



Size-dependent distribution and inhalation cancer risk of particle-bound polycyclic aromatic hydrocarbons at a typical e-waste recycling and an urban site



Pei Luo ^{a, d}, Lian-Jun Bao ^a, Shao-Meng Li ^c, Eddy Y. Zeng ^{a, b, *}

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b School of Environment, Jinan University, Guangzhou 510632, China

^c Air Quality Research Division, Environment Canada, 4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

^d University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 7 January 2015

Received in revised form

6 February 2015

Accepted 7 February 2015

Available online

Keywords:

Particle size distribution

Polycyclic aromatic hydrocarbons

Atmospheric deposition

Cancer risk

ABSTRACT

Atmospheric particle size distribution of polycyclic aromatic hydrocarbons (PAHs) in a typical e-waste recycling zone and an urban site (Guangzhou) in southern China featured a unimodal peak in 0.56–1.8 μm for 4–6 ring PAHs but no obvious peak for 2–3 ring PAHs at both sites. The atmospheric deposition fluxes of PAHs were estimated at $5.4 \pm 2.3 \mu\text{g m}^{-2} \text{d}^{-1}$ in the e-waste recycling zone and $3.1 \pm 0.6 \mu\text{g m}^{-2} \text{d}^{-1}$ in Guangzhou. In addition, dry and wet deposition fluxes of PAHs were dominated by coarse ($D_p > 1.8 \mu\text{m}$) and fine particles ($D_p < 1.8 \mu\text{m}$), respectively. Fine particles predominated the deposition of PAHs in the lung. The results estimated by incremental inhalation cancer risk suggested that particle-bound PAHs posed serious threat to human health within the e-waste recycling zone and Guangzhou.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Air pollution has become a significant environmental and health concern in China (Chan and Yao, 2008; Chen et al., 2013). It was estimated that the life expectancy has been approximately 5.5 years lower for residents of northern China than for those living in southern China, likely because of sustained exposure to higher atmospheric total suspended particulates (Chen et al., 2013). In addition, atmospheric particulate matter has been shown to associate with abundant toxic pollutants, with polycyclic aromatic hydrocarbons (PAHs) accounting for the largest portion of the lung cancer risks (Hemminki and Pershagen, 1994). To demonstrate the severity of the situation, Zhang et al. (2009) estimated that incremental annual lung cancer risk due to inhalation exposure to PAHs was up to 6.5 per million people in China. Furthermore, the annual emission of PAHs in China (114 Gg y^{-1}) accounted for 22% of the total global emission in 2004 (Zhang and Tao, 2009), which is largely dissipated in the atmosphere initially.

Particle size distribution is a critical parameter for assessing health risks via inhalation, which has been shown to be size-dependent (Kameda et al., 2005; Luo et al., 2014a; Zhang et al., 2012c). Therefore, it is essential to consider the relative contributions of different sized particles to inhalation cancer risk by particle-bound PAHs in the atmosphere. In recent years, a number of studies on the size distribution of particle-bound PAHs have been conducted (Allen et al., 1996; Bi et al., 2005). However, the health risk of exposure to size-fractionated particle-bound PAHs is less well understood, especially in urbanized densely populated areas and primitive e-waste recycling zones. In addition, atmospheric dry and wet deposition is an important pathway for pollutants to cross the air-earth interface and to be removed from the atmosphere, which implicates greatly for the long-range transport potential of pollutants (Bidleman, 1988). Dry and wet deposition fluxes of particle-bound pollutants were also particle size-dependent (Luo et al., 2014b; Zhang et al., 2012a, 2012d).

Nearly 50 million tons of e-waste are generated worldwide each year, and a large portion of it is shipped to China where it is processed often with primitive methods to recover useful materials (Schluep et al., 2009; Zhang et al., 2012b). A variety of toxic contaminants, including PAHs, are released to the surrounding environment during e-waste recycling (such as e-waste burning), and

* Corresponding author. School of Environment, Jinan University, Guangzhou 510632, China.

E-mail address: eddyzeng@gig.ac.cn (E.Y. Zeng).

unprotected workers and residents living near e-waste processing facilities are exposed to these pollutants (Wong et al., 2007; Zhang et al., 2012b). In our previous study (Luo et al., 2014a), resident exposure to halogenated flame retardants, widely used in household electronic appliances, within an e-waste recycling zone was found to be of low health risk. It was therefore hypothesized that other contaminants such as PAHs may have posed more serious threats to human health. A previous study found that the inhalation cancer risk of parent and halogenated PAHs in an e-waste recycling area was 740–1200 cases per million people (Wang et al., 2012). However, this previous study only characterized PAHs in total suspended particulates.

To verify whether PAHs posed substantial human health risk in e-waste recycling areas as compared to typical urban regions, we conducted a sampling campaign in a typical e-waste recycling zone and an urban site. The main objectives of the present study were to examine the size distribution of particle-bound PAHs and estimate the atmospheric deposition fluxes and cancer risk of PAHs in the e-waste recycling zone and urban site. The acquired information is expected to aid a better understanding of the fate and health risk of PAHs associated with e-waste recycling activities.

2. Materials and methods

2.1. Sample collection

Size-fractionated particle samples were collected directly with a Micro-Orifice Uniform Deposit Impactor (MOUDI; MSP Corporation, Shoreview, MN, USA) from an e-waste recycling site in Qingyuan and an urban site in Guangzhou, Guangdong Province of southern China (Fig. S1 of the Supplemental Material; “S” indicates tables and figures in the Supplemental Material afterwards), in September–November 2012. Particle samples were separated into 11 fractions: >18, 10–18, 5.6–10, 3.2–5.6, 1.8–3.2, 1.0–1.8, 0.56–1.0, 0.32–0.56, 0.18–0.32, 0.10–0.18, and 0.056–0.10 μm on glass microfibre filters (Whatman International, Maidstone, England). Sampling took place at the ground level (1.5 m) and two rooftop levels (5 and 20 m) in Qingyuan and at 1.5 m and a rooftop level (20 m) in Guangzhou. Overall, 8 sets of size-fractionated samples were collected at each height in the e-waste recycling zone, and 7 and 4 sets of samples were at 1.5 m and 20 m in Guangzhou, respectively. Because outdoor activities mainly occur on the ground where mechanical processes and dust resuspension are significant, the data acquired at 20 and 1.5 m of both sampling sites were used for estimating atmospheric deposition fluxes and conducting human risk assessment, respectively.

2.2. Sample analysis

The size-fractionated samples were spiked with surrogate standards (acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , perylene- d_{12} , benzo[*g,h,i*]perylene- d_{12} , and coronene- d_{12}) and ultrasonically extracted three times with a mixed solvent containing *n*-hexane, dichloromethane, and acetone (1:1:1 in volume). Water was removed from the extracts with anhydrous sodium sulfate. After being concentrated to 50 μL under nitrogen flow, the internal standards (fluoranthene- d_{10} , pyrene- d_{10} , and dibenzo[*a,h*]anthracene- d_{14}) were added before instrumental analysis.

The concentrations of PAHs were determined with gas chromatographic mass spectrometry (Shimadzu QP2010 Plus, Kyoto, Japan) using electron impact ionization. Chromatographic separation of PAHs was achieved with a 30 m (0.25 mm i.d. and 0.25 μm film thickness) TG-5MS column (Thermo Scientific; West Palm Beach, FL, USA). The oven temperature was programmed starting from 60 $^{\circ}\text{C}$ (held for 1 min), increased to 200 $^{\circ}\text{C}$ at a rate of

6 $^{\circ}\text{C min}^{-1}$ (held for 2 min), to 300 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C min}^{-1}$ (held for 20 min). Mass spectra were scanned from 50 to 500 mass units in the full-scan mode.

2.3. Quality assurance and quality control

The recoveries of the surrogate standards acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , perylene- d_{12} , benzo[*g,h,i*]perylene- d_{12} , and coronene- d_{12} were $65 \pm 13\%$, $79 \pm 11\%$, $102 \pm 16\%$, $104 \pm 21\%$, and $101 \pm 22\%$ in field samples and $64 \pm 12\%$, $75 \pm 12\%$, $101 \pm 12\%$, $97 \pm 14\%$, and $95 \pm 20\%$ in all blank samples. Concentrations of PAHs in all field samples were corrected by the corresponding procedural blanks in the same batch, but not corrected for the surrogate standard recoveries. The lowest calibration concentration divided by the actual sample volume was used as the reporting limit for a target compound. In the present study with an average air sampling volume of 21.6 m^3 and a final extract volume of 50 μL , the reporting limit was 11.6 pg m^{-3} for all PAHs.

2.4. Estimation of atmospheric deposition fluxes

Dry and wet deposition fluxes (F_{dry} and F_{wet} , respectively) of particle-bound PAHs were calculated by (Luo et al., 2014b; Zhang et al., 2012d)

$$F_{\text{dry}} = \sum (C_i \times V_i) \quad (1)$$

$$F_{\text{wet}} = W_T \times \sum (C_i \times \eta_i) \times Q \quad (2)$$

where C_i is the concentration of PAH in a specific size fraction i ; V_i and η_i are dry deposition velocity and removal efficiency of a specific size fraction; W_T is the wet washout ratio (a conservative value of 10^5 was chosen for all PAHs because the W_T data of PAHs span several orders of magnitude from 10^3 to 10^7 (Birgöl et al., 2011; Guo et al., 2014; Offenberger and Baker, 2002)); and Q is the monthly precipitation amount. Because wet deposition flux was highly dependent on rain amount, an average value of the monthly precipitation amounts in the past ten years was selected, i.e., 55 mm in October and November for Qingyuan (<http://www.gdqy.gov.cn> and therein) and 179 mm in September for Guangzhou (<http://data.gzstats.gov.cn/gzStat1/chaxun/njsj.jsp>). The V_i and η_i data were directly adopted from Zhang et al. (2012d) and Radke et al. (1980) (Table S1). The sum of dry and wet deposition flux is defined as total deposition flux.

2.5. Health risk assessment

Size-fractionated particles can be divided into three fractions in terms of their efficiencies of entering into the regions of the human respiratory system, i.e., inhalable (inhaled through the nose and/or mouth), thoracic (penetrating progressively into the lung), and respirable (reaching beyond the gas exchange region) fractions, based on the criteria given by the International Standards Organization and American Conference of Governmental Industrial Hygienists (Hinds, 1999). Particles can deposit in different regions of the human respiratory tract. The fractions of PAHs deposited in the head airway, tracheobronchial, and alveolar regions were estimated with the simplified equations from the International Commission on Radiological Protection (ICRP) model (Hinds, 1999; International Commission on Radiological Protection, 1994). More details about the models are provided in the Supplemental Material.

Human incremental lifetime cancer risk (CR) was estimated by

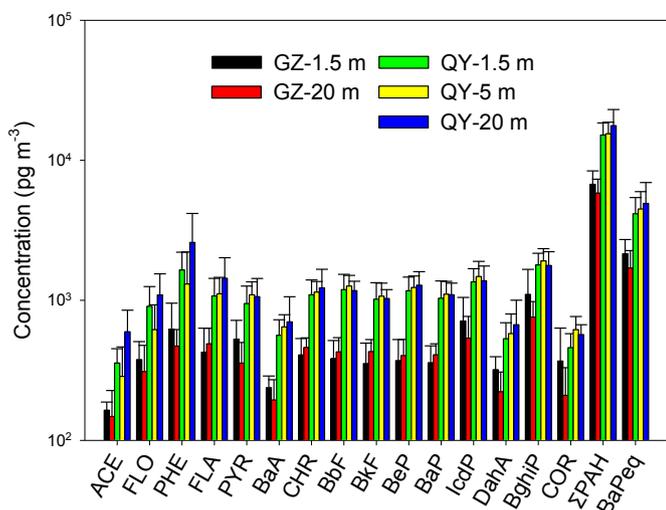


Fig. 1. Concentration of particle-bound PAHs at different heights in the e-waste recycling zone (QY) and Guangzhou (GZ) (Fig. S1). All acronyms are defined in Table S2.

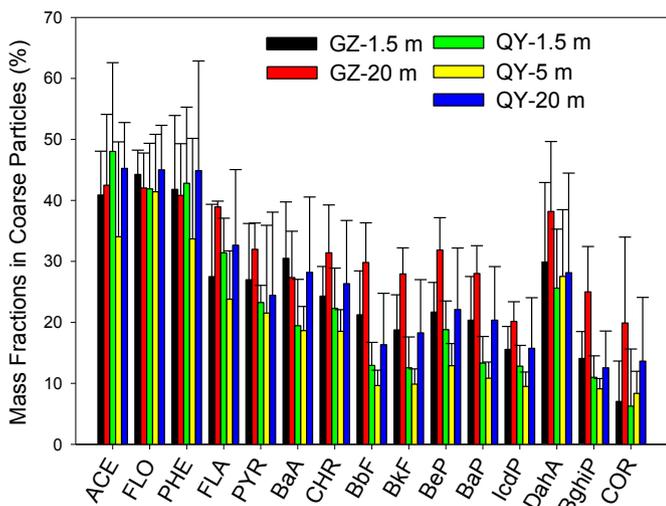


Fig. 2. Mass fractions of PAHs in coarse particles (aerodynamic diameters > 1.8 μm) at different heights in the e-waste recycling zone (QY) and Guangzhou (GZ) (Fig. S1). All acronyms are defined in Table S2.

$$CR = \sum (C_{PAH} \times TEF_{PAH}) \times UR_{BaP} \quad (3)$$

where C_{PAH} is the concentration of a specific PAH; TEF_{PAH} is the toxicity equivalency factor of PAH based on benzo[a]pyrene (Table S2); and UR_{BaP} is the unit relative risk of benzo[a]pyrene, which is 1.1×10^{-6} per ng m⁻³ from an inhalation study using hamsters (Office of Environmental Health Hazard Assessment, 2005) or 8.7×10^{-5} per ng m⁻³ from epidemiology studies on coke-oven workers (World Health Organization, 2000) over a lifetime of 70 years. The bulk and deposition concentrations of PAHs, defined as the sum concentrations of PAHs distributed in all size fractions and in three regions of the human respiratory tract, respectively, were selected as C_{PAH} in the present study for exposure assessment. Detailed calculation procedures are provided in the Supplementary material. A Monte Carlo simulation method was used to deal with the uncertainty in the incremental lifetime cancer risk assessment. The concentrations of PAHs were assumed as log-

normal distribution and TEF_{PAH} values were presumably constant for specific PAHs.

3. Results and discussion

3.1. Concentration and size distribution of particle-bound PAHs

The average concentrations of total PAHs at all heights were 15.1–17.7 and 5.8–6.7 ng m⁻³ in the e-waste recycling zone and Guangzhou, respectively (Fig. 1 and Table S3). The concentrations of PAHs in the e-waste recycling zone were significantly higher (t -test; $p < 0.05$) than those in Guangzhou, implicating e-waste recycling activities as an additional source of PAHs. The concentrations of PAHs at both sites were not significantly different among different heights (t -test; $p > 0.05$), suggesting vertically well mixed air within the range of the heights under investigation.

Size distributions of PAHs were similar in all samples, with an unimodal peak at 0.56–1.8 μm for 4–6 ring PAHs but no appreciable peaks for 2–3 ring PAHs (except for fluoranthene) (Figs. S2–S6). On average, 72–94% and 61–93% of 4–6 ring PAHs were affiliated with fine particles ($D_p < 1.8$ μm) in the e-waste recycling zone and Guangzhou, respectively (Fig. 2). In particular, 0.56–1.8 μm particles contained the most abundant 4–6 ring PAHs. The relatively high fractions of low molecular weight PAHs in coarse particles ($D_p > 1.8$ μm) can be ascribed to volatilization and condensation of these PAHs, which can revolatilize and re-adsorb to coarse particles after being emitted from combustion such as in vehicle exhausts (Zhang et al., 2012c, 2012d).

To depict the size distribution of PAHs concisely, mass geometric aerodynamic diameter (GMD) and geometric standard deviation (GSD) were calculated for each PAH compound. The GMD values of individual PAHs in particles were in the ranges of 0.46–1.86 and 0.58–1.40 μm, respectively, in the e-waste recycling zone and Guangzhou (Table S4). In addition, higher molecular weight PAHs had lower GMDs and GSDs (Table S4), i.e., GSD is larger for

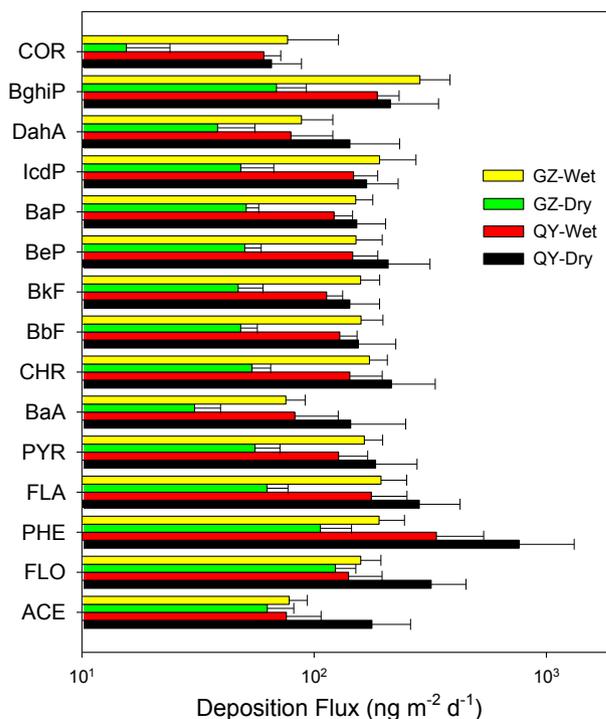


Fig. 3. Estimated dry and wet deposition fluxes of particle-bound PAHs in the e-waste recycling zone (QY) and Guangzhou (GZ) (Fig. S1). All acronyms are defined in Table S2.

compounds with higher saturation vapor pressures due to volatilization. Another possibility was gas adsorption onto the collection filters on the upper stages of the MOUDI sampler for high vapor pressure compounds.

Mass fractions of 4–6 ring PAHs in fine particles in Guangzhou were lower than those in the e-waste recycling zone (Fig. 2), attributed to different input sources of PAHs (Wang et al., 2012). Generally, e-waste recycling and dismantling activities, such as open burning of plastics and e-waste, may constitute an important source of PAHs in addition to biomass burning in the e-waste recycling zone (Wang et al., 2012). On the other hand, combustion of fossil fuel, motored-vehicle exhausts (which contain submicron particles), and biomass burning are the primary sources of PAHs in urban areas of China (Zhang and Tao, 2009). Another possible reason was the influence of temperature on the gas-particle partition of PAHs in the atmosphere (Tsapakis and Stephanou, 2005). Sampling was conducted in Guangzhou in September (average daily temperatures of 26–28 °C) and in the e-waste recycling zone in October and November (average daily temperatures of 18–22 °C). Higher temperatures in Guangzhou may have facilitated the transfer of PAHs from particles to the gaseous phase and subsequently allowed more PAHs to redeposit in all sized particles. As a result, more PAHs were transferred into the coarse particles from fine particles (Zhang et al., 2012d).

3.2. Implications for atmospheric deposition

The total atmospheric deposition fluxes of PAHs in the e-waste recycling zone and Guangzhou were 5.4 ± 2.3 and $3.1 \pm 0.6 \mu\text{g m}^{-2} \text{d}^{-1}$, respectively (Table S5), comparable with previously reported results. For example, the dry and wet deposition fluxes of PAHs in Guangzhou in September 2010 were 0.26 and $2.0 \mu\text{g m}^{-2} \text{d}^{-1}$, respectively (Guo et al., 2014). The mean deposition flux of PAHs was $1.55 \mu\text{g m}^{-2} \text{d}^{-1}$ in Guangzhou in September, 2001 (Li et al., 2009). It is noted that the estimated dry deposition flux of PAHs was 1.6 times higher than the wet deposition flux in the e-waste recycling zone, but the opposite was true in Guangzhou (Fig. 3 and Table S5). This pattern was consistent with the previous findings that dry and wet deposition fluxes of PAHs were relatively higher in dry and wet weather seasons, respectively (Guo et al., 2014; Li et al., 2009).

Coarse particles accounted for $57 \pm 14\%$ and $54 \pm 9\%$ of total dry deposition fluxes of PAHs in the e-waste recycling zone and Guangzhou, respectively, and $36 \pm 11\%$ and $41 \pm 3\%$ of wet deposition fluxes (Figs. S7–S8). Our previous studies also indicated that coarse and fine particles dominated dry and wet deposition fluxes, respectively (Luo et al., 2014b; Zhang et al., 2012d).

The mean dry deposition velocities of PAHs were $0.13\text{--}0.34 \text{ cm s}^{-1}$ in the e-waste recycling zone and $0.079\text{--}0.35 \text{ cm s}^{-1}$ in Guangzhou (Table S5). More volatile PAHs had higher dry deposition velocities (Table S5), as they were more abundant in larger-sized particles. These values were close to those ($0.12\text{--}0.35 \text{ cm s}^{-1}$) in Guangzhou in 2010 and other values (0.2 and 0.28 cm s^{-1}) assumed in previous studies (Hillery et al., 1998; Miller et al., 2000; Zhang et al., 2012d), but were slightly lower than another empirical value (0.5 cm s^{-1}) (Eisenreich et al., 1981; Zhang et al., 2012d). Therefore, deposition fluxes of particle-bound PAHs may be underestimated or overestimated with the use of bulk concentrations in the atmosphere and total deposition velocities.

3.3. Inhalation exposure to PAHs

The efficiencies for particles entering into a human body and deposition of inhaled particles in the respiratory tract were highly particle-size dependent. The inhalable, thoracic, and respirable

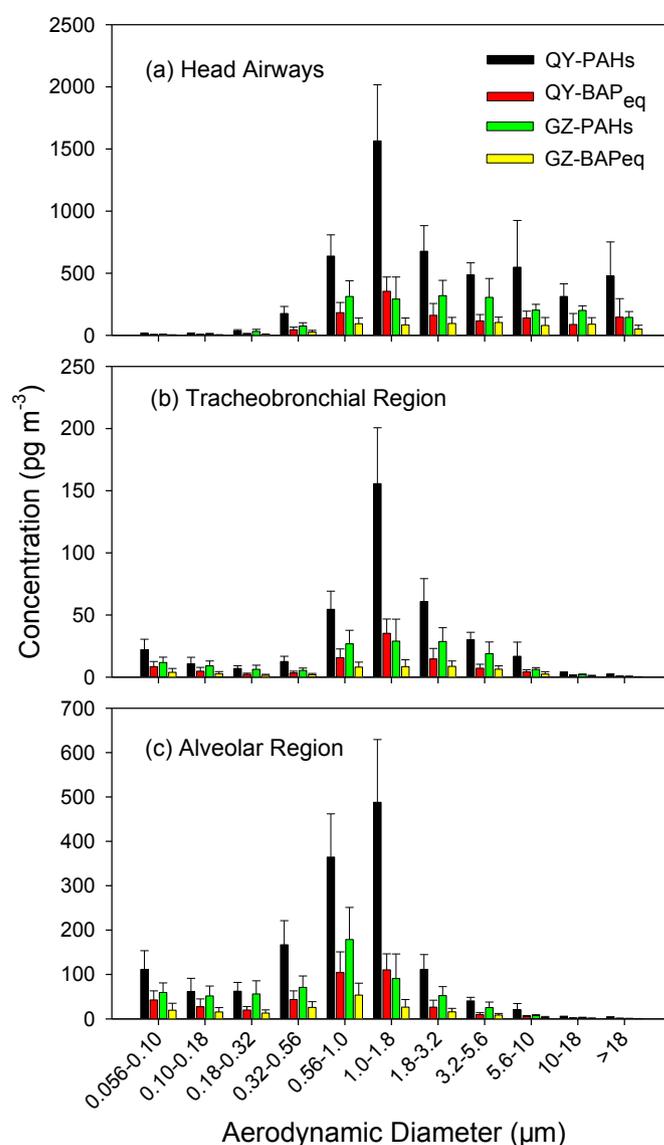


Fig. 4. Size-dependent concentrations of particle size-fractionated PAHs deposited in different regions of the human respiratory tract in the e-waste recycling zone (QY) and Guangzhou (GZ) (Fig. S1).

fractions of PAHs were estimated based on the criteria given by the International Standards Organization and American Conference of Governmental Industrial Hygienists (Hinds, 1999). The deposited fractions of PAHs in the human respiratory tract for a normal adult with a breathing frequency of 12 breaths per minute were estimated with the simplified ICRP model (Hinds, 1999; International Commission on Radiological Protection, 1994). The calculated inhalable, thoracic, and respirable fractions of PAH concentrations were 90–97%, 78–97%, and 66–94% in Qingyuan and 91–97%, 80–95% and 67–93% in Guangzhou (Table S6). By comparison, only 37–52% and 30–50% of PAHs in the e-waste recycling zone and Guangzhou could deposit in the human respiratory tract as determined from the ICRP model. This result was due to the presence of abundant PAHs in fine particles, which not only carry more PAHs deep into the human respiratory tract but also can exhale PAHs out from human body. Therefore, inhalation exposure risk would be overestimated using the bulk, inhalable, thoracic, or respirable concentrations of PAHs.

Head airways retained the most abundant fraction of PAHs,

followed by the alveolar and tracheobronchial regions (Table S7). In particular, 8.1–10.0% and 7.9–9.2% of inhaled PAHs were found to deposit in the alveolar region of humans in the e-waste recycling zone and Guangzhou, respectively, which were lower than those at roadside and suburban sites in Japan (16–19%) (Kawanaka et al., 2009) but close to that at an indoor environment of Guangzhou (8.6–10.2%) (Zhang et al., 2012c). It should be noted that the concentrations of PAHs deposited in different respiratory tract regions were size-dependent based on the ICRP model (Fig. 4). Apparently, coarse particles contributed the most to deposition fractions of PAHs in the head airways (69–91%), while fine particles were dominant in the alveolar (62–80%) and tracheobronchial regions (44–68%) at both sites. The PAHs deposited in the human respiratory tract, especially in the alveolar region, can be rapidly transferred into blood and tissues of the human body (Nemmar et al., 2002), inducing a systemic exposure to PAHs. When the concentrations of individual PAHs were converted to toxicity equivalent BaP_{eq} and summed together, the size distributions of bulk and deposition concentrations of BaP_{eq} were unimodal, peaking in the 0.56–1.8 μm at both sites (Fig. S9). Most BaP_{eq} concentrations were distributed in accumulation mode particles (D_p : 0.10–1.8 μm), i.e., accumulation mode particles were the predominant carriers of the carcinogenic toxicity of PAHs when benzo[a]pyrene was used as an indicator.

3.4. Health risk assessment

BaP_{eq} concentrations in the e-waste recycling zone were 4.2–5.0 ng m^{-3} , which exceed European Union's annual average BaP_{eq} standard (1 ng m^{-3}) (European Union, 2014) and China

National Daily BaP_{eq} standard (2.5 ng m^{-3}) (Minsrty of Environmental Protection of the People's Republic of China, 2012). On the other hand, BaP_{eq} concentrations (1.7–2.1 ng m^{-3}) in Guangzhou were lower than China National Daily BaP_{eq} standard, but higher than European Union's standard. As a result, residents living in the neighborhood of both study sites are subject to potential health risk with the e-waste recycling zone posing slightly higher risk than Guangzhou. The BaP_{eq} concentrations from the present study were close to previous results based on total suspended particulate measurements, e.g., 3.1–24 and 3.1–17 ng m^{-3} for 12 priority PAHs in an e-waste recycling zone and Guangzhou during 2010–2011 (Wang et al., 2012) and 13–27 ng m^{-3} for 16 priority PAHs in Beijing in 2005 (Liu et al., 2007).

Incremental lifetime cancer risk of inhalation exposure to PAHs was estimated by bulk concentrations and deposition concentrations. Two different UR_{BaP} values, 1.1×10^{-6} per ng m^{-3} (Office of Environmental Health Hazard Assessment, 2005) and 8.7×10^{-5} per ng m^{-3} (World Health Organization, 2000), were used in the assessment. With the bulk concentrations of PAHs in Table S3 and an UR_{BaP} value of 1.1×10^{-6} per ng m^{-3} , the average estimated incremental cancer risks were 4.6 (95% confidence interval (CI): 2.5–7.9) and 2.3 (95% CI: 1.36–3.8) cancer cases per million people with an average lifetime of 70 years in the e-waste recycling zone and Guangzhou, respectively. Alternatively, if an UR_{BaP} value of 8.7×10^{-5} per ng m^{-3} was used, the incremental cancer risks became 360 (95% CI: 195–620) and 184 (95% CI: 110–305) cases per million people in the e-waste recycling zone and Guangzhou. If the deposition concentrations (Table S7) were used, the incremental cancer risks were 1.9 (95% CI: 1.12–3.0) and 0.95 (95% CI: 0.56–1.52) ($UR_{BaP} = 1.1 \times 10^{-6}$ per ng m^{-3}) or 150 (95% CI: 92–230) and 75 (95% CI: 45–120) ($UR_{BaP} = 8.7 \times 10^{-5}$ per ng m^{-3}) per million people in the e-waste recycling zone and Guangzhou, respectively. The results corroborated the hypothesis made in our previous study (Luo et al., 2014a) that PAHs posed greater cancer risk than halogenated flame retardants within the e-waste recycling zone.

Cancer risks estimated by bulk and deposition concentrations of BaP_{eq} in the e-waste recycling zone and Guangzhou were also size-dependent (Fig. 5). With bulk concentrations, the most contributions to total cancer risk were made by the 0.32–1.8 μm fraction in both the e-waste recycling zone and Guangzhou. On the one hand, the most important contributor to the total cancer risk at both sites was PAHs in the 0.56–3.2 μm fraction if the deposition concentrations were used. In general, accumulation mode particles contributed the most to cancer risk.

The concentrations and masses of particle-bound pollutants collected with MOUDI samplers were 12–41% lower than those by total suspended particulate samplers in our previous studies (Zhang et al., 2012a, 2012d). In addition, indoor pollution by PAHs was more severe than outdoor pollution in China due to indoor use of solid fuels and cigarette smoking (Liu et al., 2001; Zhu et al., 2009). Therefore, incremental lifetime cancer risk due to inhalation of PAHs in a combined indoor and outdoor exposure scenario may be larger than that in the outdoor situation only.

In the present study, samples were collected only during a short time duration; therefore the results derived may not be reflective of long-term averages and/or seasonal variability. An additional limitation is that the cancer risk was estimated from the unit relative risk of benzo[a]pyrene, which was extrapolated from epidemiological or toxicological data for animals. Furthermore, the size-dependent toxicity of particles to human health should be critical for human health assessment, which was beyond the scope of the present study. Further studies are needed to acquire more data for a more accurate assessment of human health risk from inhalation of PAHs.

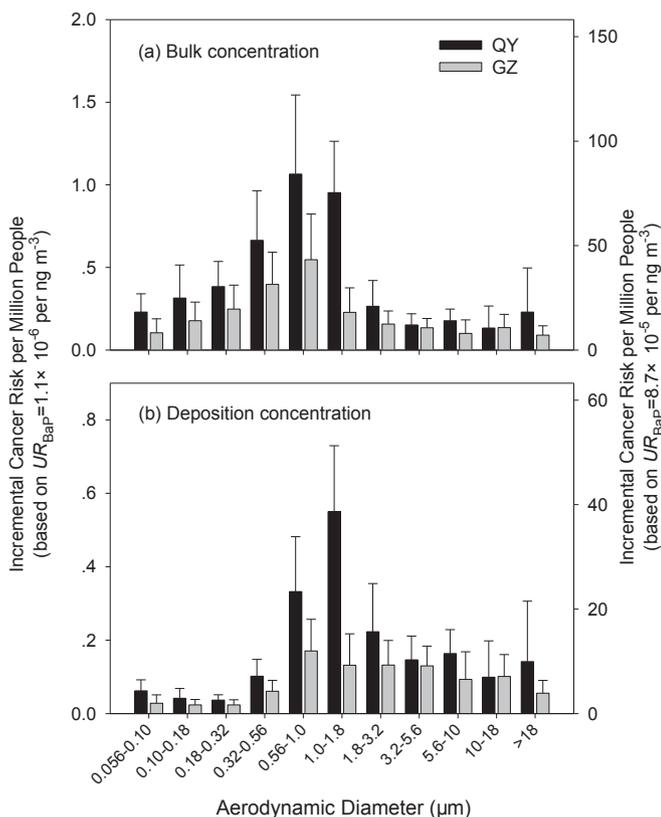


Fig. 5. Estimated incremental lifetime cancer risk of particle size-fractionated PAHs for residents in the e-waste recycling zone (QY) and Guangzhou (GZ) (Fig. S1) based on (a) bulk concentrations and (b) deposition concentrations using UR_{BaP} of 1.1×10^{-6} per ng m^{-3} (left y axes) (Office of Environmental Health Hazard Assessment, 2005) and 8.7×10^{-5} per ng m^{-3} (right y axes) (World Health Organization, 2000).

The results from the present study point to the need to further curtail the emissions of PAHs from any source, which is the most fundamental and critical strategy for lowering cancer risk from inhalation exposure to PAHs. Aside from implementation of strict control measures on conventional input sources such as coal combustion, vehicle emission, and cooking fuel in urban areas (Wang et al., 2012), proper handling of increasing amounts of e-waste is the key to battling additional sources of human health hazards in regions where large scale e-waste processing activities exist. Apparently, robust and low-cost dismantling and recycling technologies and strong government support are urgently needed in the new battle field.

4. Conclusions

Particle size-dependent profiles of both PAHs and BaP_{eq} concentrations peaked in the 0.56–1.8 μm fraction, and fine particles contributed most of the concentrations and respiratory deposition fractions for individual PAHs. In addition, use of total bulk concentrations and total deposition velocities may lead to large uncertainties in the estimated atmospheric deposition fluxes of particle-bound PAHs. The lifetime incremental cancer risks for inhalation of PAHs were size-dependent, with accumulation mode particles contributing the most, and were up to 360 and 184 cases per million people on average in the e-waste recycling zone and Guangzhou.

Acknowledgments

This study was financially supported by the National Natural Science Foundation of China (Nos. 41390240 and 41329002) and Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (No. GIGCAS 135 project Y234081001). We thank Kai Zhang, Xiang-Hong Guan, Si-Hao Huang and Ru-Lang Shen for assistance in sample collection. This is contribution No. IS-2034 from GIGCAS.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.02.007>.

References

- Allen, J.O., Dookeran, N.M., Smith, K.A., Sarofim, A.F., Taghizadeh, K., Lafleur, A.L., 1996. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts. *Environ. Sci. Technol.* 30 (3), 1023–1031.
- Bi, X., Sheng, G., Peng, P., Chen, Y., Fu, J., 2005. Size distribution of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban and rural atmospheres of Guangzhou, China. *Atmos. Environ.* 39 (3), 477–487.
- Bidleman, T.F., 1988. Atmospheric processes. *Environ. Sci. Technol.* 22 (4), 361–367.
- Birgül, A., Tasdemir, Y., Cindoruk, S.S., 2011. Atmospheric wet and dry deposition of polycyclic aromatic hydrocarbons (PAHs) determined using a modified sampler. *Atmos. Res.* 101 (1–2), 341–353.
- Chan, C.K., Yao, X., 2008. Air pollution in mega cities in China. *Atmos. Environ.* 42 (1), 1–42.
- Chen, Y., Ebenstein, A., Greenstone, M., Li, H., 2013. Evidence on the impact of sustained exposure to air pollution on life expectancy from China's Huai River policy. *Proc. Natl. Acad. Sci. U. S. A.* 110 (32), 12936–12941.
- Eisenreich, S.J., Looney, B.B., Thornton, J.D., 1981. Airborne organic contaminants in the Great Lakes ecosystem. *Environ. Sci. Technol.* 15 (1), 30–38.
- European Union, 2014. Air Quality Standards (accessed 10.10.14.). <http://ec.europa.eu/environment/air/quality/standards.htm>.
- Guo, L.-C., Bao, L.-J., She, J.-W., Zeng, E.Y., 2014. Significance of wet deposition to removal of atmospheric particulate matter and polycyclic aromatic hydrocarbons: a case study in Guangzhou, China. *Atmos. Environ.* 83, 136–144.
- Hemminki, K., Pershagen, G., 1994. Cancer risk of air pollution: epidemiological evidence. *Environ. Health Perspect.* 102 (Suppl. 4), 187–192.
- Hillery, B.R., Simcik, M.F., Basu, I., Hoff, R.M., Strachan, W.M.J., Burniston, D., Chan, C.H., Brice, K.A., Sweet, C.W., Hites, R.A., 1998. Atmospheric deposition of toxic pollutants to the Great Lakes as measured by the integrated atmospheric deposition network. *Environ. Sci. Technol.* 32 (15), 2216–2221.
- Hinds, W.C., 1999. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, second ed. Wiley Interscience, New York.
- International Commission on Radiological Protection, 1994. Publication 66: Human Respiratory Tract Model for Radiological Protection. *Annals of the ICRP* 24 (1–3).
- Kameda, Y., Shirai, J., Komai, T., Nakanishi, J., Masunaga, S., 2005. Atmospheric polycyclic aromatic hydrocarbons: size distribution, estimation of their risk and their depositions to the human respiratory tract. *Sci. Total Environ.* 340 (1), 71–80.
- Kawanaka, Y., Tsuchiya, Y., Yun, S.-J., Sakamoto, K., 2009. Size distributions of polycyclic aromatic hydrocarbons in the atmosphere and estimation of the contribution of ultrafine particles to their lung deposition. *Environ. Sci. Technol.* 43 (17), 6851–6856.
- Li, J., Cheng, H., Zhang, G., Qi, S., Li, X., 2009. Polycyclic aromatic hydrocarbon (PAH) deposition to and exchange at the air–water interface of Luhu, an urban lake in Guangzhou, China. *Environ. Pollut.* 157 (1), 273–279.
- Liu, Y., Tao, S., Yang, Y., Dou, H., Yang, Y., Coveney, R.M., 2007. Inhalation exposure of traffic police officers to polycyclic aromatic hydrocarbons (PAHs) during the winter in Beijing, China. *Sci. Total Environ.* 383 (1–3), 98–105.
- Liu, Y., Zhu, L., Shen, X., 2001. Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China. *Environ. Sci. Technol.* 35 (5), 840–844.
- Luo, P., Bao, L.-J., Wu, F.-C., Li, S.-M., Zeng, E.Y., 2014a. Health risk characterization for resident inhalation exposure to particle-bound halogenated flame retardants in a typical e-waste recycling zone. *Environ. Sci. Technol.* 48 (15), 8815–8822.
- Luo, P., Ni, H.-G., Bao, L.-J., Li, S.-M., Zeng, E.Y., 2014b. Size distribution of airborne particle-bound polybrominated diphenyl ethers and its implications for dry and wet deposition. *Environ. Sci. Technol.* 48 (23), 13793–13799.
- Miller, S.M., Green, M.L., DePinto, J.V., Hornbuckle, K.C., 2000. Results from the Lake Michigan mass balance study: concentrations and fluxes of atmospheric polychlorinated biphenyls and trans-nonachlor. *Environ. Sci. Technol.* 35 (2), 278–285.
- Minsrty of Environmental Protection of the People's Republic of China, 2012. Ambient air quality standards (accessed 10.10.14.). <http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/dqhjlzlb/201203/W020120410330232398521.pdf>.
- Nemmar, A., Hoet, P.M., Vanquickenborne, B., Dinsdale, D., Thomeer, M., Hoylaerts, M., Vanbilloen, H., Mortelmans, L., Nemery, B., 2002. Passage of inhaled particles into the blood circulation in humans. *Circulation* 105 (4), 411–414.
- Offenberg, J.H., Baker, J.E., 2002. Precipitation scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons along an urban to over-water transect. *Environ. Sci. Technol.* 36 (17), 3763–3771.
- Office of Environmental Health Hazard Assessment, 2005. Air Toxics Hot Spots Program Risk Assessment Guidelines. California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section, Oakland, CA.
- Radke, L.F., Hobbs, P.V., Eltgroth, M.W., 1980. Scavenging of aerosol particles by precipitation. *J. Appl. Meteorol.* 19 (6), 715–722.
- Schluep, M., Hagelueken, C., Kuehr, R., Magalini, F., Maurer, C., Meskers, C., Mueller, E., Wang, F., 2009. Recycling: From e-waste to Resources. United Nations Environment Programme and United Nations University, Bonn, Germany.
- Tsapakis, M., Stephanou, E.G., 2005. Occurrence of gaseous and particulate polycyclic aromatic hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect on the gas/particle concentration and distribution. *Environ. Pollut.* 133 (1), 147–156.
- Wang, J., Chen, S., Tian, M., Zheng, X., Gonzales, L., Ohura, T., Mai, B., Simonich, S.L.M., 2012. 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.* 46 (17), 9745–9752.
- Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Luksemburg, W.J., Wong, A.S., 2007. Export of toxic chemicals—a review of the case of uncontrolled electronic-waste recycling. *Environ. Pollut.* 149 (2), 131–140.
- World Health Organization, 2000. Air Quality Guidelines for Europe Regional Office for Europe, second ed. World Health Organization, Copenhagen.
- Zhang, B.-Z., Zhang, K., Li, S.-M., Wong, C.S., Zeng, E.Y., 2012a. Size-dependent dry deposition of airborne polybrominated diphenyl ethers in urban Guangzhou, China. *Environ. Sci. Technol.* 46 (13), 7207–7214.
- Zhang, K., Schnoor, J.L., Zeng, E.Y., 2012b. E-waste recycling: where does it go from here? *Environ. Sci. Technol.* 46 (20), 10861–10867.
- Zhang, K., Zhang, B.-Z., Li, S.-M., Wong, C.S., Zeng, E.Y., 2012c. Calculated respiratory exposure to indoor size-fractionated polycyclic aromatic hydrocarbons in an urban environment. *Sci. Total Environ.* 431, 245–251.
- Zhang, K., Zhang, B.-Z., Li, S.-M., Zhang, L.-M., Staebler, R., Zeng, E.Y., 2012d. Diurnal and seasonal variability in size-dependent atmospheric deposition fluxes of polycyclic aromatic hydrocarbons in an urban center. *Atmos. Environ.* 57, 41–48.
- Zhang, Y., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmos. Environ.* 43 (4), 812–819.
- Zhang, Y., Tao, S., Shen, H., Ma, J., 2009. Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population. *Proc. Natl. Acad. Sci. U. S. A.* 106 (50), 21063–21067.
- Zhu, L., Lu, H., Chen, S., Amagai, T., 2009. Pollution level, phase distribution and source analysis of polycyclic aromatic hydrocarbons in residential air in Hangzhou, China. *J. Hazard Mater.* 162 (2–3), 1165–1170.