Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies

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Abstract

The concentration, distribution, profile and possible source of polycyclic aromatic hydrocarbons (PAHs) in soil were studied in Guiyu, an electronic waste (E-waste) recycling center, using primitive technologies in Southeast China. Sixteen USEPA priority PAHs were analyzed in 49 soil samples (0–10 cm layer) in terms of individual and total concentrations, together with soil organic matter (SOM) concentrations. The concentrations of a sum of 16 PAHs ranged from 44.8 to 3206 $\mu g\,kg^{-1}$ (dry weight basis), in the descending order of E-waste open burning sites (2065 $\mu g\,kg^{-1}$) > areas near burning sites (851 $\mu g\,kg^{-1}$) > rice fields (354 $\mu g\,kg^{-1}$) > reservoir areas (125 $\mu g\,kg^{-1}$). The dominant PAHs were naphthalene, phenanthrene and fluoranthene, which were mainly derived from incomplete combustion of E-waste (e.g. wire insulations and PVC materials), and partly from coal combustion and motorcycle exhausts. All individual and total PAH concentrations were significantly correlated with SOM except for naphthalene and acenaphthylene. Principal component analysis was performed, which indicated that PAHs were mainly distributed into three groups in accordance with their ring numbers and biological and anthropogenic source. In conclusion, PAH concentrations in the Guiyu soil were affected by the primitive E-waste recycling activities.
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1. Introduction

With the rapid growth of the electronic industry, a large quantity of electronic products becomes obsolete each year. Electronic waste (E-waste), including the end of life computers, printers, photocopy machines, televisions (TV) and mobile phones, becomes the most rapidly growing waste problem in the world (Halluite et al., 2005). E-waste contains many toxic materials, such as heavy metals, PCBs, and brominated flame retardants, and creates serious pollution during recycling and disposing. It is estimated between 1997 and 2007, 500 million computers will become obsolete in the United States (Silicon Valley Toxics Coalition, 2001). Between 50% and 80% of the E-wastes collected for recycling in the western US are being exported to Asia, and 90% of that are destined for China, because of cheaper labor in China (The Basel Action Network, 2002). The US is the only developed country in the world that has not ratified the UN Basel Convention, which bans the export of hazardous wastes to developing countries.

Guiyu, a blooming E-waste processing center since 1995, is such a destination of E-waste imported from the US and Japan, where thousands of farmers without protective equipments are now engaged in primitive and highly polluting E-waste recycling operations: piles of wires are burnt

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in the open air near rice fields or riversides to recover metals; circuit boards are melted over coal grills to release valuable chips; residual useless plastics are either burnt or dumped in the rice fields, irrigation canals and along waterways. These extremely hazardous and dangerous E-waste "recycling" operations render the air, water and soil of Guiyu heavily polluted, which also poses a threat to the health of workers and local residents.

Guiyu's ground water is now so polluted that drinking water has to be trucked in from 30 km distance. A preliminary investigation of The Basel Action Network (2002) found that a water sample collected from the river near E-waste open burning sites contained 1.9 mg l^{-1} lead (Pb), which is 190 times over the World Health Authority Organization (WHO) Pb threshold. A survey among 165 children aged between one and six at four Guiyu kindergartens found that 82% of the Guiyu children had blood Pb levels of more than 100 μg l^{-1}, which will affect young children's IQ and the development of their central nervous systems (Peng et al., 2005). A report by the Shantou Medical University Hospital found a high incidence of skin damage, headaches, vertigo, nausea, chronic gastritis, and gastric and duodenal ulcers in the population of the Guiyu area (Qiu et al., 2004).

However, up to now, there are no systematic studies about pollution of the Guiyu soil, air and water caused by primitive E-waste recycling, especially for those persistent toxic substances (PTS), such as PAHs, PCBs, PBDEs, dioxins and furans, which may be released from the open burning of PVC and plastic waste.

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds composed of fused aromatic rings. Some high molecular weight (greater than four fused rings, HMW) PAHs are considered to be carcinogenic, mutagenic and teratogenic even at low concentrations (IARC, 1983). Because of their hydrophobic nature and low solubility, PAHs are resistant to biodegradation and can bioaccumulate in the environment through the food chain. Therefore, PAHs in the environment represent a long-term threat to human health and have received more and more environmental concern. In China, extensive investigations on PAH concentration and distribution in the atmosphere (Lee et al., 2001), water (Zhou and Maskaoui, 2003), sediment (Wu et al., 2003), soil (Tao et al., 2004) and dust (Wu et al., 2005) have been carried out. Most PAHs are released from anthropogenic sources, such as wastewater irrigation (Wang et al., 2004), vehicle exhausts (Chen et al., 2005; Ma et al., 2005), hydrocarbon spillage (Ou et al., 2004), residential coal combustion (Chen et al., 2004a), use of organic waste as compost and fertilizer (Smith et al., 2001), industrial activities including coke ovens, gasworks, petroleum refineries, wood conservation plants, power plants and blast furnaces (Van Brummelen et al., 1996; Stalikas et al., 1997).

The major objective of the present study is to investigate the distribution, concentration, profile and source of PAHs in the Guiyu soil affected by E-waste recycling.

2. Materials and methods

2.1. Sampling site description

Guiyu town is located in the Chaoyang District, Shantou City, Guangdong, Southeast China, with a total area of 52 km^2 and a population of 150 000. It is a rice-growing countryside and its industry has been dominated by E-waste recycling since the early 1990s. Eighty percent of families in Guiyu are engaged with individual recycling workshops, with nearly 10 000 migrant laborers being employed. There are at least three large scale E-waste open burning sites distributed in the rice fields and riversides, which are still in operation daily.

Guiyu soils are Ferric Acrisols according to the Soil Map of the People's Republic of China (Revised Version, 1990, base on the FAO/Unesco Soil Map of the Word). Guiyu belongs to the sub-tropical climate, with an annual average temperature of 21.5 °C, relative humidity of 80% and a mean annual rainfall of 1721 mm. The prevailing wind is from north–east except in summer with a southwesterly direction. In the northern area of Guiyu, there is a reservoir and a large area of woodland distributed in the hills.

2.2. Sampling

A total of 49 soil samples (0–10 cm soil layer) were collected from different locations throughout the Guiyu area between June and December, 2004. According to the location (Fig. 1), the samples can be divided into four groups: reservoir (RS) areas, rice fields (RF), areas near open burning sites (NOBS, within 500 m of the E-waste open burning site) and at the open burning site (OBS).

About 500 g of each soil sample was collected with a stainless steel scoop. Each sample was the mixture of five soil samples collected at the four corners and the center in an area of about 10×10 m^2. Samples were packed with aluminium foil and placed in polyethylene bags (Ziploc®) and transported to the laboratory. They were then air dried at room temperature (Belkessam et al., 2005), sieved through a 2 mm sieve and stored at 4 °C before analysis.

2.3. Sample extraction and analysis

Samples (5 g) of air dried soil were extracted for 18 h with acetone and dichloromethane (*v:v* 1:1, 80 ml) in a Soxhlet apparatus according to the EPA Standard Method 3540C (USEPA, 1996a). Florisil column clean-up was used for purification of the concentrated extract (EPA Standard Method 3620B) (USEPA, 1996b). The eluant was evaporated to less than 2 ml prior to analysis. Deuterated PAHs (acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were used as internal standards for quantitation. The standard curve was obtained by using 20, 50, 100, 500, 1000, 2000 ng ml^{-1} PAH standards. The response curves for the 16 PAHs were linear and the correlation coefficients were higher than 0.99.
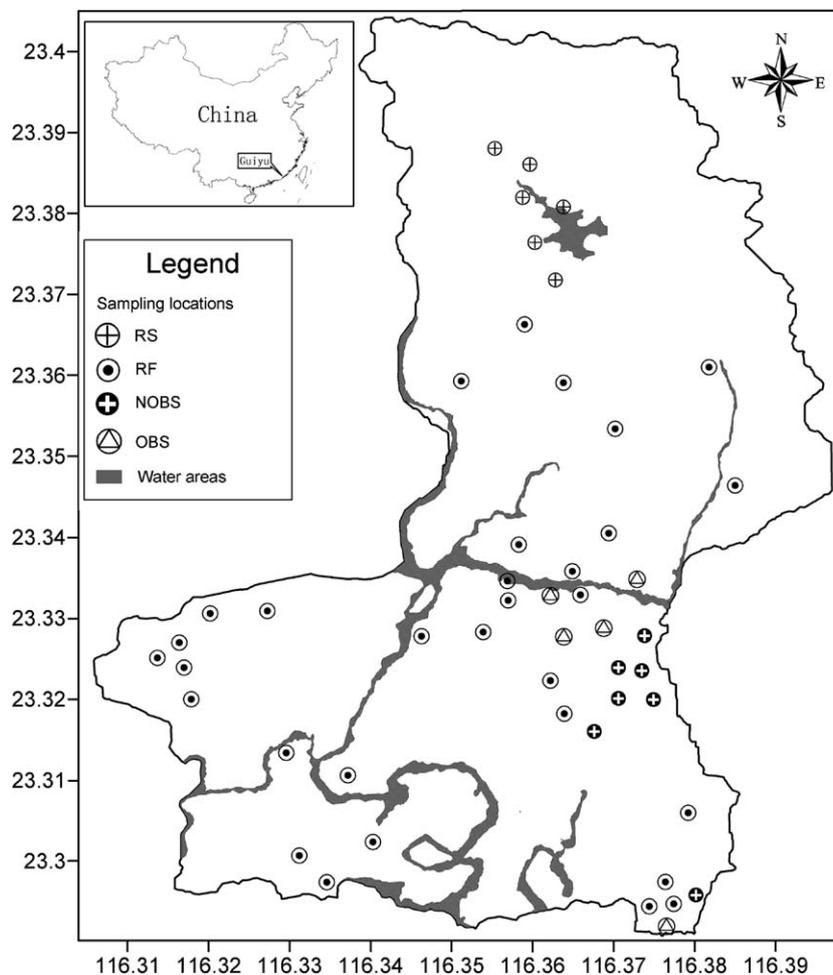
Fig. 1. The map of the soil sampling sites in Guiyu. RS, reservoir area; RF, rice field; NOBS, area near the open burning site; and OBS, at the open burning site.

GC-MS analysis was performed on a Hewlett Packard 6890 GC system equipped with a mass selective detector and a $30 \, \text{m} \times 0.25 \, \text{mm} \times 0.25 \, \mu\text{m}$ DB-5 capillary column (J & W Scientific Co. Ltd., USA). The EPA Standard Method 8270C (USEPA, 1996c) was used to determine the following 16 PAHs: naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ane), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz(*a*)anthracene (BaA), chrysene (Chr), benzo(*a*)pyrene (BaP), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), indeno(1,2,3-*cd*)pyrene (IcdP), dibenz(*a,h*)anthracene (DahA) and benzo(*g,h,i*)perylene (BghiP). The peaks of BbF and BkF were extremely close to each other and difficult to be distinguished; therefore, these two compounds were combined as one, namely, BbkF.

The dry weight of the soil was determined by drying subsamples (about 5.0000 g) at 105 °C overnight and the soil organic matter (SOM) was determined by a loss on ignition at 450 °C until a constant weight was achieved (Howsam et al., 2000).

Statistical analyses, including variance analysis, Pearson correlation and principal component analysis (PCA), were carried out with SPSS 11.0 for windows. Variance analysis ($p < 0.05$) of total PAH concentrations among four sampling sites was performed using a one-way ANOVA test (Tukey HSD). The means of LMW PAHs (low molecular weight PAHs, 2–3-ring PAHs) and HMW PAHs were compared using paired-sample *T*-Test. The contour map based on distribution and concentration of PAH was constructed using a Surfer 7.0 (Golden software, CO., USA).

2.4. Quality control

Using the certified reference material (CRM104-100, bought from Resource Technology Corporation, US) as a reference, it was observed that the recoveries of individual PAHs ranged from 83% for Nap to 114% for BghiP. The concentrations of PAHs were not corrected for the recovery ratios for the CRM. Solvent blanks and duplicate samples were also analyzed. The variation coefficient of PAH concentrations between duplicate samples was less than 10%. The limit of detection (LOD) defined as the standard deviation from the mean blank ($n = 3$) ranged from 5 to 9 $\mu\text{g} \, \text{kg}^{-1}$.

3. Results

3.1. Distribution and concentration of PAHs in the Guiyu soil

The concentrations of PAHs in the Guiyu soil are listed in Table 1. The total 16 PAH concentrations ranged from 44.8 µg kg^{-1} at the reservoir area to 3206 µg kg^{-1} at the E-waste open burning site. Fig. 2 shows the spatial distribution map of the total concentrations of PAHs in Guiyu soil. In general, the open burning site and its surrounding area had high levels of PAHs (higher than 1000 µg kg^{-1}), while in the northern area near the reservoir and woodlands, concentrations were lower than 200 µg kg^{-1}. The mean concentrations of PAHs in the four sampling areas are listed in Table 2. Total concentrations increased sharply

Table 1
Concentrations of individual and total PAHs in Guiyu soil (µg kg^{-1}, dry weight basis, $n = 49$)

| PAH	Mean ± Standard deviation	Median	Minimum	Maximum
Naphthalene (Nap)	156 ± 309	47.5	5.0	1498
Acenaphthylene (Any)	3.4 ± 7.1	1.4	ND	42.4
Acenaphthene (Ane)	1.5 ± 3.0	0.8	ND	19.3
Fluorine (Fle)	16.7 ± 27.5	9.6	1.4	155
Phenanthrene (Phe)	127 ± 194	78.9	9.7	1176
Anthracene (Ant)	5.9 ± 10.3	2.5	ND	45.2
Fluoranthene (Fla)	68.5 ± 54.6	67.0	4.4	297
Pyrene (Pyr)	40.3 ± 33.3	35.8	3.9	203
Benz(a)anthracene (BaA)	14.4 ± 16.9	9.7	ND	93.6
Chrysene (Chr)	54.1 ± 66.4	40.6	2.0	385
Benzo($b + k$)fluoranthene (BbkF)	37.1 ± 30.8	33.1	ND	158
Benzo(a)pyrene (BaP)	7.2 ± 9.4	4.8	ND	49.5
Indeno(1,2,3-cd)pyrene (IcdP)	13.3 ± 14.0	10.3	ND	64.0
Dibenz(a,h)anthracene (DahA)	16.9 ± 45.4	5.5	ND	312
Benzo(g,h,i)perylene (BghiP)	19.1 ± 24.7	13.6	ND	122
Total PAH	582 ± 663	389	44.8	3206

ND: Not detected.
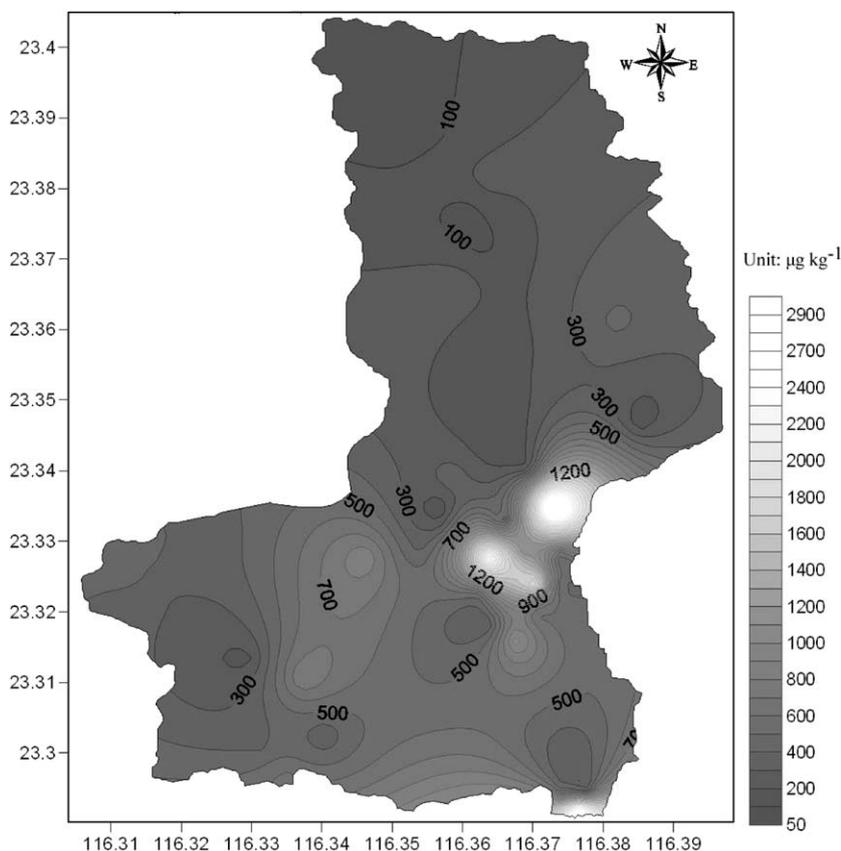
Fig. 2. Contour map of total concentrations of PAHs in the Guiyu soil.

Table 2
The mean concentrations of soil PAHs in different sampling areas ($\mu g\ kg^{-1}$)

PAHs	RS	RF	NOBS	OBS
Naphthalene (Nap)	87.6 ± 82.2	38.7 ± 15.0	349 ± 466	635 ± 534
Acenaphthylene (Any)	0.1 ± 0.2	1.5 ± 0.8	4.4 ± 6.0	16.6 ± 16.6
Acenaphthene (Ane)	0.5 ± 0.3	0.8 ± 0.3	1.6 ± 1.4	7.1 ± 7.5
Fluorine (Fle)	2.1 ± 0.6	8.8 ± 5.2	23.4 ± 12.7	71.7 ± 62.9
Phenanthrene (Phe)	15.4 ± 3.3	74.1 ± 53.4	137 ± 53.3	563 ± 388
Anthracene (Ant)	0.5 ± 0.4	2.6 ± 1.3	7.2 ± 7.8	30.2 ± 16.7
Fluoranthene (Fla)	6.5 ± 1.3	59.5 ± 24.1	92.0 ± 13.6	159 ± 117
Pyrene (Pyr)	6.3 ± 1.5	35.5 ± 18.2	53.3 ± 17.2	88.5 ± 72.2
Benz(*a*)anthracene (BaA)	0.9 ± 0.6	10.4 ± 8.0	17.8 ± 6.9	49.5 ± 30.5
Chrysene (Chr)	3.9 ± 1.8	38.1 ± 16.4	60.7 ± 11.9	200 ± 136
Benzo(*b* + *k*)fluoranthene (BbkF)	1.0 ± 0.9	35.7 ± 21.0	48.9 ± 17.0	70.3 ± 63.7
Benzo(*a*)pyrene (BaP)	ND	6.6 ± 8.2	7.8 ± 3.7	18.2 ± 18.2
Indeno(1,2,3-*cd*)pyrene (IcdP)	ND	13.8 ± 11.2	13.4 ± 8.7	26.2 ± 29.0
Dibenz(*a,h*)anthracene (DahA)	0.1 ± 0.3	9.4 ± 11.4	15.8 ± 10.0	83.9 ± 131
Benzo(*g,h,i*)perylene (BghiP)	ND	18.6 ± 15.1	18.8 ± 12.3	45.9 ± 63.0
Total PAHs	125 ± 76.3 c	354 ± 147 c	851 ± 472 b	2065 ± 1062 a
LMW PAHs	106 ± 79.5 A	127 ± 59.3 B	522 ± 469 A	1323 ± 604 A
HMW PAHs	18.7 ± 5.0 B	228 ± 115 A	329 ± 35.9 A	742 ± 607 A
Sample no.	6	30	8	5

RS, reservoir area; RF, rice field; NOBS, area near the open burning site; OBS, at the open burning site. LMW PAHs, low molecular weight PAHs (2–3-ring PAHs); and HMW PAHs, high molecular weight PAHs (4–6-ring PAHs). ND: Not detected. Values are means with standard deviations.
 Values of Total PAHs in the same row followed by the same small letter are not significantly ($p < 0.05$) different. Values of LMW PAHs and HMW PAHs in the same column followed by the same capital letter are not significantly ($p < 0.05$) different.

in the order of RS < RF < NOBS < OBS. In RS, NOBS and OBS, the sum concentration of LMW PAHs was higher than that of HMW PAHs, though the difference was not significant ($p > 0.05$) in NOBS and OBS due to the large standard deviations. But in RF, the LMW PAHs concentration was significantly ($p < 0.05$) lower than HMW PAHs.

3.2. Profile of PAH in Guiyu soil

Fig. 3 shows the PAH profiles (distribution patterns of 16 PAHs) in four sampling areas were similar, with Nap and Phe being the most abundant, while Any, Ane and Ant being the least abundant. Nap was dominant in the RS area, which accounted for 70% of the total PAHs, while Phe and Fla were dominated in RF, each accounting for 21% and 17% of the total PAHs, respectively. In NOBS and OBS, Nap, Phe, Fla and Chr were the most abundant, which accounted for 41%, 16%, 11% and 7% in NOBS, 32%, 27%, 8% and 10% in OBS, respectively.

3.3. Correlations among individual, total PAH and SOM concentrations

Soil organic matter (SOM) varied greatly among 49 soil samples ranging from 3.7% to 14.3% with a mean of 7.8%
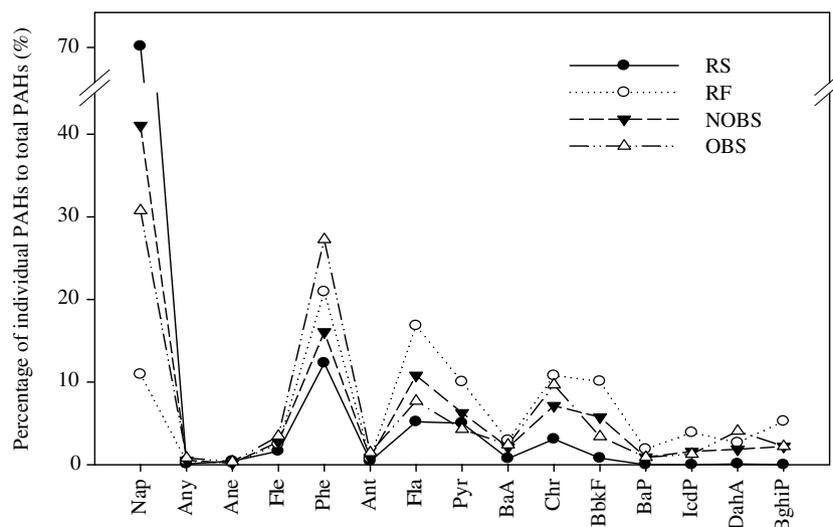

Fig. 3. Profiles of PAHs of the four sampling areas in the Guiyu soil. RS, reservoir area; RF, rice field; NOBS, area near the open burning site; and OBS, at the open burning site.

Table 3
Correlation coefficient matrix for PAHs and SOM concentrations in Guiyu soil ($n = 49$)

	Nap	Any	Ane	Fle	Phe	Ant	Fla	Pyr	BaA	Chr	BbkF	BaP	IcdP	DahA	BghiP	Total PAHs	LMW PAHs	HMW PAHs	SOM
Nap	1.000																		
Any	0.485**	1.000																	
Ane	0.243	0.534**	1.000																
Fle	0.309*	0.691**	0.944**	1.000															
Phe	0.385**	0.582**	0.926**	0.934**	1.000														
Ant	0.644**	0.827**	0.710**	0.777**	0.803**	1.000													
Fla	0.255	0.593**	0.800**	0.898**	0.862**	0.666**	1.000												
Pyr	0.262	0.728**	0.658**	0.808**	0.761**	0.687**	0.906**	1.000											
BaA	0.449**	0.512**	0.800**	0.795**	0.861**	0.819**	0.805**	0.716**	1.000										
Chr	0.423**	0.602**	0.891**	0.915**	0.949**	0.834**	0.899**	0.788**	0.940**	1.000									
BbkF	0.267	0.334*	0.598**	0.638**	0.632**	0.504**	0.790**	0.702**	0.803**	0.778**	1.000								
BaP	0.151	0.205	0.598**	0.537**	0.557**	0.384**	0.613**	0.512**	0.760**	0.671**	0.853**	1.000							
IcdP	0.092	0.364*	0.499**	0.556**	0.485**	0.365**	0.677**	0.692**	0.641**	0.644**	0.867**	0.813**	1.000						
DahA	0.173	0.220	0.884**	0.790**	0.830**	0.513**	0.724**	0.507**	0.783**	0.829**	0.745**	0.737**	0.564**	1.000					
BghiP	0.127	0.465**	0.651**	0.698**	0.608**	0.464**	0.750**	0.747**	0.669**	0.729**	0.865**	0.790**	0.962**	0.676**	1.000				
Total PAHs	0.745**	0.670**	0.771**	0.827**	0.876**	0.878**	0.793**	0.731**	0.871**	0.908**	0.701**	0.570**	0.530**	0.694**	0.616**	1.000			
LMW PAHs	0.894**	0.650**	0.626**	0.682**	0.757**	0.856**	0.605**	0.566**	0.736**	0.763**	0.497**	0.375**	0.307*	0.519**	0.394**	0.954**	1.000		
HMW PAHs	0.303*	0.549**	0.849**	0.890**	0.883**	0.709**	0.943**	0.854**	0.906**	0.953**	0.900**	0.785**	0.802**	0.843**	0.866**	0.845**	0.647**	1.000	
SOM	0.174	0.418**	0.928**	0.944**	0.938**	0.649**	0.824**	0.611**	0.796**	0.912**	0.672**	0.606**	0.414**	0.943**	0.604**	0.745**	0.563**	0.868**	1.000

LMW PAHs, low molecular weight PAHs (2–3-ring PAHs); HMW PAHs, high molecular weight PAHs (4–6-ring PAHs); SOM, soil organic matter.
* Significant at 0.05 level (2-tailed).
** Significant at 0.01 level (2-tailed).

(data not shown). The result of the correlation test among individual, total PAHs and SOM (Table 3) shows all individual PAHs were significantly correlated ($p < 0.01$) with LMW, HMW and total PAHs, and most individual PAHs in soils were significantly correlated ($p < 0.01$) with each other, except Nap and Any in some cases (some HMW PAHs). All individuals, LMW, HMW and total PAHs were significantly ($p < 0.01$) correlated with SOM except for Nap.

3.4. Principal component analyses (PCA)

The PCA results showed that 88.1% of the variance could be explained by three principal components. Principal component 1 explained 68.7% of the total variance, PC2 12.5%, and PC3 6.9%. The principal component plot (Fig. 4) shows three distinct groups according to the number of aromatic rings. The first group contained Ane, Fle, Phe, Fla, Pyr, BaA and Chr, which were 3- and 4-ring PAHs. The second group contained BbkF, BaP, IcdP, DaA and BghiP, which were 5- and 6-ring PAHs. The third group included Nap, Any and Ant, which were 2- and 3-ring PAHs.

4. Discussion

4.1. Distribution and concentration of PAH in the Guiyu soil

The average concentration of PAHs in the Guiyu soil ($582 \, \mu g \, kg^{-1}$) was much higher than the background concentration ($100 \, \mu g \, kg^{-1}$ dry weight) at remote or rural sites without anthropogenic activities (Trapido, 1999), and the endogenous concentration (1–$10 \, \mu g \, kg^{-1}$ for individual PAHs) resulting from biosynthesis and forest fires (Edwards, 1983). When compared with other cities in southeast China, such as Shantou ($317 \, \mu g \, kg^{-1}$, Hao et al., 2004), Guangzhou

($376 \, \mu g \, kg^{-1}$, Chen et al., 2005), Hong Kong ($55 \, \mu g \, kg^{-1}$, Zhang et al., 2006) and Hangzhou ($298 \, \mu g \, kg^{-1}$, Chen et al., 2004b), the average concentration of Guiyu soil was the highest. According to the criteria established by Maliszewska-Kordybach (1996), four classes of soil contamination were identified based on a total of 16 PAHs: non-contaminated soil ($<200 \, \mu g \, kg^{-1}$), weakly contaminated soil (200–$600 \, \mu g \, kg^{-1}$), contaminated soil (600–$1000 \, \mu g \, kg^{-1}$) and heavily contaminated soil ($>1000 \, \mu g \, kg^{-1}$). In general, Guiyu soil was weakly contaminated by PAHs.

However, the soils at OBS were heavily contaminated by PAHs. In OBS piles of plastic waste were combusted daily and resulted in heavy smoke. The remaining ash gave rise to the high concentration of PAHs in OBS soil, where the highest concentrations of all individual PAHs were detected. It is commonly observed that soil concentrations of PAHs were generally higher near emission sources, such as urban soils (Jones et al., 1989), road soils (Pathirana et al., 1994) and old gas works (Wilson and Jones, 1993). Similar results were also noted in the present study which indicated that the surrounding areas of the burning site were contaminated due to deposition of fly ash and emissions from E-waste open burning, and OBS was the point sources of pollution.

Although far away from the open burning site, RF soil still contained a high level ($354 \, \mu g \, kg^{-1}$), which exceeded the typical concentration (around $200 \, \mu g \, kg^{-1}$) of arable topsoil (Berset and Holzer, 1995). Contamination of agricultural soil was mostly due to the long-range atmospheric movement of PAHs from point sources of pollution to remote rural sites (Aamot et al., 1996). It was believed that the gaseous, fly ash and suspended particles containing PAHs generated from open burning may lead to the rather high levels of PAHs in rice fields through long-range transport and deposition. The traveling distance of PAHs decreases with increasing molecular weight (Yang et al., 1991; Meharg et al., 1998), and therefore gaseous PAHs
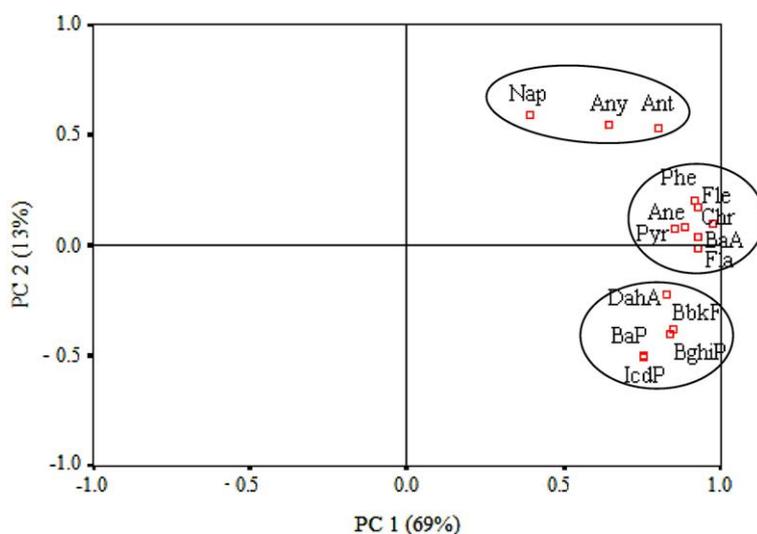

Fig. 4. Principal component analyses loading plot for individual components of PAHs.

such as Nap may be distributed over longer distances (Wilcke, 2000). This may partially explain why in RS Nap was 87.6 μg kg^{-1} (accounting for 70% of total PAHs), while some HMW PAHs were not detected. The gaseous Nap generated by open burning may affect the northern RS area, especially in summer when the prevailing wind is from the southwest. The biological source from woody plants (Wilcke et al., 2003) near the RS area would also serve as an additional Nap input.

Once deposited into soil, most PAHs will be absorbed by soil organic matter (Wilcke, 2000) and the strong sorption will inhibit PAH degradation and leaching (Beck et al., 1996). Therefore, the total concentration of PAHs was often strongly correlated with SOM or TOC (Total organic carbon) (Wilcke et al., 1999; Tang et al., 2005) except in some soils which were not heavily polluted (Jones et al., 1989; Zhang et al., 2006). In this study, significant correlations ($p < 0.01$) among SOM, individual (except Nap) and total PAHs were revealed. Jones et al. (1989) also observed significant correlations between TOC and all individual PAHs, with more significant correlations with HMW PAHs. Wilcke and Amelung (2000) interpreted this correlation as a result of the partitioning of PAHs from the atmosphere to SOM. Therefore, the correlation between concentrations of SOM and PAHs in the Guiyu soil confirmed that soil PAHs were mainly derived from point sources such as open burning through atmospheric transport and deposition. While the weak correlation between Nap and SOM may be due to its volatile characteristic and biological sources especially in RS area.

4.2. Profiles and sources of PAHs in the Guiyu soil

In general, very similar profiles were found in the four sampling areas, dominated by relatively volatile representatives: Nap (from 11% to 70% of total concentrations) and Phe (from 12% to 27%). Besides these, Fla, Chr, Pyr and BbkF were the most abundant compounds and the sum of these in RS, RF, NOBS and OBS accounted for 14%, 48%, 30% and 25% of the total concentrations, respectively. The sum of LMW was higher than that of HMW PAHs except for RF, as plowing may enhance the loss of LMW PAHs or dilute its concentration (Bierl et al., 1984), and rice leaves may also prevent a portion of atmospheric deposition to soil. This may explain why Phe was more abundant than Nap in rice fields, with LMW PAHs much lower ($p < 0.05$) than HMW PAHs in RF soil.

The similar PAH profiles in the four sampling areas indicated similar sources of PAHs. The highly significant correlations ($p < 0.01$) among individual PAHs, LMW, HMW and total PAHs further confirmed that the profile is fairly constant at different sampling sites and PAHs must come from similar sources (Ma et al., 2005), in our case OBS. Similar correlations among PAHs were also observed in other studies (Wilcke et al., 1997; Amagai et al., 1999). In this study, volatile Nap did not correlate with some HMW PAHs due to its special long-range transport and

addition of biological source from woody plants near RS or loss (by plowing) in RF.

PAHs in soil were mostly derived from atmospheric deposition (Wild and Jones, 1995). Therefore, the abundance of volatile and most easily degradable LMW PAHs (Nap and Phe) in the Guiyu soil suggested that the loss of PAH in soil was smaller than deposition from the atmosphere (Wilcke, 2000) due to the continuous emission of PAHs derived from the open burning of E-waste. Wilcke et al. (1999) also explained that the predominance of LMW PAHs was attributed to a more recent contamination and the replacement of contamination.

PAHs derived from different sources have distinct compositions, and hence the characteristic profile of PAHs could be used as a fingerprint to identify their sources (Khalili et al., 1995), e.g., Nap and Phe (LMW PAHs) are more thermodynamically stable compounds mainly derived from petrogenic sources (from the release of uncombusted petroleum product such as gasoline, diesel fuel and fuel oil from vehicle traffics). Their dominance in the Guiyu soil indicates the petrogenic source. However, Fla, Chr, Pyr and BbkF (HMW PAHs) are typical pyrogenic products derived from high temperature condensation of lower molecular weight aromatic compounds (Khalili et al., 1995; Soclo et al., 2000). Their large contributions (from 14% to 48%) to the total PAHs in the Guiyu soil suggest a pyrogenic source (from combustion of fossil fuels). Therefore, the PAH profile in the Guiyu soil suggests both petrogenic and pyrogenic sources of soil PAHs.

The incomplete combustion of plastic wastes (petroleum product) in the open burning sites should be the main source of PAHs in the Guiyu soil. Beside this, coal combustion and motorcycle exhausts are other PAH sources (Tang et al., 2005). In E-waste recycling workshops, coal was used to melt circuit boards for releasing valuable chips, while motorcycles were popularly the main traffic vehicles in Guiyu.

4.3. Principal component analyses (PCA)

PCA is a multivariate analytical method that is used to reduce a set of original variables and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables (Goloboĉanin et al., 2004).

The 16 PAHs were grouped into three distinct groups based on the number of aromatic rings. The first group contains Ane, Fle, Phe, Fla, Pyr, BaA and Chr, and all are 3-ring and 4-ring PAHs. Their concentrations were correlated significantly with each other ($p < 0.01$) and with total PAHs ($p < 0.01$) (Table 3). The sum of their mean concentrations accounted for 55% of those of total PAHs in Guiyu soils (Table 1). Ane, Fle and Phe are LMW PAHs and resulted from petrogenic sources, while all Fla, Chr, Pyr and BaA are pyrogenic products (Khalili et al., 1995; Soclo et al., 2000). Therefore, the first group represents the mixture of petrogenic and pyrogenic sources. The second group includes 5-ring and 6-ring PAHs: BbkF, BaP,

IcdP, DahA and BghiP. In the RS area their concentrations were not detected or less than $1\,\mu g\,kg^{-1}$, while in the OBS, the sum reached $245\,\mu g\,kg^{-1}$ (Table 2). Therefore, this group represents carcinogenic HMW PAHs derived from anthropogenic source such as E-waste open burning. The third group includes 2-ring and 3-ring PAHs: Nap, Any and Ant. Nap and Any showed a weak correlation with some HMW PAHs (Table 3). Nap ($156\,\mu g\,kg^{-1}$) dominated the PAH profile of the Guiyu soil, while the mean concentrations of Any ($3.4\,\mu g\,kg^{-1}$) and Ant ($5.9\,\mu g\,kg^{-1}$) were very low (Table 1). Hence, the third group represents volatile LMW PAHs derived from both biological and anthropogenic sources.

5. Conclusion

In general, the Guiyu soil was weakly contaminated by PAHs, but in OBS, the soil was heavily contaminated. Total PAH concentrations increased sharply in the order of RS < RF < NOBS < OBS. The significant correlations among individual, LMW, HMW and total PAHs, and the very similar PAH profiles in four sampling areas indicated the similar sources of PAHs, while the abundance of volatile LMW PAHs (Nap and Phe) in the Guiyu soil suggests the continuous PAH sources. The primitive E-waste recycling activities especially open burning and coal combustion were the main sources of PAHs in Guiyu.

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