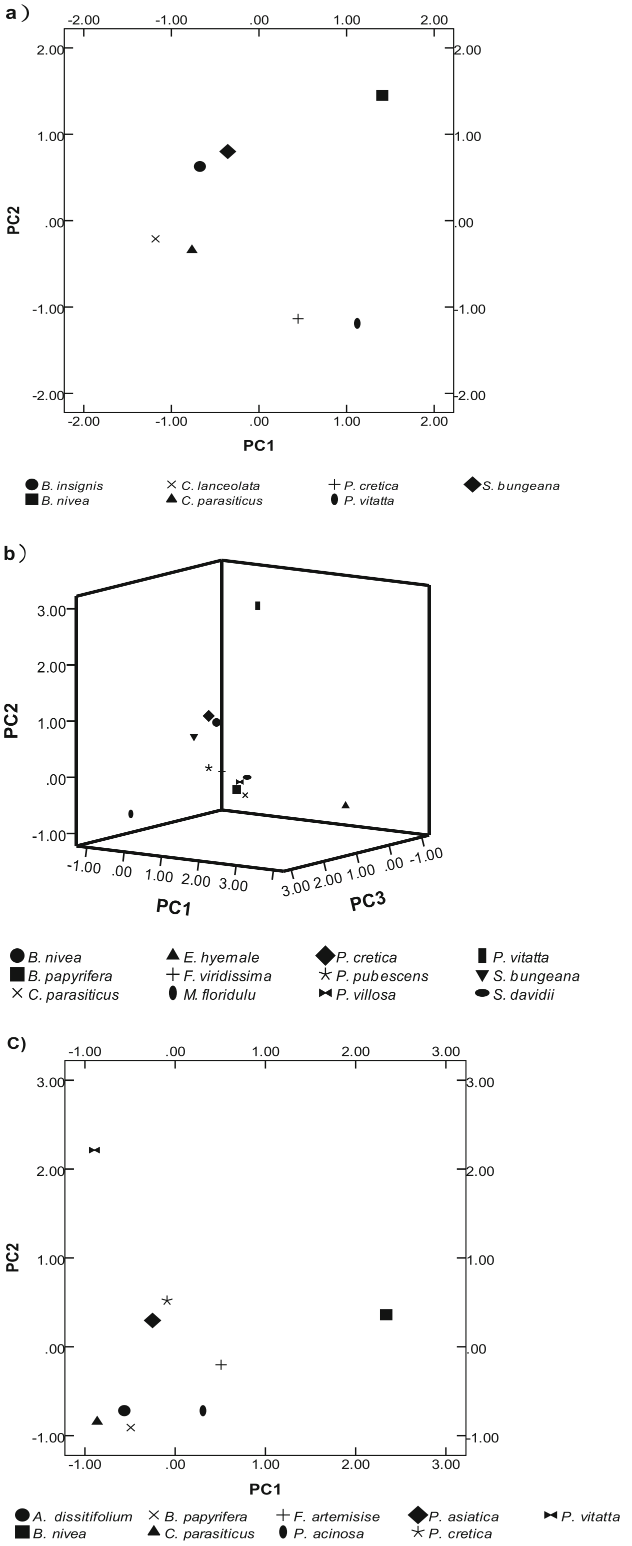


Fig. 5 Biplots of principal components based on heavy metal and ∑16 PAHs concentrations in plant species at **a** coke power site, **b** smelting site, and **c** coal mining site

accumulated statistically higher As and PAHs. In particular, *B. nivea* was characterized as high accumulation for As, Pb, Cu, Zn, and ∑16 PAHs as all the data were in the positive PC sectors both at coke power and coal mining sites. At smelting site, *M. floridulu* showed high positive loading in PC3 indicative of the high accumulation for Cu and PAHs. *P. cretica* and *S. bungeana* showed accumulation of As, Cu, and PAHs due to the positive loading in PC2 and PC3. *P. vitatta* was characterized as accumulator for As, Cd, Pb, and Zn with positive loading in PC1 and PC2.

Based on the results obtained from PCA, together with heavy metal and PAHs contents in plant samples, the accumulation potential of plant species was compared. Generally, the species of *P. vitatta*, *P. cretica*, and *B. nivea* with significantly higher contents of As and PAHs wherever these species were located showed excellent As accumulating capacity and positive potential for PAHs uptake. In addition, *P. vitatta* was capable of simultaneously accumulating high levels of As, Pb, Zn, and PAHs. The species *B. nivea* was characterized by high accumulation ability for Pb, As, and PAHs. *M. floridulu* showed the maximum and significant Cu accumulation and a relative accumulation capacity for PAHs. It is well recognized that the promising plant material for phytoremediation would be characterized by the applicability to extensive geographical areas in abundant communities, the resistance to combined pollution, and great phytoaccumulating potential for contaminants (Jørgensen et al. 2005). The species *P. vitatta*, *P. cretica*, *B. nivea*, and *M. floridulu* are generally identified as growing widely and colonizing contaminated sites in South Central China. The applications of these plant species for phytoremediation of heavy metal contamination have also been documented (Wei and Chen 2002; Yang et al. 2010). Recently, a variable of researches have demonstrated that, even at low doze, the combination of heavy metal and PAHs could strongly cause oxidative stress and cellular organelle deformation in plant, resulting in the suppression of heavy metal uptake (Maier et al. 2002; Li et al. 2010). In the present study, it seemed that, at the levels of heavy metal and PAHs determined in plant species, these indigenous species were tolerant to high heavy metal and PAH co-exposure with good growth conditions and showed high accumulation potential for various heavy metals and PAHs and, therefore, would serve as good phytoremediators for heavy metal and PAH combined pollution.

Conclusion

The present study clearly demonstrates that endemic plant species growing at the industrial sites can colonize and survive in soils with multiple heavy metals and PAHs. Although spatial distributions of the heavy metal and PAHs varied greatly among industrial sites, it is possible to conclude that the species *P. vitatta*, *P. cretica*, *B. nivea*, and *M. floridulu* have potential in co-exposure tolerating and accumulating heavy metals and PAHs. Based on the examination of plant species for possible application of phytoremediation technologies, the plant strategy indicated that *P. vitatta* and *P. cretica* would be the promising remediation material for As and PAH combined pollution. *B. nivea* would be a candidate for Pb, As, and PAH combined pollution remediation while *M. floridulu* for Cu and PAH combined pollution remediation. It should also be noted that plants usually have significant metabolic activities in the rhizosphere for degrading PAHs. Thus, field-scale studies of heavy metal and PAH removal efficiency in soil should also be undertaken to further evaluate the phytoremediation capability of these plant species.

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