Seasonal variations and source apportionment of complex polycyclic aromatic hydrocarbon mixtures in particulate matter in an electronic waste and urban area in South China

She-Jun Chen ^{a,*}, Jing Wang ^{a,b}, Tao Wang ^{a,b}, Ting Wang ^{a,b}, Bi-Xian Mai ^b, and Staci L.

Massey Simonich ^{c,d*},

^a *State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

^b *University of Chinese Academy of Sciences, Beijing 100049, China*

^c *Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, United States*

^d *Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, United States*

Abstract

Complex polycyclic aromatic hydrocarbon (PAH) mixtures including parent PAHs, high molecular weight PAHs (MW 302 PAHs), and halogenated PAHs (HPAHs) were measured in particulate matter (PM) in an urban area and a rural electronic waste area in

* Corresponding author. Tel: +86-20-85291509; fax: +86-20-85290706; +1-541-737-9194. Fax: +1-541-737-0497.

E-mail address: chenshejun@gig.ac.cn (S.J. Chen)

E-mail address: staci.simonich@orst.edu (S. Simonich)

South China. The concentrations of MW < 302 PAHs at two sites were not significantly different with annual means of 23.2 ± 17.2 and 33.7 ± 29.0 ng/m³, respectively. However the concentrations of both MW 302 PAHs (5.35 ± 3.72 ng/m³) and HPAH (49.9 pg/m³) were significantly higher at the e-waste site than the urban site (2.81 ± 2.36 ng/m³ and 28.2 ± 28.5 pg/m³), suggesting e-waste recycling being a significant source of these PAHs. The majority of PAHs exhibited higher concentrations in winter and spring and lower concentrations in fall and summer. Meteorological conditions and increased emissions of PAHs in northern China due to domestic heating in colder seasons are important factors influencing the PAH seasonal variations. Source apportionment by the chemical mass balance (CMB) model indicated that residential stoves (coal combustion), industrial boilers (coal combustion), biomass burning, and vehicular emission accounted for $38 \pm 14\%$, $30 \pm 11\%$, $22 \pm 22\%$, and $10 \pm 7\%$ of the PAHs in the urban PM, respectively. Comparable contributions from these sources were also observed for PM at the e-waste site. PAH emission factors are needed for primitive e-waste recycling to further understand the importance of this source to ambient air.

Key words: Polycyclic aromatic hydrocarbon; Particulate matter; E-waste; Urban; Source apportionment

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic contaminants that are formed mainly from incomplete combustion or pyrolysis of organic matter such as fossil fuel, wood, and municipal waste (Shen et al., 2010). Although they have been extensively studied, PAHs in the environment still attract great attention because PAHs are ubiquitous in both urban and rural environments and many of them are mutagenic and carcinogens (Armstrong et al., 2004). Perera et al. found that prenatal exposure to airborne PAHs can adversely affect child behavior (Perera et al., 2012). A study from Chongqing, China indicated that environmental concentration of PAH exposure is associated with increased sperm DNA damage (Han et al., 2011). In addition, substituted PAH derivatives (e.g., nitrated, oxygenated, and halogenated PAHs) and high molecular-weight PAHs (MW 302 Da) PAHs have also attracted concern in recent years (Jariyasopit et al., 2014; Reisen and Arey, 2005; Zimmermann et al., 2013). These PAHs have been found in municipal waste incinerator gas and various environmental matrices (Tsapakis and Stephanou, 2007; Watanabe and Noma, 2009; Witter and Nguyen, 2016), and some of them are identified to be more persistent, mutagenic, and carcinogenic compared to parent PAHs (Kawanaka et al., 2008; Ohura et al., 2009).

Due to the rapid economic development and huge population, China consumes significant amount of energy for industry, transportation, and domestic combustion, and resulted in substantial emissions of PAHs to the atmosphere (Zhang et al., 2007). It was

estimated that China emitted 21% of the global atmospheric emission (Shen et al., 2013). The Pearl River Delta (PRD), located in Guangdong province, South China, is one of the most highly urbanized and industrialized regions in China. The PAH emission density in the PRD region was reported to be much higher than the average PAH emission density for China (Zhang et al., 2007). The contamination of PAHs in the urban air of the PRD region has been reported in previous studies (Bi et al., 2003; Gao et al., 2012; Li et al., 2006; Liu et al., 2015; Yang et al., 2010). These studies indicated that the PAH concentrations elevated significantly in winter season and coal combustion and vehicular emission were the main sources of PAHs in the urban air (Li et al., 2006; Yang et al., 2010; Liu et al., 2015). Nevertheless, in most of these studies, the samples were collected in short periods (one or two seasons), whereas year-round data are limited. Furthermore, the PAH sources in the PRD air are largely identified using molecular diagnostic ratios but quantitative information on the sources is rare (Gao et al., 2013). A large electronic waste (e-waste) recycling site is located in the rural area adjacent to the PRD. Primitive e-waste recycling has been proved to be significant source of PAHs to the ambient environment (Ma et al., 2009; Wang et al., 2012b; Wei et al., 2012).

Particulate matter (PM) samples were collected year round from an urban site in Guangzhou and an e-waste site in a rural area in South China and analyzed for complex PAH mixtures including 32 MW < 302 PAHs, 16 MW 302 PAHs, and 27 halogenated (16 chlorinated and 11 brominated) PAHs (HPAHs). In a previous study, we reported the benzo[a]pyrene equivalent (BaPeq) concentration of these PAHs in the PM and the

associated human inhalation cancer risk (Wang et al., 2012a). In this study, we aim to understand the seasonal variations and spatial differences in the contamination of these PAHs and the characteristics of PM in the air at the two sites where distinct sources may exist. The chemical mass balance (CMB) model is performed to conduct source apportionment of PAHs in the air. To our knowledge, this is the first effort to compare the simultaneous air pollution of PAHs at urban and e-waste sites.

2. Materials and methods

The detailed materials and methods have been given in a previous study (Wang et al., 2012a) and are described briefly here.

2.1 Sampling

The urban area air sampling site was located in Guangzhou, the capital of Guangdong province and the largest city in South China (Fig. S1 in the Supplementary Material). The samples were collected from the rooftop of building (approximately 20 m tall) on the Guangzhou Institute of Geochemistry campus. This site is representative of residential areas in Guangzhou without major industrial sources nearby. The e-waste area air sampling site is approximately 70 km north of the urban site, which is one of the three largest e-waste recycling sites in China. The e-waste recycling processing is concentrated mainly in a number of villages in two towns with an area of 330 km². The samples were collected from the rooftop of a building (10 m above the ground) in a small village.

Total suspended particles were collected on quartz fiber filters for 24 h using a high volume air sampler on five consecutive days of each month. The sampling was conducted

simultaneously at the e-waste and urban sites from May 2010 to April 2011 and 60 samples were obtained, respectively. After sampling, the filters were wrapped in aluminum foil, sealed in polyethylene bags, returned to the lab, and stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.2 Analysis methods.

PM mass was weighed using a balance with accuracy of 0.01 mg after the filters were conditioned in a desiccator for 24 h. A small sample punch ($1 \times 1.5\text{ cm}^2$) was taken from the quartz filters to determine the contents of organic carbon (OC) and elemental carbon (EC) using National Institute of Occupational Safety and Health (NIOSH) 5040 method by an OC-EC aerosol analyzer (Sunset Laboratory Inc., US) (Birch and Cary, 1996).

The PM-loaded filters were spiked with recovery standards and extracted with a 1:1 mixture of hexane and acetone using pressurized liquid extraction (ASE300, Dionex Corp., Sunnyvale, CA, USA). The extracts were solvent exchanged to hexane and concentrated to 1 mL using Turbovap II (Biotage, Charlotte, NC, USA). The extracts were further purified with 20 g silica solid phase extraction (SPE) columns (Varian, Inc., Santa Clara, CA). The eluates were spiked with internal standards (d_{10} -acdnaphthene, d_{10} -fluoranthene, d_{12} -benzo[k]fluoranthene, and $^{13}\text{C}_{12}$ -PCB138), and concentrated to 1 mL for analysis.

The target compounds were listed in Table S1. The parent PAHs and MW 302 PAHs were analyzed using an Agilent 5890 gas chromatograph (GC) (Agilent Technologies) coupled to an Agilent 5973 mass spectrometer (MS) operated in selected ion monitoring

mode and using electron impact ionization. The HPAHs were analyzed using the same instrument operated in negative chemical ionization mode. Measurement of the HPAHs was achieved using a DB-5MS (30 m $\times$ 0.25 mm i.d., 0.25 μ m film thickness) capillary column (J&W Scientific, Palo Alto, CA). The initial column temperature was held at 60 $^{\circ}$ C for 1 min, ramped to 200 at 25 $^{\circ}$ C/min, ramped to 300 at 3 $^{\circ}$ C/min, and held for 10 min. Injection of 1 μ L sample was conducted with an automatic sampler in the splitless mode. The method detection limits (MDLs) were 0.2–1.2 pg/m³ for ClPAHs and 0.3–1.8 for BrPAHs pg/m³.

2.3 *Quality control.*

A procedural blank was processed for every five field samples. The target compounds were not detected in the blanks. The average recoveries were $76.6 \pm 19.1\%$ for ¹³C₆-1-chloropyrene, $50.4 \pm 16.0\%$ for *d*₁₀-fluorene, $63.3 \pm 19.4\%$ for *d*₁₀-phenanthrene, $74.8 \pm 21.6\%$ for *d*₁₀-pyrene, $89.3 \pm 24.6\%$ for *d*₁₂-triphenylene, $62.8 \pm 15.2\%$ for *d*₁₂-benzo[a]pyrene, and $97.8 \pm 29.2\%$ for *d*₁₂-benzo[g,h,i]perylene. The reported concentrations were recovery corrected and the recoveries of individual samples are given in Table S2.

2.4 *The CMB model and statistical analysis.*

The CMB model developed by the US EPA (EPA-CMB8.2) was used to apportion the major sources in the particular matter. The fingerprints of PAHs from four sources were considered, i.e., residential stoves (coal combustion), industrial boilers (coal combustion), biomass burning, and vehicular emission that were recently reported in the literature (in

China or South Asia) (Chen et al., 2013; Shen et al., 2010; Wiriya et al., 2016; Zhang et al., 2008). The 16 US EPA's priority PAHs (except for naphthalene) that were commonly measured in the literature were used as the fitting species (Fig. S2). The model parameters were used basically as the US EPA recommendations. More information on the CMB model is given in the Supplementary Material.

Statistical analyses were performed using SPSS software version 19 (SPSS Inc., Chicago, US). Principal component analysis (PCA) was used for all log-transformed PAH concentrations with detection frequency over 60% (except for naphthalene and its methylated derivatives), as well as the OC and EC concentration of the PM from the two sites, respectively. For results below the limit of detection (LOD), a value of LOD/2 was assigned. The Mann-Whitney Rank Sum test was used to compare differences in measurements between the two sites.

3. Results and discussion

3.1 Characteristics of PM

The average annual concentrations of PM were 163 and 192 $\mu\text{g}/\text{m}^3$ at the urban and e-waste sites, respectively (Fig. 1). At the e-waste site, the maximum and minimum daily average concentrations occurred in April 2011 (314 $\mu\text{g}/\text{m}^3$) and August 2010 (109 $\mu\text{g}/\text{m}^3$), respectively. The PM concentrations in other months were between the Grade I (120 $\mu\text{g}/\text{m}^3$) and II (300 $\mu\text{g}/\text{m}^3$) of Chinese National Ambient Air Quality Standard (NAAQS). At the urban site, the highest average concentration (255 $\mu\text{g}/\text{m}^3$) was observed in December 2010 and the lowest occurred in July 2010 (97.7 $\mu\text{g}/\text{m}^3$). The PM

concentrations from September 2010 to April 2011 were higher than other months, which were between the NAAQS Grade I and II. At the both sites, the PM concentrations were highest in winter and lowest in summer.

OC and EC constitute a major portion of atmospheric particles. EC is produced by incomplete combustion, and OC can be emitted directly into the air from anthropogenic or biogenic sources or formed in the atmosphere through reactions (Satsangi et al., 2012). The contents of OC in the urban PM were ranged from 60.5 to 236 mg/g (mean = 120 mg/g), which were not significantly different from those from the e-waste site (44.6–181 mg/g with a mean of 116 mg/g). Nevertheless, the EC contents in PM from the urban site (10.0–87.9 mg/g with a mean of 36.7 mg/g) were significantly higher than those from the e-waste site (7.90–58.1 mg/g with a mean of 22.7 mg/g) ($p < 0.001$). Thus, the OC/EC ratios in the urban air (4.10 ± 2.26) were significantly lower than those in the rural air (5.82 ± 2.51) ($p < 0.001$). This was probably due to more PM associated with fossil emissions from coal combustion and vehicle exhaust in the urban area than in the e-waste area, which are thought to be the primary sources of EC (Liu et al., 2014; Zhang et al., 2015) and/or different emission sources of PM at the two sites. In addition, at both urban and rural sites, the OC/EC ratios in dry seasons (winter and fall) (4.30 ± 1.49 and 7.33 ± 2.46 , respectively) were significantly higher than those in wet seasons (summer and spring) (3.02 ± 2.28 and 5.18 ± 1.72 , respectively). This suggests more secondarily formed aerosols in dry seasons (because of longer retention of PM in the air) or seasonality in PM sources in the study area. The amount of secondary OC was calculated

by the minimum OC/EC ratio method that commonly use in the literature (Cao et al., 2007). The result indicated that the contributions of secondary OC to OC in the PM in the urban air ($67.8 \pm 18.3\%$) were significantly higher than those in the rural air ($60 \pm 18.1\%$) ($p = 0.011$), though the OC contents were not significantly different at the two sites.

Correlation analysis were conducted among the concentrations of PM, OC, and EC (Fig. S3). At the urban site, it was shown that the OC contents in the bulk particles varied less with the increase of PM concentrations in the air ($p = 0.200$), whereas the EC contents were significantly negatively correlated with the PM concentrations ($r = -0.499$, $p < 0.001$). It can be inferred that the increase of PM mass in the urban air was significantly attributed to particles with lower EC content. In contrast, at the rural e-waste site there was a negative correlations between the PM and OC concentrations ($r = -0.331$, $p = 0.010$), but the EC contents varied less with PM ($p = 0.755$). This implied that the increase of PM in the rural air could be contributed largely by mineral particles from soils, which usually have lower organic matter content (less than 5%) (Zeraatpishe and Khormali, 2012). Alternatively, this could also be attributed to the low OC content particles released from e-waste recycling or to secondary inorganic ions that have been found to be significant components of PM. EC was not correlated with OC in the urban air, it has a moderate correlation with OC in the rural air ($r = 0.401$, $p = 0.002$).

3.2 Concentrations of PAHs and seasonal variations

The daily concentrations of MW < 302 PAHs ranged from 5.07 to 79.7 ng/m³, with a median of 17.9 ng/m³ at the urban site (Table 1). The concentrations were between 5.96

and 114 ng/m³, with a median of 23.6 ng/m³ at the e-waste site, which were not statistically significantly higher than those at the urban site. The concentrations of MW 302 PAHs ranged from 0.28 to 7.86 ng/m³ (median = 1.42 ng/m³) at the urban site, which were significantly lower than the MW 302 PAH concentrations at the e-waste site, which ranged from 0.54 to 11.8 ng/m³ (median = 3.05 ng/m³) ($p < 0.001$). At both site, the highest mean concentrations were observed for naphtho[1,2-b]fluoranthene, followed by dibenzo[e,l]pyrene, dibenzo[j,l]fluoranthene, and dibenzo[a,e]pyrene (Table S3). The HPAH concentrations were also significantly higher at the e-waste site (median = 29.3 pg/m³) than the urban site (15.9 pg/m³) ($p = 0.003$) (Table S4). However, the HPAH concentrations were substantially lower than the MW < 302 and MW 302 PAH concentrations at both sites. The HPAHs were dominated by CIPAHs (medians = 11.2 and 17.3 pg/m³) relative to BrPAHs (medians = 2.81 and 8.72 pg/m³) at the both sites. The result suggests the presence of stronger sources of MW 302 PAHs and HPAHs at the e-waste site.

The concentrations of MW < 302 PAHs at the e-waste site showed clear seasonal variations with medians of 60.5, 30.1, 16.2, and 10.3 ng/m³ in winter, spring, fall, and summer, respectively ($p < 0.056$) (Fig. 2). Similar trend was also observed for MW 302 PAHs and CIPAHs, except that the concentrations of CIPAHs in fall declined significantly compared to other PAHs. At the urban site, significantly higher MW < 302 PAH concentrations were also observed in winter (40.6 ng/m³) and spring (18.5 ng/m³) and the concentrations in summer and fall are similar (11.5-12.0 ng/m³). The concentrations of

MW 302 PAHs also exhibited similar seasonal pattern except for the relatively elevated concentrations in fall. Different patterns were observed for ClPAHs, which exhibited significantly higher concentrations in winter (51.8 pg/m^3) than other seasons ($8.40\text{-}9.85 \text{ pg/m}^3$) ($p < 0.001$). The concentrations of BrPAHs had lower detection frequencies in the air of both site, showing different seasonal variations.

The study area has a subtropical climate and nearly has no domestic heating in winter which usually increases emission of PAHs to the air. The e-waste recycling activities have little seasonality, but does depend on the amount of e-waste received at this site. The seasonal variations of PAHs and PM (both higher in winter and spring) indicated that meteorological conditions would be an important factor influencing the atmospheric concentrations. The lower boundary layer and lower temperature in winter favor the retention of PM and PAHs in the air and partitioning of PAHs into particles from gaseous phase. In a recent study, Yang et al. (2010) also observed elevated air concentrations and enhanced gas/particle partitioning of PAHs in winter in this city. We also compared the temporal variation of PAH mass fractions in the PM ($\mu\text{g/g}$) and the air concentrations ($\mu\text{g/m}^3$). Their trends were generally similar (Fig. S4), indicating the air concentrations were largely dependent on the mass of PAHs bound to PM. However, the air concentrations in the December samples increase substantially, but the mass fractions increased only moderately compared to the November sampling. Clearly, the increase in the air PAH concentration in December was enhanced by the elevated PM concentration in the air. In addition, increased PAH emission due to domestic heating in northern China

also contributed to episodic elevated PAH concentrations in the study region in colder season when northerly wind is prevalent (Fig. S6). A previous study by Tan et al. (2011) found that the PAH concentrations in Guangzhou air substantially increased in haze days when the air masses came from the north and northeast compared to non-haze days or haze days when the air mass came from the south (Tan et al., 2011).

Several studies have reported the PAH concentrations in Guangzhou air. The average concentrations of $\sum_{16}\text{PAHs}$ in the urban air (19.2 ng/m^3) in 2010-2011 in the present study was a little lower than that in PM collected in 2001-2002 (23.7 ng/m^3), very close to that in 2005-2006 PM (19.5 ng/m^3), and a little higher than that in 2009 $\text{PM}_{2.5}$ (15.5 ng/m^3). This suggests that the PAH concentrations in Guangzhou air didn't decline significantly in recent year. These concentrations were all lower than the average concentration at the e-waste site (27.6 ng/m^3). The air concentrations at the e-waste site in the present study were between the concentrations in 2012 ($15.1\text{--}17.7 \text{ ng/m}^3$) and in 2004 (148 ng/m^3) at the other two Chinese e-waste sites (Deng et al., 2006; Luo et al., 2015). However, the PAH concentrations in the present study are much lower than the concentrations in urban PM recently reported in northern China such as Beijing (annual mean = 76.3 ng/m^3), Xi'an (107 ng/m^3), and Taiyuan (126 ng/m^3) (Wang et al., 2011b; Wei et al., 2015; Xia et al., 2013), and lower than that in Nanjing in eastern China (52.9 ng/m^3) (He et al., 2014).

Previous reports on concentrations of MW 302 PAHs in ambient air are scarce. Four dibenzopyrene isomers (DBaP, DBaP, DBaP, and DBaP), which are considered to be

potential human carcinogens by the International Agency for Research on Cancer, were more commonly reported in the literature. The mean concentrations of the four isomers were 0.014, 0.07, 0.02, and 0.01 ng/m³ in the urban air in Rome (Menichini and Merli, 2012) and were 0.003, 0.024, 0.006, and 0.002 ng/m³ in the urban air in Stockholm (Bergvall and Westerholm, 2007), respectively. These concentrations were much lower than their concentrations in the air in the present study, with values of 0.034, 0.170, 0.055, 0.008 ng/m³ at the urban site and 0.072, 0.333, 0.123, and 0.019 ng/m³ at the e-waste site, respectively. The concentrations of these isomers in PM_{2.5} in Beijing (0.049, 0.255, 0.111, and 0.025 ng/m³) (Wang et al., 2011a) were close to those at our e-waste site. However, despite their potentially different sources at these sites, the relative contributions of the isomers were similar.

3.3 Source identification and apportionment

Five PAH molecular diagnostic ratios were applied to identify the sources of PAHs in the air (Table 2). The ratios of ANT/(ANT+PHE) (> 0.1) and BaA/(BaA+CHR) (0.34-0.72) consistently indicated a dominant pyrogenic rather than petrogenic sources at the both sites (Fig. S5). At the urban site, the FLA/(FLA+PYR) ratios were above 0.5 in all the samples except one, indicating clear dominance of coal/biomass combustion sources. However, the IcdP/(IcdP + BghiP) ratios, ranging from 0.41 to 0.57 (median = 0.50), indicated both contributions from liquid fuel combustion and coal/biomass combustion. The BaP/BghiP ratios, with a median of 0.64, also suggest both traffic and non-traffic emissions. Similar results were also observed at the rural site. The results

indicated that molecular diagnostic ratios may not be valid markers for identifying the PAH sources in the air, which was also suggested in a recent study from the UK (Katsoyiannis et al., 2011).

PCA was also performed to identify the PAH sources in the PM and the loadings are listed in Table S5. At the urban site, four components were extracted which accounted for 88.9% of the variance in the data set. Principal component 1 (PC1) had high correlations with MW 302 PAHs, C1PAHs, and a few MW < 302 PAHs. PC2 showed good loadings for most MW < 302 PAHs, and PC3 showed good loadings for some 4 and 5-ring PAHs such as benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, and benzo(a)pyrene. PC4 was correlated well with OC, while EC showed no good correlations with the four components. At the e-waste site, MW 302 PAHs, C1PAHs, 4 and 5-ring PAHs, and OC were associated with PC1, and MW < 302 PAHs and C1PAHs were associated with PC2. EC was correlated well with PC3. The PCA results for the PAHs may be more a result of their environmental behaviors than of the sources. PCA thus may not be a good tool to identify the sources of PAHs in the air of the study area. The weak correlations between OC/EC and PAHs in the urban air suggest that they had different origins. At the e-waste site, heavier PAHs concentrations (including MW 302 PAHs and most 4 and 5-ring PAHs) showed moderate correlations with OC concentrations. However, no PAH concentrations were correlated with EC concentration, similar to that in the urban air.

Source apportionment by the CMB model showed that the major sources of particle-associated PAHs in the urban air were residential stoves, industrial boilers,

biomass burning, and vehicular emission, which accounted for $38 \pm 14\%$, $30 \pm 11\%$, $22 \pm 22\%$, and $10 \pm 7\%$, respectively (Table 3). This indicated that coal combustion (coal power plants and residential coal combustion) was the dominant source of PAHs in the air (68%). The coal consumption in Guangdong Province was 171 million tons (over 60% of the total energy consumption) and approximately 80% of the coal was consumed in the PRD region (GDSY, 2012). The high contribution from residential stoves may be due to use of coal in some low-income homes in Guangzhou and in the suburb and rural areas around the city. The much higher (approximately 100 times) PAH emission factors of residential coal combustion than industrial combustion, as observed in previous studies (Zhang et al., 2008), may also be a reason for the large contributions from residential coal use. The estimated contributions from biomass burning showed very large seasonal variations (Table 3). In the period of May to September 2010 (i.e. the warmer season), the average contribution from biomass burning was only 2.0%; while it increased to 31.4% in the cool season. This is a result of biomass burning in harvest season and for domestic heating in winter in the northern regions when the northerly wind is prevalent. Similar result was also observed in previous studies (Gao et al., 2011; Xu et al., 2006) that regional biomass burning would be a significant source of PAHs in winter in Guangzhou. The vehicular emission source constitutes roughly 10% of total PAH emissions in the urban air, which is unexpectedly lower as most previous studies in this region suggested traffic as a major PAH source, although the contributions were not quantitatively estimated in these studies. In a recent study, Gao et al. (2013) estimated the source

contributions to PM_{2.5} PAHs in Guangzhou using positive matrix factorization receptor model (Gao et al., 2013). They found that coal combustion, biomass burning, and vehicular emissions accounted for $58 \pm 4\%$, $31 \pm 4\%$, and $11 \pm 2\%$ of the total PAHs, consistent with our finding.

Although it was assumed that e-waste recycling was the dominant source of PAHs at the e-waste site, we also made source apportionment for the PAHs in this rural air based on the four sources because, to our knowledge, no PAH fingerprints of e-waste recycling emission is available. The result showed that industrial boilers, residential stoves, biomass burning, and vehicular emission accounted for $40 \pm 23\%$, $28 \pm 20\%$, $23 \pm 14\%$, and $9 \pm 8\%$, respectively (Table 3). Industrial coal combustion was the most important source in this rural area, where there are no other industrial activities except for e-waste recycling. According to our survey of e-waste recycling workers in this area, this was likely because the coal was used in the e-waste burning furnaces. Although the contributions of biomass burning in warmer season (6.6%) were also lower relative to cool season (27.3%), they were apparently higher than those in the urban area (warmer season) indicating more biomass burning in the rural area. Overall, PAH emission factors for primitive e-waste recycling, which is prevailing in many developing countries, is needed to further understand the importance of this source to the ambient air.

It should be noted that the source apportionment contains large uncertainties, which is mainly attributed to the uncertainties in the source profiles affected by combustion conditions (Lee et al., 2007), and the possible environmental degradation of PAHs in air,

and the number of source types.

4. Conclusion

This study compared the contamination of PM-bound complex PAH mixtures in an e-waste and urban area in South China. The annual concentrations of PM were higher at the e-waste site than the urban site, but the urban PM contained more EC and secondary OC. The concentrations of MW < 302 PAHs were comparable at two sites, however the concentrations of both MW 302 PAHs and HPAH were significantly higher at the e-waste site, suggesting e-waste recycling being a significant source of these PAHs. The majority of PAHs exhibited higher concentrations in winter and spring and lower concentrations in fall and summer. The seasonal variations indicated that meteorological conditions would be an important factor responsible for the PAH concentrations in the study region, in addition to the increased emissions of PAHs in northern China due to domestic heating in colder seasons. The CMB model showed that coal combustion (68%) was the dominant source of PAHs in the urban air, followed by biomass burning (22%) and vehicular emission (10%). Measuring the PAH emission fingerprints of primitive e-waste recycling is needed in order to further understand the importance of this emission source to ambient air.

Acknowledgments

This research was financially supported by the National Science Foundation of China (Nos. 41422305 and 41230639). Funding for this research was provided by the U.S. National Science Foundation (AGS-11411214). This publication was made possible in

part by National Institute of Environmental Health Sciences (NIEHS), National Institutes of Health (NIH), grants P30 ES00210 and P42 ES016465. The authors thank Dr. Takeshi Ohura from Meijo University for supplying the halogenated PAH standards. The authors thank the analytical chemistry core of OSU's Superfund Research Program for supplying some of the other standards.

References

- GDSY (Guangdong Statistical Yearbook 2012). Available at <http://www.gdstats.gov.cn/tjnj/2012/table/7/07-04.htm>.
- Armstrong B, Hutchinson E, Unwin J, Fletcher T. Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: A review and meta-analysis. *Environ Health Perspect* 2004;112:970-8.
- Bergvall C, Westerholm R. Identification and determination of highly carcinogenic dibenzopyrene isomers in air particulate samples from a street canyon, a rooftop, and a subway station in Stockholm. *Environ Sci Technol* 2007;41:731-7.
- Bi XH, Sheng GY, Peng P, Chen YJ, Zhang ZQ, Fu JM. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmos Environ* 2003;37:289-98.
- Birch ME, Cary RA. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci Tech* 1996;25:221-41.
- Cao JJ, Lee SC, Chow JC, Watson JG, Ho KF, Zhang RJ, et al. Spatial and seasonal distributions of carbonaceous aerosols over China. *J Geophys Res-Atmos* 2007;112.
- Chen F, Hu W, Zhong Q. Emissions of particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Fu Gui-shan Tunnel of Nanjing, China. *Atmos Res* 2013;124:53-60.
- Deng WJ, Louie PKK, Liu WK, Bi XH, Fu JM, Wong MH. Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM_{2.5} at an electronic waste recycling site in southeast China. *Atmos Environ* 2006;40:6945-55.
- Gao B, Guo H, Wang XM, Zhao XY, Ling ZH, Zhang Z, et al. Polycyclic aromatic hydrocarbons in PM_{2.5} in Guangzhou, southern China: Spatiotemporal patterns and emission sources. *J Hazard Mater* 2012;239:78-87.
- Gao B, Guo H, Wang XM, Zhao XY, Ling ZH, Zhang Z, et al. Tracer-based source apportionment of polycyclic aromatic hydrocarbons in PM_{2.5} in Guangzhou, southern China, using positive matrix factorization (PMF). *Environ Sci Pollut R* 2013;20:2398-409.

- Gao B, Yu JZ, Li SX, Ding X, He QF, Wang XM. Roadside and rooftop measurements of polycyclic aromatic hydrocarbons in PM_{2.5} in urban Guangzhou: Evaluation of vehicular and regional combustion source contributions. *Atmos Environ* 2011;45:7184-91.
- Han X, Zhou NY, Cui ZH, Ma MF, Li LB, Cai M, et al. Association between Urinary Polycyclic Aromatic Hydrocarbon Metabolites and Sperm DNA Damage: A Population Study in Chongqing, China. *Environ Health Perspect* 2011;119:652-7.
- He JB, Fan SX, Meng QZ, Sun Y, Zhang J, Zu F. Polycyclic aromatic hydrocarbons (PAHs) associated with fine particulate matters in Nanjing, China: Distributions, sources and meteorological influences. *Atmos Environ* 2014;89:207-15.
- Jariyasopit N, Zimmermann K, Schrlau J, Arey J, Atkinson R, Yu TW, et al. Heterogeneous Reactions of Particulate Matter-Bound PAHs and NPAHs with NO₃/N₂O₅, OH Radicals, and O₃ under Simulated Long-Range Atmospheric Transport Conditions: Reactivity and Mutagenicity. *Environ Sci Technol* 2014;48:10155-64.
- Katsoyiannis A, Sweetman AJ, Jones KC. PAH molecular diagnostic ratios applied to atmospheric sources: A critical evaluation using two decades of source inventory and air concentration data from the UK. *Environ Sci Technol* 2011;45:8897-906.
- Kawanaka Y, Matsumoto E, Wang N, Yun SJ, Sakamoto K. Contribution of nitrated polycyclic aromatic hydrocarbons to the mutagenicity of ultrafine particles in the roadside atmosphere. *Atmos Environ* 2008;42:7423-8.
- Li J, Zhang G, Li XD, Qi SH, Liu GQ, Peng XZ. Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Sci Total Environ* 2006;355:145-55.
- Liu JJ, Man RL, Ma SX, Li JS, Wu Q, Peng JY. Atmospheric levels and health risk of polycyclic aromatic hydrocarbons (PAHs) bound to PM_{2.5} in Guangzhou, China. *Mar Pollut Bull* 2015;100:134-43.
- Liu JW, Li J, Zhang YL, Liu D, Ding P, Shen CD, et al. Source apportionment using radiocarbon and organic tracers for PM_{2.5} carbonaceous aerosols in Guangzhou, South China: Contrasting local- and regional-scale haze events. *Environ Sci Technol* 2014;48:12002-11.
- Luo P, Bao LJ, Li SM, Zeng EY. Size-dependent distribution and inhalation cancer risk of particle-bound polycyclic aromatic hydrocarbons at a typical e-waste recycling and an urban site. *Environ Pollut* 2015;200:10-5.
- Ma J, Horii Y, Cheng JP, Wang WH, Wu Q, Ohura T, et al. Chlorinated and parent polycyclic aromatic hydrocarbons in environmental samples from an electronic waste recycling facility and a chemical industrial complex in China. *Environ Sci Technol* 2009;43:643-9.
- Menichini E, Merli F. Dibenzopyrenes, other PAHs with molecular weight 302, and selected carcinogenic PAHs seldom determined: identification and one-year quantification in urban air. *Intern J Environ Anal Chem* 2012;92:1609-25.

- Ohura T, Sawada KI, Amagai T, Shinomiya M. Discovery of novel halogenated polycyclic aromatic hydrocarbons in urban particulate matters: Occurrence, photostability, and AhR activity. *Environ Sci Technol* 2009;43:2269-75.
- Perera FP, Tang DL, Wang S, Vishnevetsky J, Zhang BZ, Diaz D, et al. Prenatal Polycyclic Aromatic Hydrocarbon (PAH) Exposure and Child Behavior at Age 6-7 Years. *Environ Health Perspect* 2012;120:921-6.
- Reisen F, Arey J. Atmospheric reactions influence seasonal PAH and nitro-PAH concentrations in the Los Angeles basin. *Environ Sci Technol* 2005;39:64-73.
- Satsangi A, Pachauri T, Singla V, Lakhani A, Kumari KM. Organic and elemental carbon aerosols at a suburban site. *Atmos Res* 2012;113:13-21.
- Shen GF, Wang W, Yang YF, Zhu C, Min YJ, Xue MA, et al. Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China. *Atmos Environ* 2010;44:5237-43.
- Shen HZ, Huang Y, Wang R, Zhu D, Li W, Shen GF, et al. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environ Sci Technol* 2013;47:6415-24.
- Tan JH, Guo SJ, Ma YL, Duan JC, Cheng Y, He KB, et al. Characteristics of particulate PAHs during a typical haze episode in Guangzhou, China. *Atmos Res* 2011;102:91-8.
- Tsapakis M, Stephanou EG. Diurnal cycle of PAHs, nitro-PAHs, and oxy-PAHs in a high oxidation capacity marine background atmosphere. *Environ Sci Technol* 2007;41:8011-7.
- Wang J, Chen SJ, Tian M, Zheng XB, Gonzales L, Ohura T, et al. Inhalation cancer risk associated with exposure to complex polycyclic aromatic hydrocarbon mixtures in an electronic waste and urban area in South China. *Environ Sci Technol* 2012a;46:9745-52.
- Wang WT, Jariyasopit N, Schrlau J, Jia YL, Tao S, Yu TW, et al. Concentration and Photochemistry of PAHs, NPAHs, and OPAHs and Toxicity of PM_{2.5} during the Beijing Olympic Games. *Environ Sci Technol* 2011a;45:6887-95.
- Wang WT, Simonich SLM, Wang W, Giri B, Zhao JY, Xue MA, et al. Atmospheric polycyclic aromatic hydrocarbon concentrations and gas/particle partitioning at background, rural village and urban sites in the North China Plain. *Atmos Res* 2011b;99:197-206.
- Wang Y, Tian ZJ, Zhu HL, Cheng ZN, Kang ML, Luo CL, et al. Polycyclic aromatic hydrocarbons (PAHs) in soils and vegetation near an e-waste recycling site in South China: Concentration, distribution, source, and risk assessment. *Sci Total Environ* 2012b;439:187-93.
- Watanabe M, Noma Y. Influence of combustion temperature on formation of nitro-PAHs and decomposition and removal behaviors in pilot-scale waste incinerator. *Environ Sci Technol* 2009;43:2512-8.

- Wei C, Han YM, Bandowe BAM, Cao JJ, Huang RJ, Ni HY, et al. Occurrence, gas/particle partitioning and carcinogenic risk of polycyclic aromatic hydrocarbons and their oxygen and nitrogen containing derivatives in Xi'an, central China. *Sci Total Environ* 2015;505:814-22.
- Wei SL, Huang B, Liu M, Bi XH, Ren ZF, Sheng GY, et al. Characterization of PM_{2.5}-bound nitrated and oxygenated PAHs in two industrial sites of South China. *Atmos Res* 2012;109:76-83.
- Wiriya W, Chantara S, Sillapapiromsuk S, Lin N-H. Emission profiles of PM₁₀-bound polycyclic aromatic hydrocarbons from biomass burning determined in chamber for assessment of air pollutants from open burning. *Aerosol Air Qual Res* 2016;in press.
- Witter AE, Nguyen MH. Determination of oxygen, nitrogen, and sulfur-containing polycyclic aromatic hydrocarbons (PAHs) in urban stream sediments. *Environ Pollut* 2016;209:186-96.
- Xia ZH, Duan XL, Tao S, Qiu WX, Liu D, Wang YL, et al. Pollution level, inhalation exposure and lung cancer risk of ambient atmospheric polycyclic aromatic hydrocarbons (PAHs) in Taiyuan, China. *Environ Pollut* 2013;173:150-6.
- Xu SS, Liu WX, Tao S. Emission of polycyclic aromatic hydrocarbons in China. *Environ Sci Technol* 2006;40:702-8.
- Yang YY, Guo PR, Zhang Q, Li DL, Zhao L, Mu DH. Seasonal variation, sources and gas/particle partitioning of polycyclic aromatic hydrocarbons in Guangzhou, China. *Sci Total Environ* 2010;408:2492-500.
- Zeraatpishe M, Khormali F. Carbon stock and mineral factors controlling soil organic carbon in a climatic gradient, Golestan province. *J Soil Sci Plant Nut* 2012;12:637-54.
- Zhang YL, Huang RJ, El Haddad I, Ho KF, Cao JJ, Han Y, et al. Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013. *Atmos Chem Phys* 2015;15:1299-312.
- Zhang YX, Schauer JJ, Zhang YH, Zeng LM, Wei YJ, Liu Y, et al. Characteristics of particulate carbon emissions from real-world Chinese coal combustion. *Environ Sci Technol* 2008;42:5068-73.
- Zhang YX, Tao S, Cao J, Coveney RM. Emission of polycyclic aromatic hydrocarbons in China by county. *Environ Sci Technol* 2007;41:683-7.
- Zimmermann K, Jariyasopit N, Simonich SLM, Tao S, Atkinson R, Arey J. Formation of nitro-PAHs from the heterogeneous reaction of ambient particle-bound PAHs with N₂O₅/NO₃/NO₂. *Environ Sci Technol* 2013;47:8434-42.

Figure caption

Fig. 1 Seasonal variations of the mean concentrations of PM, OC, and EC in the air in the urban area (A column) and e-waste area (B column) in South China. Error bars represent standard deviations.

Fig. 2 Seasonal variations of the mean concentrations of PAHs in PM in the urban area (A column) and e-waste area (B column) in South China. Error bars represent standard deviations.

Table 1 Concentrations of PAHs (ng/m³), OC (mg/g), and EC (mg/g) in particulate matter at the urban and rural e-waste sites in South China in 2010-2011.

Target	Urban site			E-waste site		
	Range	Median	Mean	Range	Median	Mean
Organic carbon (OC)	60.46-235.6	119.4	120.5	44.63-181.1	116.3	115.6
Elemental carbon (EC)	10.04-87.86	30.72	36.73	7.903-58.10	20.49	22.68
Acenaphthene (ACE)	0.018-0.184	0.060	0.072	0.021-0.679	0.074	0.113
Acenaphthylene (ACY)	0.012-0.210	0.033	0.049	0.005-0.148	0.021	0.030
Anthracene (ANT)	0.022-0.613	0.101	0.139	0.012-0.892	0.077	0.156
Benz[a]anthracene (BaA)	0.120-3.767	0.584	0.968	0.109-6.570	0.685	1.454
Benz[c]fluorene (BcF)	0.034-1.315	0.139	0.215	0.029-2.789	0.183	0.374
Benzo(e)pyrene (BeP)	0.368-10.16	1.752	2.406	0.412-15.59	2.154	3.584
Benzo(a)pyrene (BaP)	0.265-8.109	1.098	1.824	0.439-11.40	1.919	3.125
Benzo(b)fluoranthene (BbF)	0.701-11.60	2.832	3.712	0.766-16.31	3.308	5.143
Benzo(ghi)perylene (BghiP)	0.521-13.56	1.964	2.647	0.735-13.84	3.163	4.009
Benzo(k)fluoranthene (BkF)	0.192-8.519	0.991	1.498	0.202-19.45	1.212	2.449
Chrysene (CHR)/ Triphenylene (TRI)	0.122-5.658	0.575	1.204	0.090-7.641	0.652	1.580
Dibenz(a,h)anthracene (DahA)	0.025-0.982	0.115	0.182	0.037-1.018	0.241	0.306
Dibenzo[a,c]anthracene (DacA)	0.068-2.567	0.282	0.485	0.114-3.340	0.622	0.875
Dibenzothiophene (DBT)	n.d.-0.237	0.029	0.040	0.003-0.174	0.023	0.034
Fluoranthene (FLA)	0.300-11.48	1.476	1.929	0.164-13.66	1.510	2.474
Fluorene (FLU)	n.d. ^a -0.376	0.056	0.074	0.007-0.410	0.046	0.072
Indeno(1,2,3-cd)pyrene (IcdP)	0.607-12.52	1.822	2.423	1.029-10.86	3.133	3.701
Naphthalene (NAP)	0.007-0.264	0.076	0.093	0.010-0.157	0.042	0.053
Phenanthrene (PHE)	0.217-6.672	0.645	0.944	0.063-7.014	0.514	0.948
Pyrene (PYR)	0.282-9.696	0.855	1.460	0.132-12.79	1.175	2.024
Retene (RET)	n.d.-1.796	0.229	0.315	0.045-3.016	0.324	0.469
Coronene (COR)	0.125-2.078	0.479	0.639	0.209-3.321	0.906	1.067
Picene (PIC)	0.046-1.404	0.198	0.293	0.103-2.029	0.463	0.600
Methylated PAHs ^b	0.063-2.093	0.397	0.532	0.080-3.444	0.374	0.750
Total MW < 302 PAHs	5.074-79.67	17.89	24.14	5.962-114.1	23.55	35.39
∑ ₁₆ PAHs ^c	3.953-61.41	14.30	19.22	4.434-89.66	18.30	27.64
Total MW 302 PAHs ^d	0.282-7.855	1.422	1.881	0.538-11.76	3.045	3.686
CIPAHs ^e	0.001-0.075	0.011	0.022	0.002-0.171	0.017	0.033
BrPAHs ^f	n.d.-0.051	0.003	0.006	n.d.-0.253	0.009	0.017
HPAHs ^g	0.001-0.122	0.016	0.028	0.003-0.307	0.029	0.050

^a Not detectable.

^b Include 1,3-DMNAP, 1-MNAP, 1-MPHE, 1-MPYR, 2-MANT, 2-MNAP, 2-MPHE, 2,6-DMNAP, 3,6-DMPHE, and 6-MCHR.

^c The 16 US EPA's priority PAHs.

^d Include BbP, DBaeF/DBbkF, DBaeP, DBahP, DBaiP, DBalP, DBelP, DBjlF, DBakF, N12bF, N23aP, N23bF, N23eP, N23jF, N23kF.

^e Include 1,3-CIFLU, 1,9-CIPHE, 1-CIPYR, 2-CIANT, 3,4-CIFLU, 3,8-CIFLU, 3,9,10-CIPHE, 3-CIBZA, 3-CIFLU, 6,12-CICHR, 6 ClBaP, 7,12-ClBaA, 7-ClBaA, 8-CIFLU, 9,10-CIANT, 9-CIANT.

^f Include 1BrPYR, 2 BrFLU, 4,7-BrBaA, 5,7-BrBaA, 5,7-BrBaA, 7,11-BrBaA, 7,12-BrBaA, 7-BrBaA, 9,10-BrANT, 9-BrANT, 9-BrPHE.

^g Sum of CIPAHs and BrPAHs.

Table 2 PAH molecular diagnostic ratios in the particulate matter at the urban and rural e-waste sites in South China.^a

Ratio	Urban site			E-waste site		
	Range	Median	Mean	Range	Median	Mean
ANT/(ANT+PHE)	0.04-0.50	0.14	0.14	0.05-0.53	0.15	0.16
BaA/(BaA+CHR)	0.37-0.60	0.45	0.47	0.34-0.72	0.52	0.52
FLA(FLA+PYR)	0.49-0.82	0.58	0.58	0.47-0.83	0.55	0.56
IcdP/(IcdP+BghiP)	0.41-0.57	0.50	0.49	0.41-0.58	0.49	0.50
BaP/BghiP	0.13-1.25	0.64	0.68	0.30-1.20	0.76	0.71

^a ANT/(ANT+PHE): <0.1, petrogenic, >0.1 pyrogenic; BaA/(BaA+CHR): <0.2, petrogenic, >0.35 pyrogenic; FLA(FLA+PYR): <0.4, petrogenic, 0.4-0.5, liquid fuel combustion, >0.5 coal/biomass combustion; IPY/(IPY+BghiP): <0.2, petrogenic, 0.2-0.5, liquid fuel combustion, >0.5 coal/biomass combustion; BaP/BghiP: <0.6, nontraffic, >0.6 traffic (Katsoyiannis et al., 2011).

Table 3 Source apportionment (%) of PAHs in the particulate matter in each month
(between May 2010 and April 2011) at the urban and rural e-waste sites in South China.

Sampling month	Urban site				E-waste site			
	Industrial boilers	Biomass burning	Residential stoves	Vehicular exhaust	Industrial boilers	Biomass burning	Residential stoves	Vehicular exhaust
MAY	36.0±2.0	7.39±11	46.2±7.5	10.4±5.4	79.7±15	13.9±7.4	4.75±7.1	1.68±2.9
JUN	38.0±3.0	0.00	48.3±4.6	13.8±1.9	71.8±25	9.06±7.8	12.4±21	6.80±11
JUL	41.0±7.4	0.00	43.8±11	15.2±4.6	56.2±29	3.53±6.1	30.8±27	9.45 ±8.4
AUG	37.7±2.0	0.13±0.3	45.7±2.5	14.4±2.0	46.6±5.6	0.00	37.5±4.1	15.9±2.0
SEP	38.6±6.9	2.36±4.1	45.1±9.1	14.0±5.5	67.3±22	15.6±15.1	10.7±15	6.43±8.3
OCT	24.3±3.7	31.8±9.0	43.6±5.3	0.30±0.7	25.6±5.5	21.4±11.6	45.8±11	7.23±6.0
NOV	29.5±11	31.5±7.6	32.3±12	6.65±7.9	35.0±11	22.5±4.8	30.0±15	12.48±5.3
DEC	27.4±1.1	33.2±3.2	21.3±3.5	18.2±3.2	24.6±3.3	46.1±7.1	13.2±10	16.05±6.9
JAN	6.2±1.4	71.6±13	22.2±14	0.00	14.1±3.4	32.7±4.1	51.3±7.2	1.85±4.0
FEB	27.8±5.1	31.8 ±3.5	26.5±14	13.9±10	28.6±6.1	30.4±10	28.0±12	13.0 ±9.1
MAR	29.2±8.5	25.8 ±17	38.7±17	6.39±6.7	28.6±14	26.5±6.2	35.6±27	9.32±9.7
APR	28.6±8.3	23.1 ±21	39.1±12	9.29±7.3	38.8±11	23.6±7.1	25.2±14	12.4±7.4

Figure 1 (2-column)

Figure 2 (2-column)