

## Source identification and health risk of polycyclic aromatic hydrocarbons associated with electronic dismantling in Guiyu town, South China

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### ABSTRACT

In this study the concentrations and distribution of sixteen polycyclic aromatic hydrocarbons (PAHs) were investigated in gas and total suspended particle (TSP) samples collected during daytime and night time. The sampling locations included an electronic waste dismantling workshop (EW), a plastic recycling workshop (PW) and a waste incineration field (WF) in Guiyu, China. A large residential area (RA) in this region was used as a control site. In the daytime, the highest concentration was found at WF (1041 ng m<sup>-3</sup>); while in the night time the highest concentration was found outside of EW (744 ng m<sup>-3</sup>). Comparison between work hours (daytime) and rest hours (night time) displayed that the total PAHs (gas + particulate phase) concentrations and the percentages of PAHs associated with TSP were higher at night than those in the daytime in all sampling workshops except WF. Source diagnostic-ratio analysis revealed that unwanted materials and smoldering honeycomb coals were the main sources of PAHs in EW, WF and PW. Benzo[*a*]pyrene equivalent [BaP<sub>eq</sub>] concentrations calculated by using the toxic equivalent factors [TEFs] suggested that the occupational exposure levels were not significantly high when compared with other occupational exposure. Additionally, our study suggested that the smoldering of unwanted materials could produce much more toxic PAHs compounds.

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### 1. Introduction

Rapid development of electronic industry results in the production of large amounts of electronic wastes (e-waste), including obsolete computers, cellular phones and televisions. Dealing with this type of toxic garbage has become a significant task for many countries. Due to lack of relevant standardized rules, e-wastes produced by developed countries are being exported to developing countries, such as China, India and Pakistan. These countries have used e-waste to create profitable business, which flourish as an unorganized sector, mainly as backyard workshops. One of the most famous e-waste recycling regions in the world is Guiyu town (23°327'N, 116°342'E), located in Guangdong Province, South China (Fig. S1). Workshops involved in this industry have been numerous

in this town since 1995. There are many workshops recycling only plastic, or managing only the circuit boards which were dismantled from computers or TV sets. E-wastes dismantling and plastic recycling have become dominant industries in Guiyu town. Millions of tonnes of waste are recycled in illegal workshops, cheap improper handling techniques including manual sorting and melting circuit boards, which use open-air incineration and acidic washing [1].

Various highly toxic pollutants, such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), and polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDDs/Fs) can be emitted or formed during these recycling procedures [2]. Because of the primitive techniques used in the recycling of e-wastes and absence of appropriate facilities to safeguard human health and the environment in Guiyu town, this region has been seriously polluted by PAHs [3,4], heavy metals [4–6], PBDEs [7–10] and other toxic chemicals [9].

PAHs (Table 1) are well known persistent, bio-accumulative, carcinogenic and mutagenic contaminants [11–13]. Once PAHs enter into the atmosphere, these compounds distribute between gas and particle phases [14]. High levels of PAHs in air; especially of the carcinogenic PAH compounds will impose serious environ-

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**Table 1**  
Physicochemical characteristics of PAHs and quality assurance information of analytical method.

Name	Symbol	Quantification ion	Confirmation ions	Retention time	Spike recovery (%) ± SD		No. of Rings	TEFs [21]
					GFFs	PUF		
Naphthalene	Nap	128		13.49	91.06 ± 9.10	92.98 ± 14.61	2	0.001
Acenaphthylene	Ace	152	76,151	25.72	82.58 ± 6.37	107.99 ± 4.43	3	0.001
Acenaphthene	Dih	154	152,76	26.90	88.04 ± 3.65	101.02 ± 8.04	3	0.001
Fluorene	Flu	166	164,165	31.05	90.30 ± 5.14	106.82 ± 8.01	3	0.001
Phenanthrene	Phe	178	188,89	39.43	111.88 ± 8.25	118.12 ± 12.16	3	0.001
Anthracene	Ant	178	188,89	39.81	78.16 ± 3.88	103.21 ± 15.95	3	0.01
Fluoranthene	Flua	202	101,200	49.43	92.71 ± 9.89	124.05 ± 20.13	4	0.001
Pyrene	Pyr	202	101,200	51.53	90.45 ± 12.63	111.07 ± 8.48	4	0.001
Benz[a]anthracene <sup>a</sup>	BaA	228	114,226	61.65	82.01 ± 5.43	89.60 ± 8.54	4	0.1
Chrysene <sup>a</sup>	Chr	228	114,226	62.20	82.30 ± 4.47	88.98 ± 6.29	4	0.01
Benzo[b]fluoranthene <sup>a</sup>	BbF	252	126,250	70.26	95.59 ± 8.69	101.39 ± 16.06	5	0.1
Benzo[k]fluoranthene <sup>a</sup>	BkF	252	126,250	70.45	89.27 ± 4.47	88.03 ± 13.07	5	0.1
Benzo[a]pyrene <sup>a</sup>	BaP	252	126,250	73.10	76.211 ± 11.12	82.05 ± 8.23	5	1
Indeno[1,2,3-c,d]pyrene <sup>a</sup>	Ind	276	277,138	84.10	95.54 ± 7.94	81.99 ± 16.91	6	0.1
Dibenzo[a,h]anthracene <sup>a</sup>	DiB	278	179,139	84.53	91.10 ± 18.50	113.38 ± 20.14	5	5
Benzo[g,h,i]perylene	BghiP	276	138,277	88.07	90.87 ± 13.54	97.36 ± 14.74	6	0.01

<sup>a</sup> Carcinogenic PAHs.

SD: standard deviation calculated from the spiked blank ( $n = 3$ ).

mental and health problems [13,15]. It has been found that in Guiyu town large amount of PAHs were associated with total suspended particles (TSPs) and the average concentration of benzo(a)pyrene was 2–6 times higher than that in other Asian cities [4]. The soil [16] and water [3] in the vicinity of this town have also been found to be highly polluted by PAHs. Biomonitoring studies [3,4] indicated that these PAHs pollutants mainly resulted from e-waste dismantling.

However, most of these published studies were focused on monitoring of PAHs concentrations in surrounding environment and these researches were not enough to identify the sources of PAHs. Furthermore no intensive research has been conducted in Guiyu town on PAHs levels in these workshops atmosphere especially in work hours (daytime) and rest hours (night time). The objective of this research is to investigate the contamination profiles, including an e-waste dismantling workshop (EW), a typical plastic recycling workshop (PW) and a waste incineration field (WF), to identify the possible sources of PAHs at different periods and estimate the occupational exposure in different representative workshops and health risk of PAHs to locals in Guiyu town (Fig. S2).

## 2. Materials and methods

### 2.1. Chemicals

Analytical-reagent grade dichloromethane (DCM) and n-hexane (Hex) were used as solvents. A mixed PAHs standard solution of 2000  $\mu\text{g ml}^{-1}$  containing 16 PAHs compounds (Supelco, US) and hexamethyl benzene standard solution (Supelco, US) (2000  $\mu\text{g ml}^{-1}$ ) were used. The surrogate standards (naphthalene- $d_8$ , acenaphthylene- $d_{10}$ , phenanthrene- $d_{10}$ , chrysene- $d_{12}$  and perylene- $d_{12}$ ) were purchased from Supelco, USA.

### 2.2. Sample collection and preparation

Sample collecting method has been published in previous literature [14,17–19]. In this research, gas phase were gathered by a 6.5 cm in diameter and 10.5 cm in thickness (a density of 0.030  $\text{g m}^{-3}$ ) polyurethane foam (PUF) plugs. Before use, the PUF were Soxhlet extracted for 72 h with DCM and solvent-cleaned PUF were kept in pre-cleaned jars. Whatman glass fiber filters (GFFs), with 0.45  $\mu\text{m}$  pore size, pre-combusted at 450 °C for 5 h. A compatible high-volume air sampler (Tianhong Intelligent Instrument Plant, Wuhan, China) was used to collect TSP and gases.

Samples were collected simultaneously from the six sites in Guiyu on October 12–14, 2007. The air volumes of 108–180  $\text{m}^3$  were drawn at the rate of 0.15–0.25  $\text{m}^3 \text{min}^{-1}$  for 12 h through GFFs first and PUF plugs subsequently. After sampling, GFFs with TSP were wrapped with pre-baked aluminum foils and sealed with double layers of polyethylene bags, and PUFs were placed in solvent rinsed glass jars with aluminum foil-lined lids. Then the GFFs and PUFs were transported to the laboratory and stored at –20 °C until extraction. All treatments were carefully handled using a pair of stainless steel tweezers.

### 2.3. Extraction, clean-up and GC/MS analysis

The extraction and clean-up methods have been used before in our laboratory [14]. Briefly, the PUF plugs and GFFs spiked with surrogate standards were Soxhlet extracted with 200 ml DCM for 72 h. The extract was evaporated to around 2 ml by a rotary evaporator (Büchi Rotavapor R-124). Then the solvent was exchanged to n-hexane. Concentrated extracts were cleaned and fractionated on neutral silica gel and alumina columns used by Bi and Luo [14,20], and eluted with 70 ml mixture of the solvent (Hex:DCM, 7:3). The 70 ml eluent was evaporated to 1 ml and then concentrated to 200  $\mu\text{l}$  under a stream of  $\text{N}_2$  for instrument analysis.

The samples were analyzed with a GC/MS system consisting of an Agilent model 6890 N gas chromatograph (GC) and an Agilent model 5973 mass spectrometer detector (MSD). The MSD operated in electron ionization mode with electron energy of 70 eV. A capillary column (DB-35MS, 30 m, 0.25 mm, 0.25  $\mu\text{m}$ ) was used.

The chromatographic conditions were as follows: injector temperature, 280 °C; ion source temperature, 180 °C; temperature program: 60 °C holding for 5 min, programmed to 295 °C at 3 °C  $\text{min}^{-1}$ , holding for 30 min. The carrier gas was helium at a constant flow rate of 1.5  $\text{ml min}^{-1}$ . Sample of 1  $\mu\text{l}$  was injected with splitless model. The MSD was run in selected ion monitoring mode (SIM) for optimum sensitivity. Identification of individual PAHs was based on the retention times of target ion peaks (within  $\pm 0.05$  min of the retention of the calibration standard) (Table 1). Identification was confirmed by the abundance of the qualifier ion relative to the target ion. If the relative intensity in the sample spectrum was within  $\pm 20\%$  of the relative intensity in the standard spectrum, identification was confirmed. Identified PAHs were quantified based on external standard calibration procedure.

## 2.4. Quality assurance and quality control

All reference substances used in the present study were analytical grade and all solvents were glass-distilled prior to use. Procedural blanks were conducted for every 5 samples, in order to monitor the contamination and interferences. Surrogate standards were added to all the analyzed samples including PUF (gas) and GFFs (particles) samples, procedural blanks and spiked blanks (include PUF and GFFs) before extraction in order to quantify the procedural recovery. Two spiked blanks (one for PUF and another for GFFs) were conducted for every ten samples.

The correlation coefficients for all calibration curves for every target compound and surrogate standard were greater than 0.99. The spiked recoveries for all target compounds were presented in Table 1. None of the target PAHs was detected in procedural blanks. Surrogate recovery of samples ranged from 68.29% to 106.52%. The limit of quantification (LOQ) was set to be the lowest concentration of the calibration standard ( $5 \mu\text{g L}^{-1}$  equal with  $0.01 \text{ ng m}^{-3}$ ). The data reported in this research was not corrected by the recoveries.

## 3. Results and discussion

### 3.1. PAHs Concentrations in EW, PW, WF

The concentrations of total PAHs during day and night times were given in Table 2. The total atmospheric PAHs (gas plus particle) concentration ( $\Sigma\text{PAHs}$ ) outside EW (OEW) was  $580.20 \text{ ng m}^{-3}$  in the daytime and  $744.04 \text{ ng m}^{-3}$  at night, higher than that of inside EW (IEW) ( $558.87 \text{ ng m}^{-3}$  and  $580.70 \text{ ng m}^{-3}$ ) and approximately twofold higher than that in the atmosphere of the PW ( $313.49 \text{ ng m}^{-3}$  and  $378.63 \text{ ng m}^{-3}$ ). The highest concentration of  $\Sigma\text{PAHs}$  ( $1040.67 \text{ ng m}^{-3}$ ) was found in samples from WF during the daytime; however, the concentration dropped to  $501.32 \text{ ng m}^{-3}$  at night time. And the lowest concentration was in the PW no matter what time day or night in the three workshops. The research of chlorinated-polycyclic aromatic hydrocarbons (ClPAHs) in these types of workshops got the similar result that is the highest concentration was found in municipal/hazardous/industrial waste incinerator and then e-waste recycling facility and last in the chemical industrial complex [21].

As shown in Table 3 the highest  $\Sigma\text{PAHs}$  concentration in this research (WF  $1040.67 \text{ ng m}^{-3}$ ) was higher than the averaged concentration of PAHs (13 targets,  $867.46 \text{ ng m}^{-3}$ ) at the road intersections [22], and lower than that of Carbon black manufacturing industry ( $2365.00\text{--}2770.00 \text{ ng m}^{-3}$ ) [23] and fastener manufacturing industry ( $88300.00 \text{ ng m}^{-3}$ ) [24]. The PAHs concentrations in other workshops in this study were a little lower than those of the cooking room in Malay ( $597.00 \text{ ng m}^{-3}$ ) [25].

As for the reference or control site (RA), the concentration was lower than any of the workshops in the present study, however the concentrations were much higher than that in previous report from urban area [15,16,18,26] and in indoor environment [27]. In general, the concentrations of  $\Sigma\text{PAHs}$  in RA, OEW, IEW and PW were higher at night, especially in the comparison site RA, where the concentration at night ( $291.68 \text{ ng m}^{-3}$ ) was almost 6 times higher than that in the daytime ( $50.13 \text{ ng m}^{-3}$ ) (Table 2). On the contrary, the  $\Sigma\text{PAHs}$  concentration in WF in the daytime was about twice as high as that at night. The concentrations of the total carcinogenic PAHs ( $\Sigma\text{cPAHs}$ ) showed the same trend as the  $\Sigma\text{PAHs}$  in all sampling sites, except WF (Table 2 and Fig. 1). At night the door was closed and exhaust fan were turned off in the EW and there was no human activity during this period, but the honeycomb coals, used in grill, changed from burning to smoldering and the exhaust gas was discharged outside of the EW by exhaust pipes. Therefore the total concentration and the percentages associated with particu-

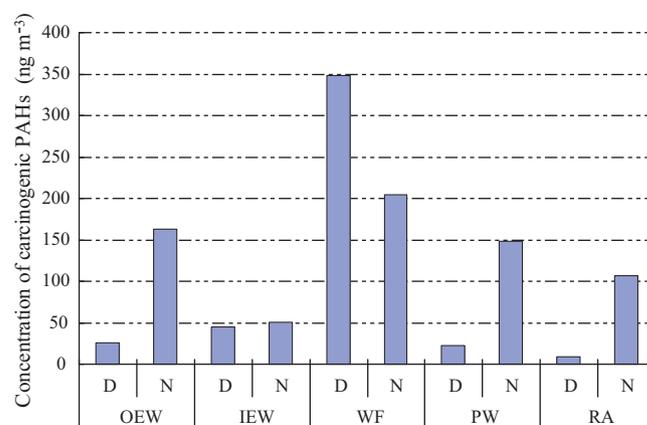


Fig. 1. The change of total carcinogenic PAHs ( $\Sigma\text{cPAHs}$ ) at different sample sites and periods (D: at day; N: at night).

late phase of PAHs in OEW were found higher at night and became lower in IEW. While in PW much waste plastic was stacked in the workshop no matter at day or night, however, the door was closed at night and there was no fan or chimney in this workshop, so the concentration of  $\Sigma\text{PAHs}$  got higher at night. As described in supporting information, the local people in WF would burn unwanted materials (plastic insulating layer and municipal solid waste) in the open air, and most importantly, the open burning was carried out at night, while in the daytime the unwanted materials were smoldering combusted. PAHs might be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Furthermore, it has been noticed that smoldering combustion could emit 4–5 times more PAHs than flaming combustion [28]. Consequently, the PAHs concentrations were much higher in the daytime than those at night in WF. Due to the transportation, deposition and other processes the vicinity of WF such as RA, the concentration of  $\Sigma\text{PAHs}$  drastically elevated at night.

### 3.2. The PAHs species distribution and gas/particle partitioning of PAHs

As shown in Fig. 2, three and four-ring compounds, dominated by Phe, Flu and Pyr in all samples. They accounted for 51.54–83.57% in total PAHs in the daytime, and 28.95–71.90% at night in RA, OEW, IEW and PW. However, the profile of PAHs was not changed remarkably in WF. The concentrations of the most carcinogenic and mutagenic PAHs including 4-ring compounds (BbF and BkF), 5-ring compounds (BaP, Ind and Dib) and 6-ring compounds (BghiP) became higher at night in these sites. Meanwhile the low molecular compounds (include 2 and 3 ring PAHs) became lower at the same period (Fig. 2). Since the compounds such as Ace, Flu, Phe, Ant and Pry were volatile, they were the dominant components of PAHs in gas phase in this research. On the contrary, high molecular weight PAHs had a higher fraction in particulate PAHs simply because of their low volatility [29]. The partition of PAHs between gas and particle phase could be different in the day and night time. It was clear that the percentage of PAHs in particle phase increased at night in all sample sites especially the high molecular PAHs (Fig. 3 and Fig. S3). The most distinct example was the IEW, where less than 10% of the PAHs compounds were existed in particulate phase in the daytime, while the ratio was changed to 80% at night (Fig. 3). Because of the use of coal and the poor atmospheric dispersion in the IEW, much e-waste was stacked in the IEW no matter at day or night. So the concentrations of PAHs in particulate phase were higher at night.

It was commonly observed that the high molecular weight PAHs (5 and 6 rings PAHs) were often associated with particulates, while

**Table 2**

The concentration of total and carcinogenic PAHs and diagnostic concentration ratios of selected PAHs at different workshops and periods.

Analyte	Total concentration (ng m <sup>-3</sup> ) during day					Total concentration (ng m <sup>-3</sup> ) during night				
	OEW	IEW	WF	PW	RA	OEW	IEW	WF	PW	RA
Σ <sub>c</sub> PAHs	26.09	44.47	348.68	22.48	8.74	162.65	50.74	204.73	148.67	106.99
ΣPAHs	580.2	558.87	1040.67	313.49	50.13	744.04	580.7	501.32	378.63	291.68
Flua/(Flua + Pyr) <sup>a</sup>	0.57	0.58	0.55	0.50	0.53	0.57	0.53	0.52	0.51	0.53
Flua/(Flua + Pyr) <sup>b</sup>	0.63	0.59	0.63	0.91	0.64	0.65	0.58	0.61	0.59	0.63
Ind/(BghiP + Ind)	0.42	0.47	0.55	0.43	0.44	0.56	0.49	0.53	0.54	0.55

Σ<sub>c</sub>PAHs: total carcinogenic PAHs.

ΣPAHs: total PAHs.

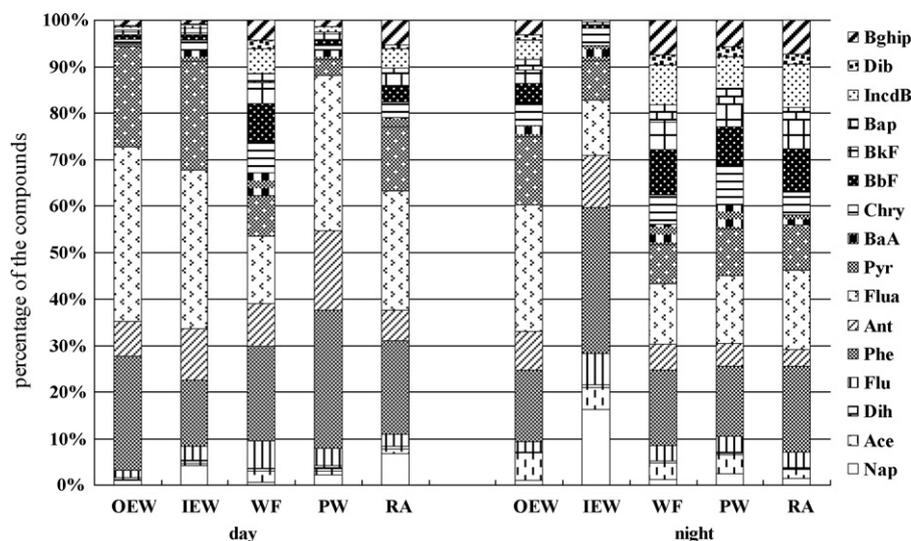
<sup>a</sup> Calculated only by compounds in particle.<sup>b</sup> Calculated by total concentration (gas + particulate).**Table 3**

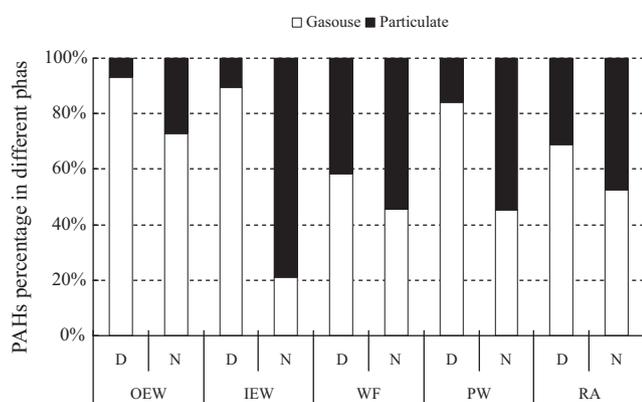
Comparison of PAHs concentrations and BaPeq (toxic equivalency quotients,TEQs) calculated for various samples from different occupational environments.

Occupational environments	Sample type/place/time	G	P	T	Reference	
Fastener manufacturing industry	Oil mists	Concentration	86,000	2300	88300.00	[24]
		BaPeq	108	126	234.00	
Carbon black manufacturing industry	Packaging	Concentration	993	1777	2770.00	[23]
		BaPeq	200	566	766.00	
	Palletizing	Concentration	1088	1277	2365.00	
		BaPeq	307	314	621.00	
Cook rooms	Chinese	Concentration		135	135.00	[25]
		BaPeq		14	14.00	
	Malay	Concentration		597	597.00	
		BaPeq		54	54.00	
	Indian	Concentration		30	30.00	
		BaPeq		2.5	2.50	
Toll station <sup>a</sup>	Taiwan	Concentration		1322	[40]	
Road intersection <sup>b</sup>	Tianjin	Concentration	8228	4771	12,999	[41]
		BaPeq	73	457	530	
IEW	D	Concentration	501.05	57.82	558.87	This research
		BaPeq	2.68	10.97	13.65	
WF	N	Concentration	122.75	457.95	580.70	
		BaPeq	0.86	5.12	5.98	
PW	D	Concentration	606.44	434.23	1040.67	
		BaPeq	2.20	136.42	138.62	
PW	N	Concentration	228.42	272.90	501.32	
		BaPeq	0.71	86.12	86.83	
PW	D	Concentration	262.97	50.51	313.49	
		BaPeq	0.87	5.52	6.39	
PW	N	Concentration	171.96	206.68	378.63	
		BaPeq	0.37	64.27	64.64	

Notes: Concentration: ng m<sup>-3</sup>.

G: gas phase, P: particulate phase, T: total = G + P, D: at day, N: at night.

<sup>a</sup> Samples were collected in winter.<sup>b</sup> Average of yearly PAHs concentrations calculated using WS = 10.**Fig. 2.** The PAH profiles distributions at different sample sites and periods.



**Fig. 3.** The partition of the PAHs in different phase at different sample sites and periods (D: at day; N: at night).

low molecular weight compounds (include 2 and 3 ring PAHs) tended to be more concentrated in the vapor phase [29]. But this could be influenced by temperature. Lower temperature at night would make much of these compounds adsorbed in particles. So in all the sites, Ace, Flu, Phe and Ant were found almost exclusively in the gas phase (92–98%), whereas the five and six-ring PAHs (BbF, BkF, BaP, Ind, Dib, and BghiP) were primarily associated with the particulate phase (>98%). Of the four-ring PAHs, Flua and Pyr were mostly found in the gas phase (>89% and >73%, respectively), whereas Nap, BaA and Chry were distributed almost equally between the two phases in the daytime except IEW. At night the two and three-ring PAHs became less in particulate phase and the shift of the distribution of four, five and six-ring PAHs to the particulate phase was observed in all the samples except IEW (Fig. 2).

### 3.3. Source identification

Specific PAHs have been suggested as indicators of certain processes that release PAHs into the environment. Therefore, the PAHs concentration profiles and ratios could be used to determine the sources of PAHs in the air. Dominance of Chry and BkF were suggested from coal combustion [30]. Pyr, Flua and Phe showed reasonably high levels in emission from incineration [31]. Diagnostic PAHs ratios, such as Flua/(Flua + Pyr) and Ind/(BghiP + Ind), have been used to investigate the origin of PAHs [32]. Generally, the Flua/(Flua + Pyr) ratio was above 0.50 in grass, most coal and wood combustion samples, below 0.50 for most petroleum samples [33–35]. The Ind/(Ind + BghiP) ratio was during 0.35 and 0.7, used for diesel emissions [36].

Previous studies [14,37] calculating the ratios were only based on the concentration in particles, which might result in a significant underestimation of the contribution of anthropogenic emissions. Therefore, the two ratios employed in this study were determined not only based on concentration in TSP, but also the total concentrations including the vapor and particulate phase. Consequently, the pollution sources could be predicted more accurately by these ratios.

As shown in Table 2, the ratios of Flua/(Flua + Pyr) calculated based on these compounds existed in TSP or the total concentrations (gas and particulate) are all bigger than 0.50 at day and night time, though there are little difference, suggesting that the ratio calculated only based on compounds in TSP can identify the potential sources and the ratios also revealed that coal combustion emission was a possible main source in these work shops. While the ratios calculated on the basis of the total concentrations (gas and particulate) were larger than that that only based on these compounds concentration in TSP especially in the WF, PW and RA in the daytime revealed that some PAHs were possibly from petroleum products

(incomplete combustion of plastic wastes). As described above, all the wastes including plastics and other unwanted materials were smoldering combusted, and the plastic wastes were recycled through shredding and low temperature melting in PW in the daytime. All these processes might produce PAHs that could affect the ratios. Research in soil PAHs pollution also suggested that the incomplete combustion of plastic wastes in the open burning sites might be the main source of PAHs in Guiyu soil environment [3]. Besides, coal combustion and burning of fossil fuels could also produce PAHs. Hence, the ratios calculated from total concentrations might be more correct than that only based on concentration in TSP to identify the potential pollution sources.

The values of Ind/(BghiP + Ind) were 0.42 in the daytime and 0.56 at night in OEW, 0.47 and 0.49 in IEW, 0.55 and 0.53 in WF, 0.43 and 0.54 in PW, and 0.44 and 0.55 in RA (Table 2). The significant change of the ratios in OEW, PW and RA at day and night proved that there was not only one pollutant source in these places, but also, the ratios changed little in IEW and WF, confirming that there was only one main pollutant source or the pollutant sources remained unchanged during the sampling period. Additionally, the ratios at all sites were larger than 0.49 at night, which might indicate that burning coal was the dominant source of PAHs in Guiyu at this period.

However, all these characteristics may be attributable to unwanted materials incineration and honeycomb coals smoldering were the main PAHs pollution sources in this area.

### 3.4. The toxic equivalency quotients and health risk of PAHs in different workshops

To date there exists no threshold for a dose–response relationship for PAHs. Hence, the assessment of health risk due to inhalation exposure to PAHs is based on atmospheric concentrations of PAHs using epidemiological results.

The toxicity of PAHs is complicated by presence of two to several fused aromatic ring compounds each with its own toxicity. The carcinogenicity of PAHs varies with structural characteristics such as relative positions of carbon atoms in space of the fused rings that determine their biological activity. The organization of carbon atoms as a bay region elicits a high degree of biochemical reactivity to some PAHs and their metabolites. Among several PAHs, the most carcinogenic PAH is benzo-a-pyrene (BaP), which is assigned the maximum carcinogenic potential factor of 1 (toxic equivalent factor, TEF), and the relative carcinogenic potential of individual PAHs has been determined relative to BaP (i.e. toxic equivalents). To date, only limited data are available for TEFs [38]. The list of TEFs finished by Nisbet and LaGoy has been demonstrated to better reflect the actual state of the toxic potency of each individual PAH species relative to BaP [21], and a TEF of 1.0 is given for BaP, adopted in this study (Table 1). PAHs in gaseous phase were dominated by PAHs with lower TEFs (Fig. S3), while PAHs in particulate phase were dominated by PAHs with higher TEFs (Fig. S3). The total BaP<sub>eq</sub> exposure levels in particulate phase were 5–100 times higher than those in gaseous phase on the aspect of inhalational exposures. Consequently, controlling the particulate-phase PAHs was crucial to decrease the toxicity of PAHs (Fig. 2). The total BaP<sub>eq</sub> exposure levels became higher at night in PW, OEW and RA, and lower in IEW and WF. The reason was the same as described above; indicating that unwanted materials incineration and honeycomb coals smoldering could produce more toxic PAH.

The occupational exposure levels in this research (Table 4) were comparatively lower than those in carbon black manufacturing industry sectors [39], relative to those in the fastener manufacturing industry [23] and booth attendants of the highway toll stations, and equal with those in cooking room [25] in some period (Table 3).

**Table 4**

The toxic equivalency quotients of PAHs and lifetime lung cancer risks in different sample sites.

			G	P	T	CR × 10 <sup>-3</sup>
OEW	D	Concentration	541.11	39.09	580.20	0.64
		BaP <sub>eq</sub>	1.15	7.99	9.14	
	N	Concentration	541.39	202.65	744.04	4.97
		BaP <sub>eq</sub>	1.79	69.26	71.05	
IEW	D	Concentration	501.05	57.82	558.87	0.96
		BaP <sub>eq</sub>	2.68	10.97	13.65	
	N	Concentration	122.75	457.95	580.70	0.42
		BaP <sub>eq</sub>	0.86	5.12	5.98	
WF	D	Concentration	606.44	434.23	1040.67	9.70
		BaP <sub>eq</sub>	2.20	136.42	138.62	
	N	Concentration	228.42	272.90	501.32	6.08
		BaP <sub>eq</sub>	0.71	86.12	86.83	
PW	D	Concentration	262.97	50.51	313.49	0.45
		BaP <sub>eq</sub>	0.87	5.52	6.39	
	N	Concentration	171.96	206.68	378.63	4.52
		BaP <sub>eq</sub>	0.37	64.27	64.64	
RA	D	Concentration	34.50	15.63	50.13	0.21
		BaP <sub>eq</sub>	0.11	2.82	2.93	
	N	Concentration	153.62	138.05	291.68	3.40
		BaP <sub>eq</sub>	0.69	47.94	48.63	

CR: lifetime lung cancer risks = the sum of BaP<sub>eq</sub> × 7.0 × 10<sup>-5</sup> [23,25].

G: gas phase, P: particulate phase, T: total = G + P, D: at day, N: at night.

Regarding the lung cancer risk via the inhalation route, in this study, the sum of BaP<sub>eq</sub> levels for PAHs was used to estimate the corresponding lifetime lung cancer risks for workers. And the unit risk  $7.0 \times 10^{-2} (\mu\text{g m}^{-3})^{-1}$  for a 25-year occupational PAHs exposure with the averaged BaP concentration of  $1 \mu\text{g m}^{-3}$  was used in this study [23,25]. It worth noting above unit risk was proposed to estimate the lung cancer risk caused by lifetime exposure; therefore, it has been adopted by a recent study for assessing the lung cancer risks of general adults' exposure to the ambient atmospheric PAHs [23,25].

As shown in Table 4 the highest sum of BaP<sub>eq</sub> ( $138.62 \text{ ng m}^{-3}$ ) was gotten in WF in the daytime. For the corresponding lifetime lung cancer risks were found as  $9.70 \times 10^{-3}$  ( $138.62 \times 7.0 \times 10^{-5} = 9.70 \times 10^{-3}$ ), this is by far below the unity  $7.0 \times 10^{-2} (\mu\text{g m}^{-3})^{-1}$ . And other workshops lifetime lung cancer risks were also found far below the unity. But recently, Goriaux [24] reported that the atmospheric PAHs concentrations measured using conventional sampling method without an ozone trap might underestimate the concentrations by more than 200%. This was especially found when the samples were collected in the vicinity of a point source of particulate PAHs and for highly reactive compounds such as BaP. As the consequence the concentrations of BaP were underestimated in this study because the conventional sampling method was used. Therefore, the real health risk of the PAHs exposure might be minimized by the data in this research.

#### 4. Conclusions

The concentrations of the total PAHs and the carcinogenic PAHs were higher at night except WF. Furthermore, it was observed that the main sources of PAHs in this region were the waste incineration at day and honeycomb coals smoldering at night. The plastic wastes recycling also emitted some PAHs to the atmosphere. The BaP<sub>eq</sub> of PAHs revealed that unwanted materials and honeycomb coals smoldering could produce more toxic PAH compounds to the environment. As the e-waste recycling workshops and other relevant workshops can be found in every corner, this area should be regarded as a large non-point source for PAHs and other toxic pollutants. Thus, further investigation will be needed to better understand the negative effect of e-waste recycling and relative activities on the environment and human health.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.109.

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**Source identification and health risk of polycyclic aromatic  
hydrocarbons associated with electronic dismantling in Guiyu town,  
South China**

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## **1. Study locations**

The study was conducted in the Guiyu town (23°327'N, 116°342'E), which is located in Chaoyang District, Shantou City, Guangdong Province, southeast of China, with a total area of 52 km<sup>2</sup> and a population of 150,000. The area belongs to a sub-tropical climate, with an annual average temperature of 21.5°C, relative humidity of 80% and mean annual rainfall of 1721 mm. The prevailing wind is from the northeast except in the summer, which is in the southwesterly direction. In the northern part of Guiyu, there is a reservoir and a large area of hilly woodlands. The traditionally rice-growing community at Guiyu has turned into an intensive e-waste recycling center since 1995. Over 75% of 300 individual workshops have been involved in the business of dismantling or processing e-waste with nearly 100,000 migrant laborers employed in Guiyu town.

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The work was divided very clearly, and there are many plants deal with the recycling the plastic and others deal with the circuit boards which dismantled from compute or TV set. These plants can be found everywhere in this town.

#### *1.1 E-waste recycling workshop (EW) (N: 23.323889 E: 116.367222)*

The EW lies in the east of Guiyu. Twenty-four grills and 35 workers are employed in this plant and 5 tons e-wastes can be managed every day. All the e-wastes are supplied by the same company and are mainly TV set circuit boards produced ten years ago. The techniques used in this process are very primitive, including dismantling copper and aluminum with rough tools such as hammers and Chinese kitchen knives from circuit boards and separating different electronic components by heating over a domestic stove using honeycombed coal blocks as fuel (coal were mixed with contaminated river sediment). Workers repeat the same work day after day without any appropriate facilities to protect their health and surroundings. .

#### *1.2 Waste plastic recycling workshop (PW) (N: 23.308056 E: 116.373611)*

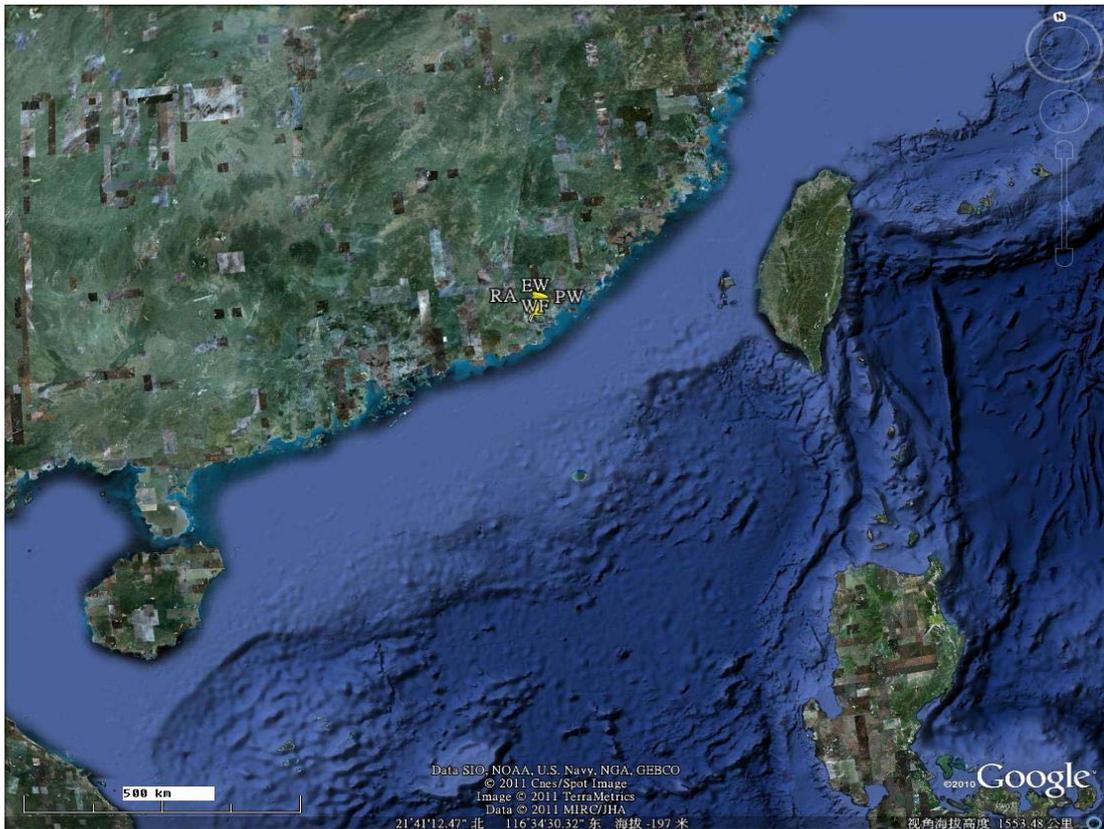
The plastics managed in this plant are produced in recent years. The techniques used in the PW include crushing plastics into pieces with a disintegrator, then washing and cooling the plastic particles with a big bucket and heating the plastic particles to be remodeled. There is no any ventilation around the integrators and the waste water was poured down to a river directly.

#### *1.3 Waste incineration field (WF) (N: 23.335556 E: 116.368333)*

The WF lies in a river bank without walls. In this place, something such as stripping of metals in open-pit acid baths, burning cables and unwanted materials in the open air and disposing unsalvageable materials in the fields and riverbanks have been done.

1.4 Residential area (RA) (N: 23.320000 E: 116.350278)

The sampling site is in the town council, located in the southwest of the EW and WF and this district is the largest residential area in this region. There is a big market and a middle school with 400 students around the town council.



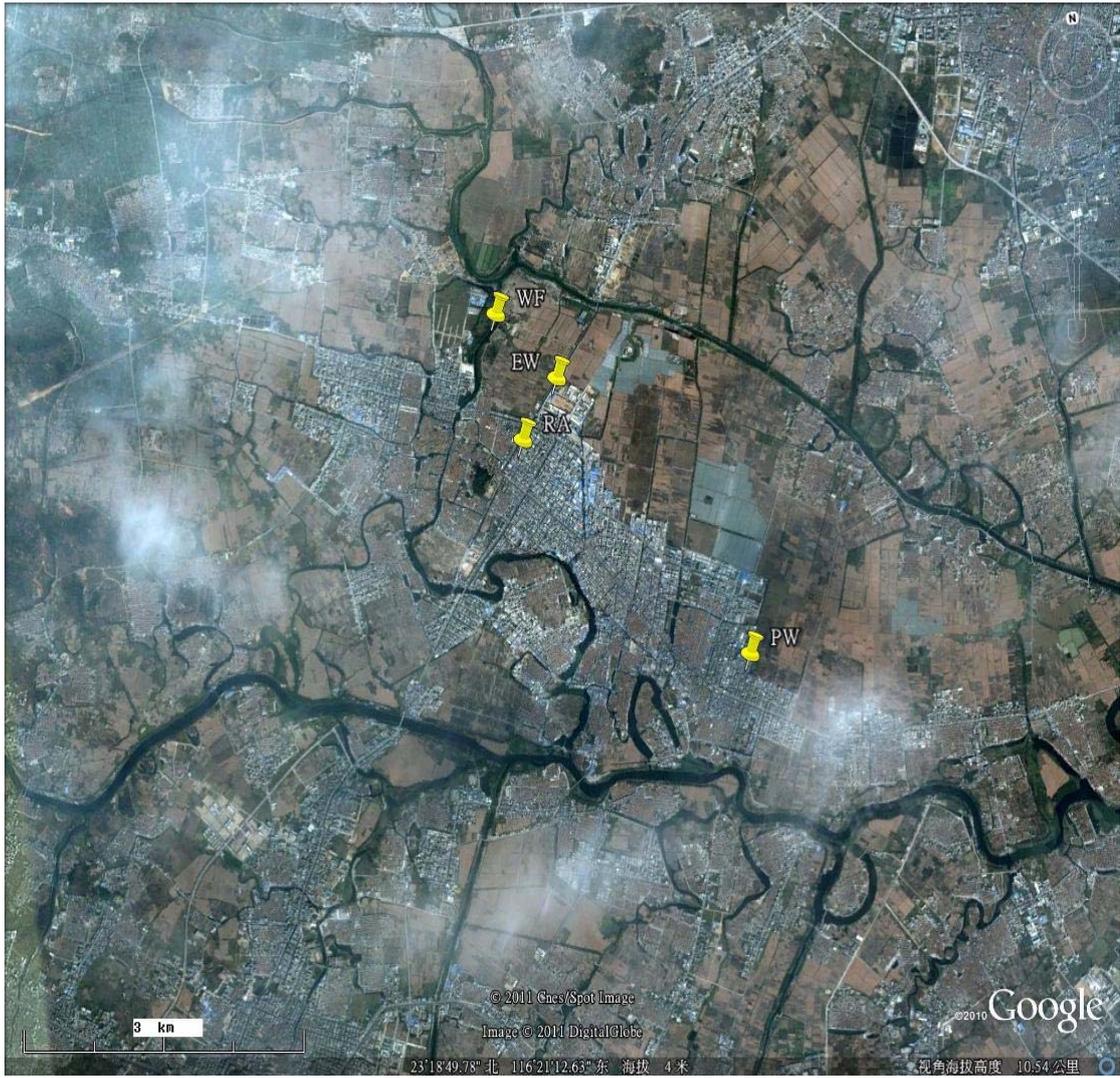


Figure S1. The location of Guiyu Town in China and sampling sites in this Town (from Google Earth):

# MAP OF GUIYU

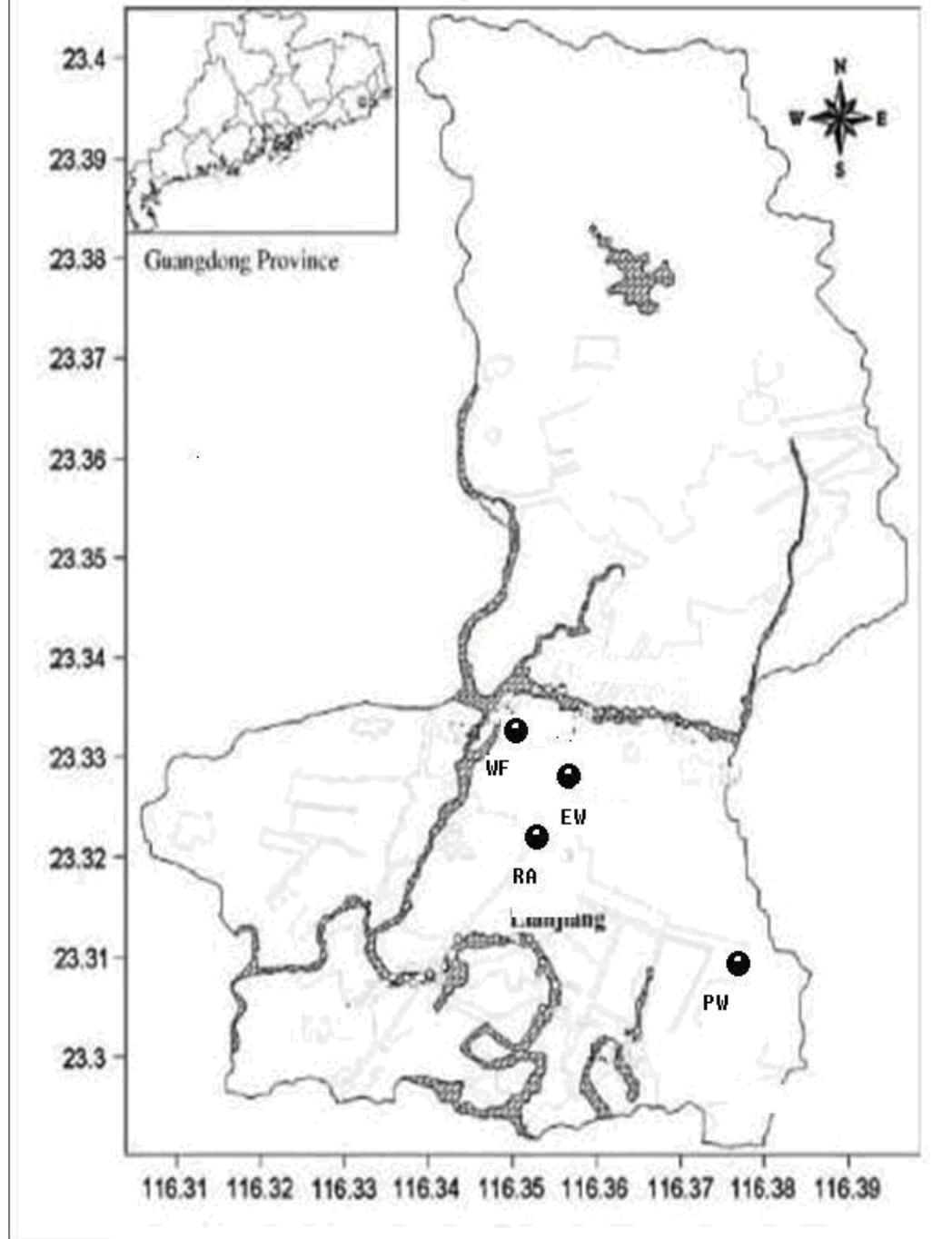
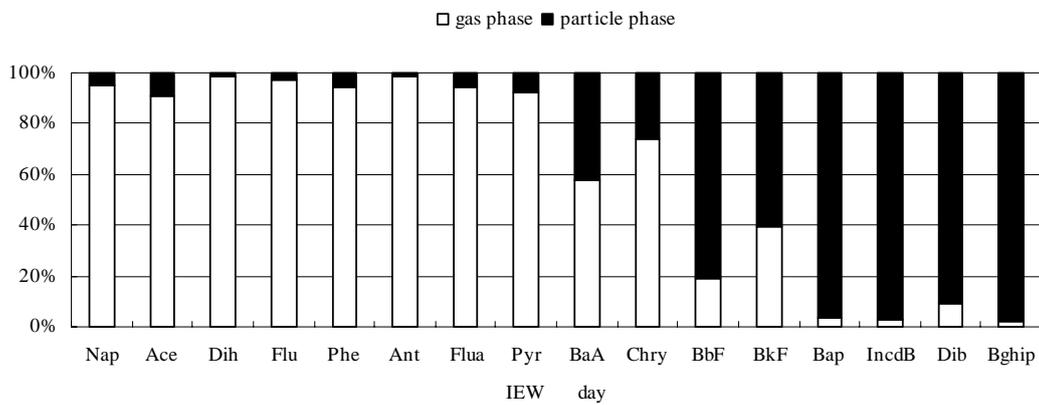
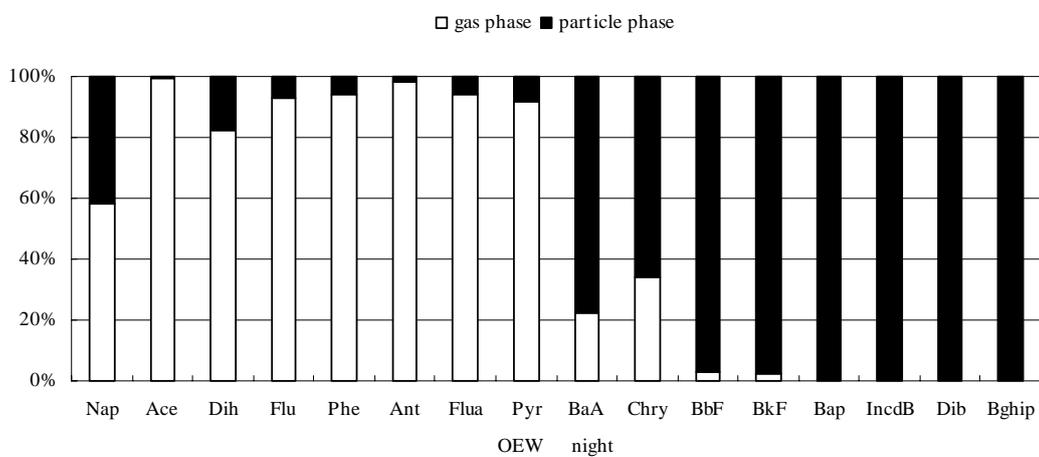
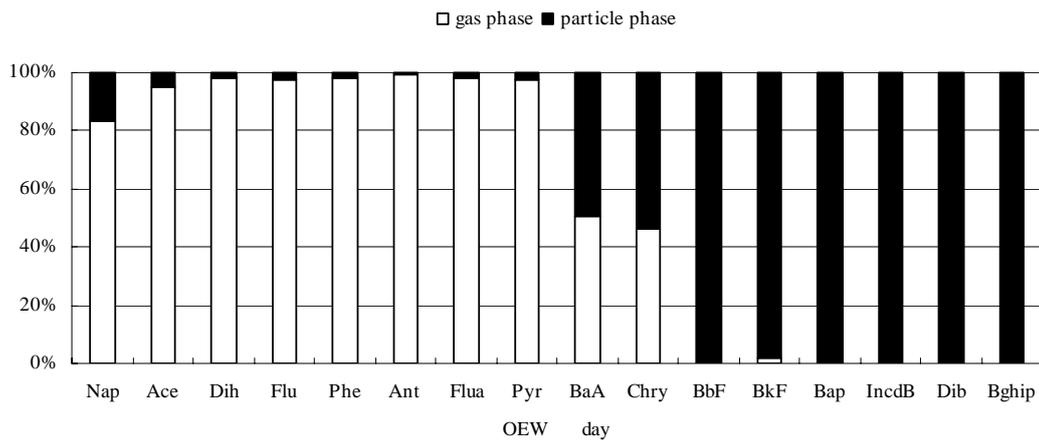
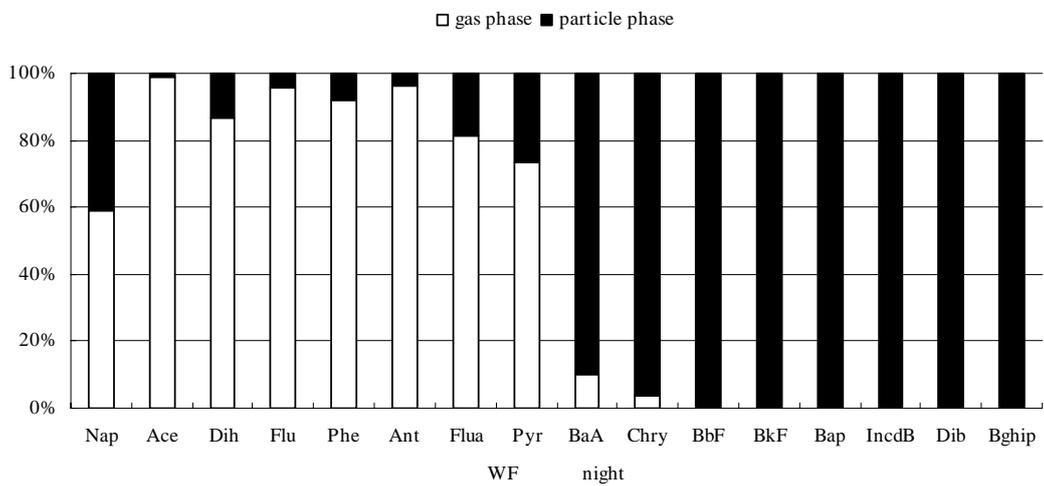
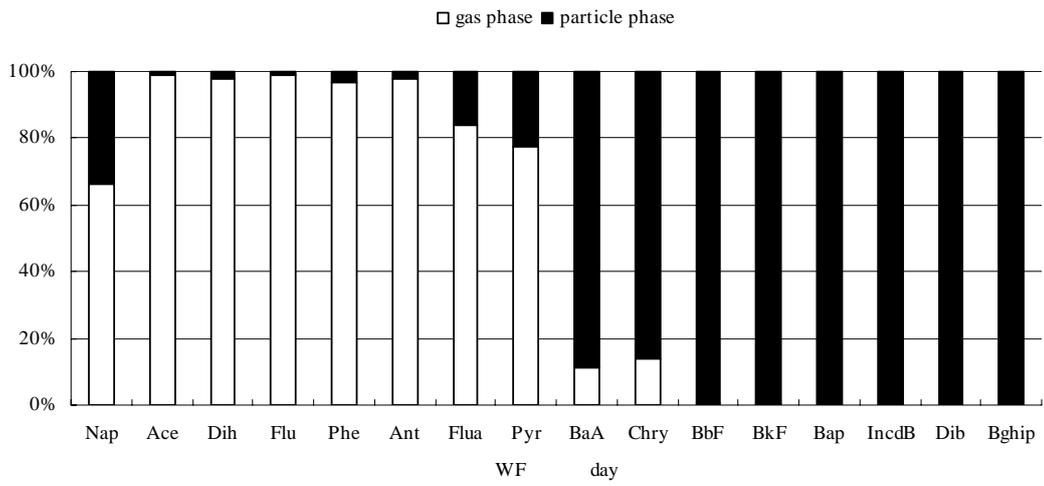
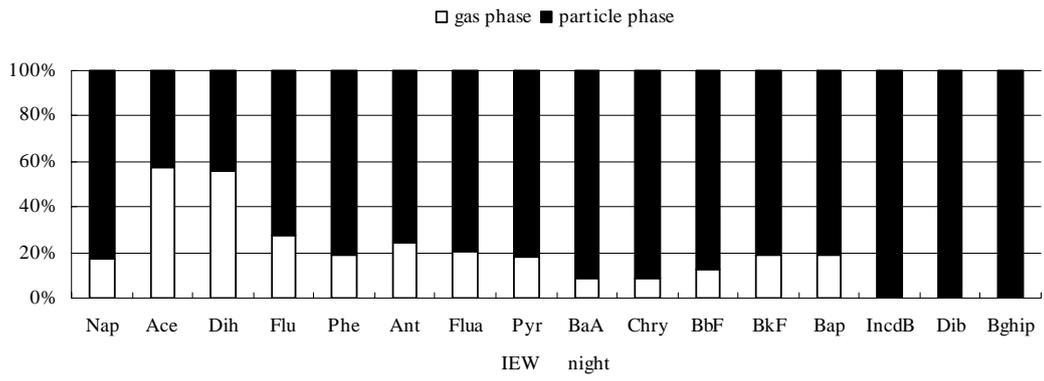
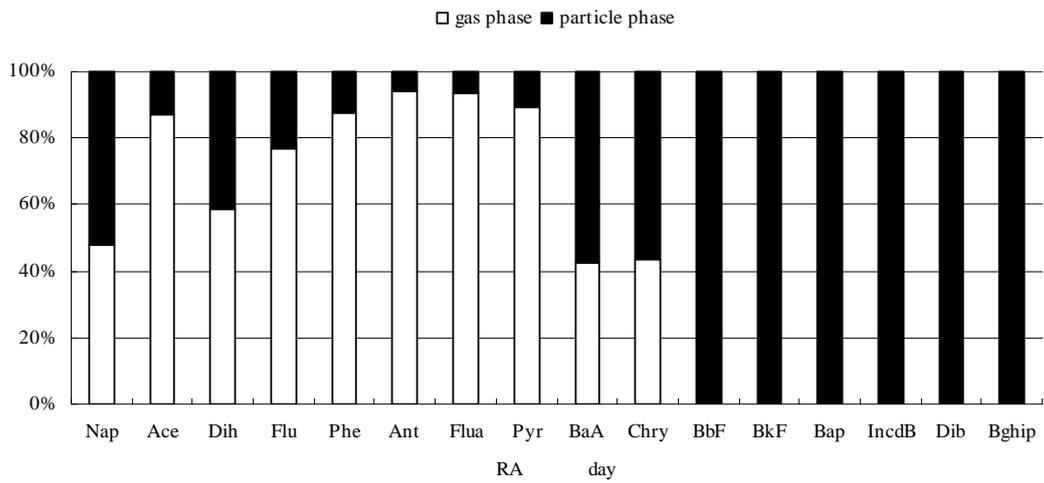
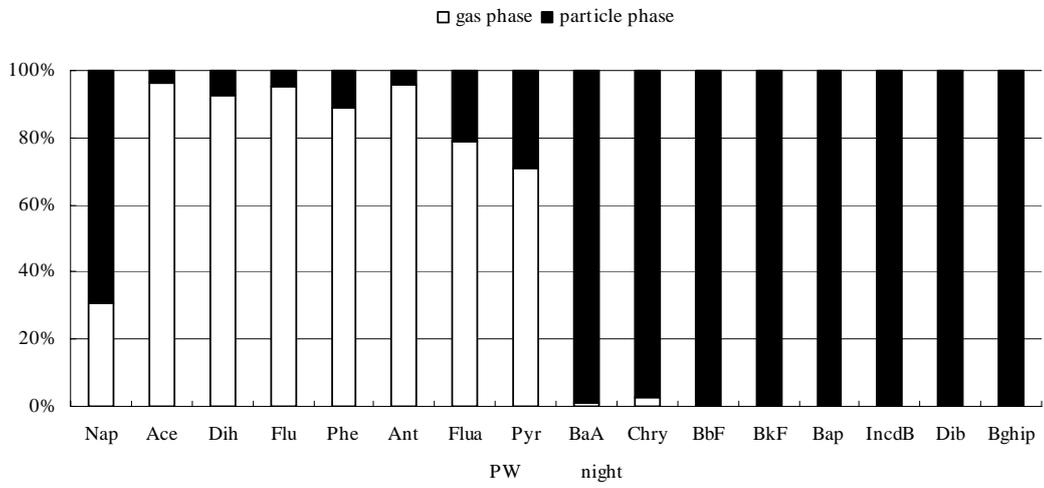
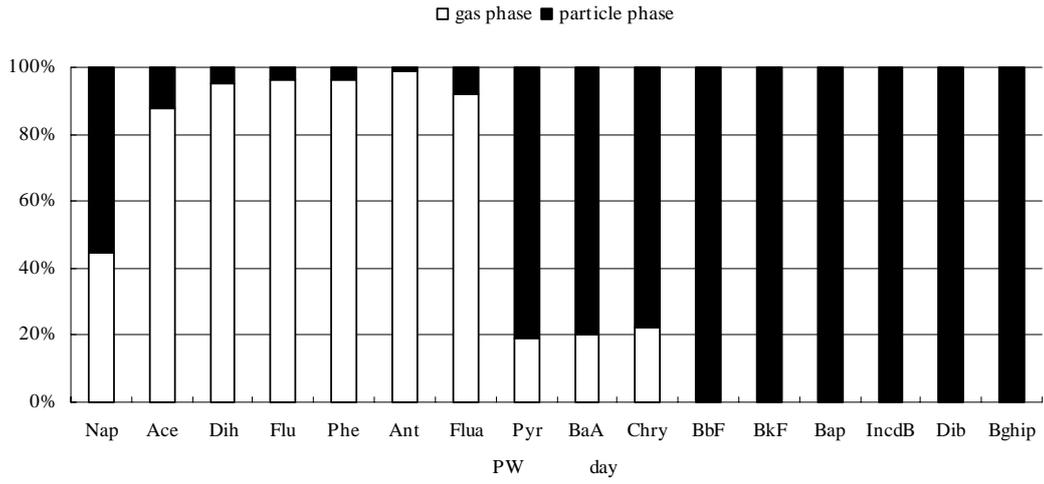
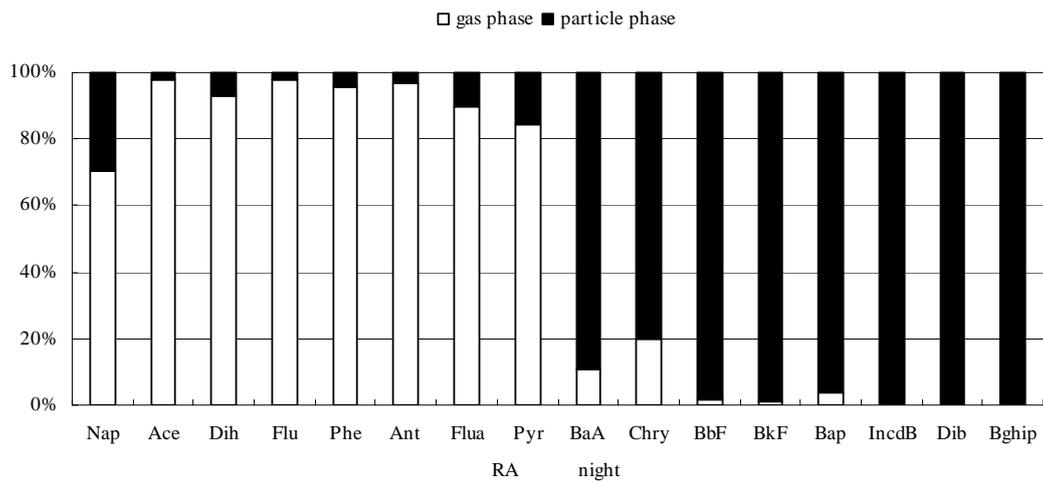


Fig.S2 Map of the sampling sites in Guiyu Town









**Fig S3.** Partition between the gas and the particle phase at day and night at different sites