

Inhalation Cancer Risk Associated with Exposure to Complex Polycyclic Aromatic Hydrocarbon Mixtures in an Electronic Waste and Urban Area in South China

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Supporting Information

ABSTRACT: Atmospheric particulate matter samples were collected from May 2010 to April 2011 in a rural e-waste area and in Guangzhou, South China, to estimate the lifetime inhalation cancer risk from exposure to parent polycyclic aromatic hydrocarbons (PAHs), high molecular weight PAHs (MW 302 PAHs), and halogenated PAHs (HPAHs). Seasonal variations in the PAH concentrations and profiles within and between the e-waste and urban areas indicated different PAH sources in the two areas. Benzo[b]fluoranthene, benzo[a]pyrene, dibenz[ah]anthracene, and dibenzo[al]pyrene made the most significant contribution to the inhalation cancer risk. MW 302 PAHs accounted for 18.0% of the total cancer risk in the e-waste area and 13.6% in the urban area, while HPAHs made a minor contribution (<0.1%) in both the areas. The number of lifetime excess lung cancers due to exposure to parent PAHs, MW 302 PAHs, and HPAHs ranged from 15.1 to 1198 per million people in the e-waste area and from 9.3 to 737 per million people in Guangzhou. PAH exposure accounted for 0.02 to 1.94% of the total lung cancer cases in Guangzhou. On average, the inhalation cancer risk in the e-waste area was 1.6 times higher than in the urban area. The e-waste dismantling activities in South China led to higher inhalation cancer risk due to PAH exposure than the urban area.



INTRODUCTION

Cancer is now the leading cause of death in Chinese cities, accounting for ~25% of all deaths, and the second leading cause of death in rural areas, accounting for ~21% of all deaths.¹ In China, lung cancer has replaced liver cancer in causing the largest number of cancer deaths each year, at approximately 23% of all cancer deaths,¹ and approximately 300,000 people die from lung cancer and heart disease each year.² Smoking is a major cause of lung cancer in China, but ambient air pollution also plays an important role in causing lung cancer.³ The carcinogenicity of ambient particulate matter has been associated with a variety of toxic chemicals and, of these, carcinogenic polycyclic aromatic hydrocarbons (PAHs) make up the largest contribution to lung cancer.⁴ The significant consumption of energy in China for industry, transportation, and electricity has resulted in an unprecedented demand for fossil fuels and unprecedented emissions of PAHs to the atmosphere.^{5,6}

PAHs are produced from incomplete combustion⁷ and are ubiquitous pollutants in both indoor and outdoor air.⁵ Prenatal exposure to airborne PAHs has been associated with neurodevelopment effects in children.⁸ PAHs can bind covalently with DNA to form PAH-DNA adducts, a biomarker of DNA damage that has been related to cancer.⁹ Epidemiologic evidence showed that high occupational exposure to PAHs results in an excess risk of lung, skin, and bladder cancers in workers.¹⁰

Recently, halogenated PAHs (HPAHs), including chlorinated and brominated PAHs, have attracted concern due to their potentially higher toxicity, lipophilicity, and persistence compared to parent PAHs.^{11,12} HPAHs have been measured in various environmental media, including municipal incinerator

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ash, urban air, sediment, and soil.^{11–14} The primary sources of HPAHs appear to include the chemical industry, waste incinerators, leaded gasoline automobile exhaust, and the incineration of electronic waste.^{11–14}

China accounts for nearly one-fourth of the global atmospheric emission of PAHs, with an annual PAH emission inventory of 114,000 tons in 2004.⁶ The Pearl River Delta (PRD), located in Guangdong province, South China, is one of the most highly urbanized and industrialized regions in China. The rapid development of this region has resulted in serious environmental problems, including air pollution.¹⁵ The PAH emission density in the PRD region was reported to be much higher than the average PAH emission density for China, and biomass and domestic coal combustion are the primary PAH sources in this region.¹⁶

The United Nations Environment Programme (UNEP) estimated that 22 to 50 million tons of e-waste are generated worldwide each year and that 70% of this e-waste is transported to China where it is often dismantled using primitive methods.¹⁷ A wide range of toxic chemicals, including PAHs, are released into the environment during the processing of e-waste (including e-waste burning), and unprotected workers and residents living in or near the e-waste area are exposed to these pollutants.^{17–19}

In this study, we measured the concentrations of 12 USEPA priority pollutant parent PAHs, 5 high molecular-weight PAHs (MW 302), 13 chlorinated PAHs (ClPAHs) and 10 brominated PAHs (BrPAHs) in 120 24-h total suspended particulate (TSP) samples, collected year round, from a site in an e-waste area located ~70 km north of Guangzhou and an urban site in Guangzhou, China. Despite their high mutagenicity, the MW 302 PAHs and HPAHs are rarely studied because of the lack of commercial standards and relatively low concentrations of these compounds compared to parent PAHs.^{12,20} The human inhalation cancer risk due to exposure to carcinogenic parent PAHs, MW 302 PAHs, and HPAHs in ambient air in the two areas was assessed. To our knowledge, this is the first effort to assess and compare the inhalation cancer risk in populations living in adjacent e-waste and urban areas in South China.

MATERIALS AND METHODS

Sampling. The e-waste area air sampling site (23°59' N, 113°03' E) was located in the rural area of Qingyuan, with a population of 0.2 million. A large amount of e-waste (~700,000 t/yr) is processed within this 330 km² area, and there are no other industrial activities nearby. The samples were collected from the rooftop of a building (~10 m above the ground) in a small village where there are a number of e-waste recycling workshops and homes. This sampling site is approximately 1 km south of an e-waste burning site.

The urban area air sampling site (23°15' N, 113°36' E) was located in Guangzhou, the capital of Guangdong province and the largest city in South China, with a population of about 13 million. The samples were collected from the rooftop of a 20 m tall building on the Guangzhou Institute of Geochemistry campus. This urban sampling site is representative of residential areas in Guangzhou without major industrial sources nearby.

Total suspended particulate (TSP) samples were collected on quartz fiber filters for 24 h using a high volume air sampler (Tisch Environmental Inc., OH, USA) operated at a flow rate of 15 m³/h. The filters were baked at 450 °C for 4 h, wrapped in aluminum foil, and stored in polyethylene bags prior to use.

After sampling, the used filters were wrapped in aluminum foil, sealed in polyethylene bags, returned to the lab, and stored at –20 °C until analysis. Because of the distant location of the e-waste sampling site, five 24-h TSP samples were collected on five consecutive days of each month (typically from the 19th to 23rd of each month), at each site, from May 2010 to April 2011 rather than on a once a week basis. A total of 120 TSP samples were collected and analyzed. PAHs are primarily associated with particulate matter less than 2.5 μm in diameter (PM_{2.5}),²⁴ which is included in the TSP that was collected.

Standards and Chemicals. The parent PAHs, MW302 PAHs, and HPAHs were measured, and the abbreviations of their chemical names and detection frequencies in samples collected from the two sampling areas are listed in Table S1, Supporting Information. Additional information on where the standards and chemicals were obtained from is given in the Supporting Information.

Sample Preparation and Instrumental Analysis. The sample extraction method has been previously described in detail^{21–23} and is summarized in the Supporting Information.

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 with CH₄ as the reagent gas. The detailed measurement of these USEPA priority pollutant parent PAHs and MW 302 PAHs has been previously described.²⁰ Measurement of the HPAHs was achieved using a DB-SMS (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column (J&W Scientific, Palo Alto, CA, USA). The initial column temperature was held at 60 °C for 1 min, ramped to 200 at 25 °C/min, ramped to 300 at 3 °C/min, and held for 10 min. Injection of 1 μL sample was conducted with an automatic sampler in the splitless mode.

Risk Assessment. PM-bound PAHs are predominantly associated with PM_{2.5} which is part of the TSP we collected and analyzed.²⁴ In total, 12 priority pollutant parent PAHs, 5 MW 302 PAHs, 13 ClPAHs, and 10 BrPAHs were included in the estimation of inhalation cancer risk (Table S1). Due to the coelution of chrysene (CHR) and triphenylene (TRI) and coelution of 9,10-Cl₂ANT and 1,9-Cl₂PHE, a ratio of CHR:TRI = 2.4 (their ratio in the National Institute of Standards and Technology (NIST) SRM 1649b urban dust standard²⁵) and a ratio of 9,10-Cl₂ANT:1,9-Cl₂PHE = 0.7 (their ratio in fly ash from a waste incineration plant in Shenzhen, South China²⁶) was assumed in order to estimate their individual concentrations in the samples. Although we measured other parent PAHs, MW 302 PAHs, and HPAHs in the samples, these compounds were not included in the inhalation cancer risk estimation because of the lack of relative potency factors (RPFs) for these compounds.

The risk assessment calculations have been previously described.²⁰ Briefly, the USEPA point-estimated approach was used to estimate the inhalation cancer risk of PAHs during the different seasons.^{27,28} The benzo[a]pyrene (BaP) equivalent (BaP_{eq}) concentration of individual PAHs was calculated by multiplying their concentration by their RPF. The inhalation cancer risk for the PAH mixture was estimated by multiplying the sum of the individual BaP_{eq} concentrations by the unit risk (UR) of exposure to BaP

$$\text{CancerRisk} = \sum_{i=1}^n (C_{\text{PAH}_i} \times \text{RPF}_i) \times \text{UR}_{\text{BaP}} \quad (1)$$

where n is the number of individual PAH used for the cancer risk assessment, C_{PAH_i} is the concentration of the i th individual PAH measured on TSP, RPF_i is the RPF of the i th PAH, and UR_{BaP} is the inhalation unit risk of exposure to BaP (specifically, “the calculated, theoretical upper limit possibility of contracting cancer when exposed to BaP at a concentration of one microgram per cubic meter of air for a 70-year lifetime”).^{29–31} RPF values for parent PAHs and MW 302 PAHs were obtained from USEPA,³⁰ while the RPF values for HPAHs were obtained from an aryl hydrocarbon receptor-mediated effects study.^{11,12} Table S1 lists the RPF values used for individual parent PAHs, MW 302 PAHs, and HPAHs. As in previous studies, two different UR_{BaP} values were used in the inhalation cancer risk assessment.^{20,32} We used an UR_{BaP} value of 1.1×10^{-6} per ng/m³ based on data for respiratory tract tumors from inhalation exposure in hamsters^{28,30} and an UR_{BaP} value of 8.7×10^{-5} per ng/m³ based on an epidemiology study on coke-oven workers.³³

RESULTS AND DISCUSSION

BaP_{eq} Concentrations. The monthly mean BaP_{eq} concentrations at the urban and e-waste sites are given in Tables S2 and S3, respectively, while the monthly mean concentrations of the individual PAHs are given in Tables S4 and S5, respectively. The monthly mean concentrations of $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$ (sum of 12 priority pollutant PAHs), $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$ (sum of 5 MW 302 PAHs), and $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ (sum of 23 HPAHs) at the e-waste site ranged from 3.15 to 24.6 ng/m³, 0.78 to 5.59 ng/m³, and 0.001 to 0.020 ng/m³, respectively (with annual means of 11.3 ± 9.5 , 2.48 ± 1.99 , and 0.007 ± 0.010 ng/m³, respectively). The monthly mean concentrations of $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$, $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$, and $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ at the urban site ranged from 2.91 to 17.1 ng/m³, 0.39 to 4.17 ng/m³, and <0.001 to 0.011 ng/m³, respectively (with annual means of 7.31 ± 5.96 , 1.15 ± 1.41 , and 0.004 ± 0.005 ng/m³, respectively). The annual mean $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$, $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$, and $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ concentrations at the e-waste site were significantly higher ($p < 0.04$) than the urban site, by factors of 1.6 ± 1.1 , 2.2 ± 15.5 , and 1.8 ± 9.9 , respectively.

The annual mean $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$, $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$, and $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ concentrations were all significantly higher ($p < 0.01$) at the e-waste site compared to the urban site, indicating that e-waste recycling is a source of these pollutants. Our result for HPAHs is in agreement with previous findings where HPAHs were measured in soil and dust at a different e-waste site in China¹³ and in fly ash from waste incinerators in South Korea,³⁵ suggesting that the burning of waste is a potential source of HPAHs. However, the annual mean $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ concentrations were 3 orders of magnitude lower than the $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$ and $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$ concentrations at both the e-waste and urban sites.

Figure 1 shows the mean monthly variation of $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$ and $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$ concentrations at the two sites. At both sites, the $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$, $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$, and $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ concentrations in winter (December, January, and February) were significantly higher ($p < 0.05$) than the concentrations in other seasons. The concentrations followed the general trend of winter > spring > autumn > summer at the e-waste site and

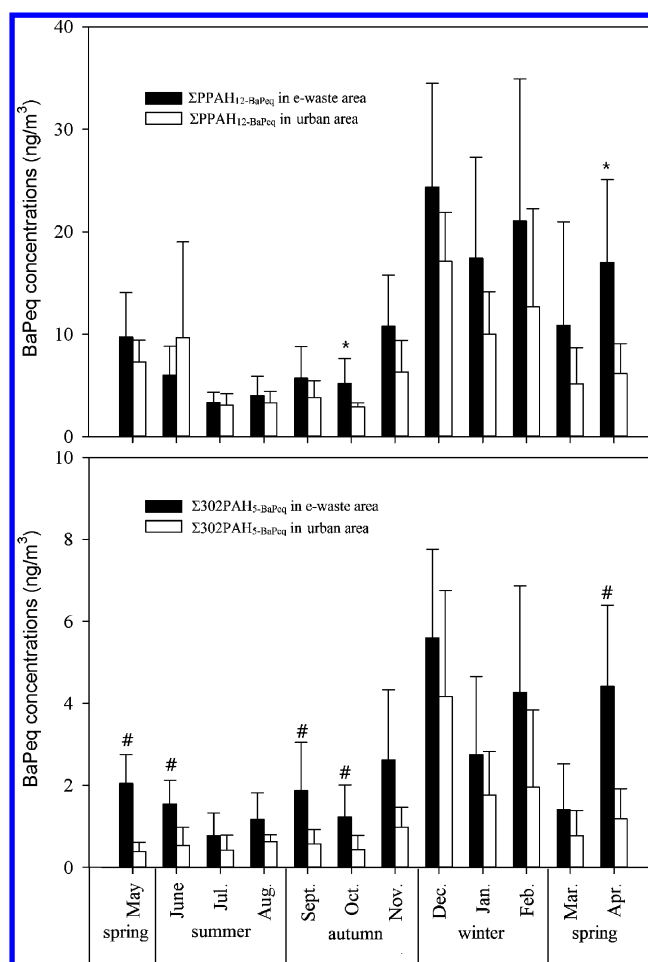


Figure 1. Monthly mean BaP_{eq} concentration of $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$ and $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$ in TSP collected from the e-waste and urban areas. The error bars represent the standard deviations of total concentration of 17 PAHs. The BaP_{eq} concentrations of $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ are not shown because of their low percentage contribution to the total BaP_{eq} concentrations. Statistically significant differences ($p < 0.05$) between the e-waste and urban areas are indicated by * for parent PAHs and # for MW 302 PAHs.

winter > spring > autumn ~ summer at the urban site. The $\Sigma\text{HPAH}_{23-\text{BaP}_{\text{eq}}}$ concentrations at the two sites followed similar seasonal patterns to the $\Sigma\text{PPAH}_{12-\text{BaP}_{\text{eq}}}$ and $\Sigma 302\text{PAH}_{5-\text{BaP}_{\text{eq}}}$ concentrations. Although our sample collection frequency (on five consecutive days) may have slightly biased certain weather events, others have measured higher winter and lower summer BaP_{eq} concentrations in ambient air in both northern and southern China.³⁶

The difference in the seasonal BaP_{eq} concentrations at the e-waste and urban sites suggest that the sites may be influenced by different PAH sources. Combustion of fossil fuels for industrial processes, motor vehicles exhaust, and biomass burning are the primary sources of PAHs in urban areas of China.³⁷ In the e-waste area, e-waste dismantling activities (including the burning of plastics) may constitute an important PAH source in addition to biomass burning for cooking. Unlike northern China in winter, there are no domestic heating sources in these areas of South China and no other seasonal PAH sources.³⁸ The elevated PAH concentrations in winter were likely due to differences in meteorological conditions. In winter, atmospheric inversions hamper the dispersion of

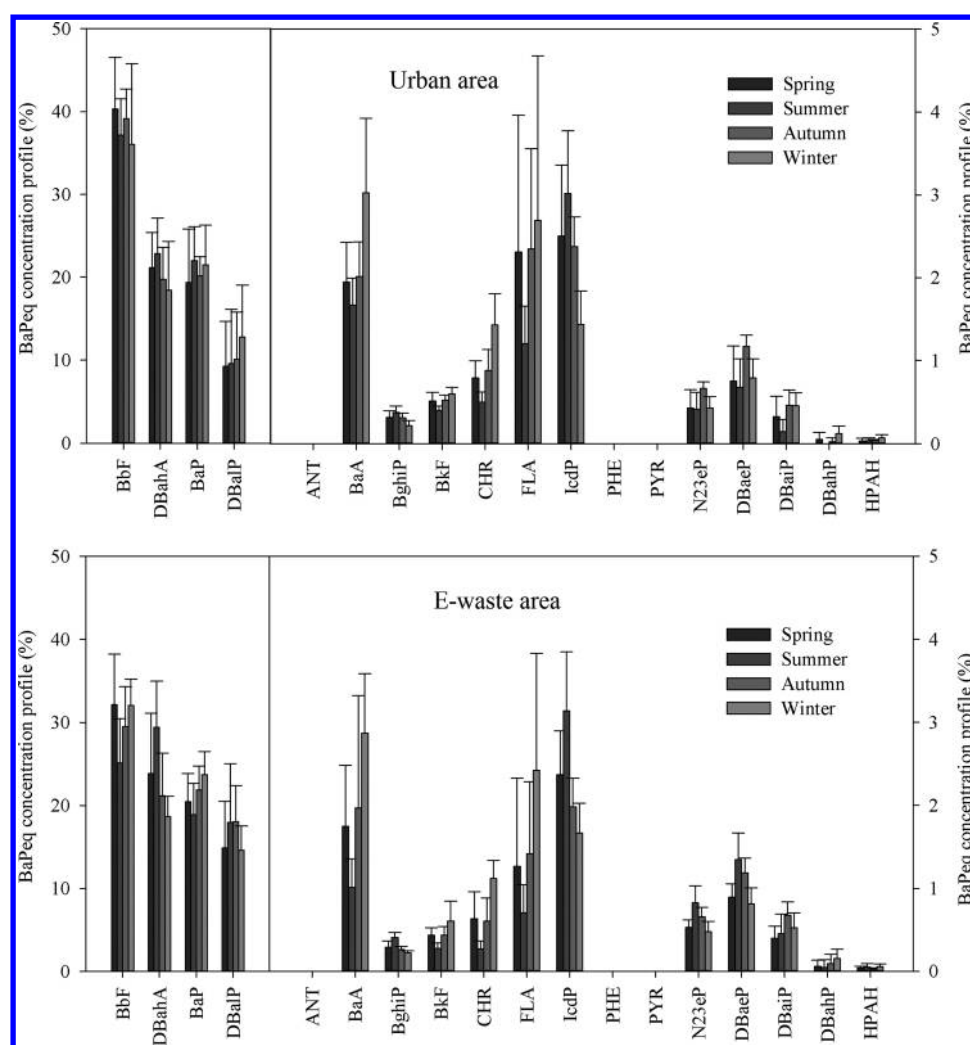


Figure 2. The mean BaP_{eq} concentration profiles of the individual PAHs and total halogenated PAHs in the e-waste and urban areas in different seasons.

pollutants and the lower temperatures favor the partitioning of PAHs to the particle phase.³⁹ In addition, during the winter heating season in northern China, PAHs may be transported from northern China to southern China due to prevalent northerly winds.

The BaP_{eq} concentrations exceeded the new national daily BaP_{eq} standard for China (2.5 ng/m^3)⁴⁰ on 59 of the 60 sampling days at the e-waste site and on 56 of the 60 sampling days at the urban site. The highest BaP_{eq} concentration at the e-waste site was 17.5 times higher than China's new standard, while it was 13.3 times higher than China's new standard at the urban site. This suggests that people living in the e-waste area are exposed to BaP_{eq} concentrations that exceed China's standard approximately 98% of the time and people living in the urban area are exposed to concentrations that exceed the standard 93% of the time. This also suggests that e-waste dismantling and burning activities lead to substantial PAH exposure, in addition to exposure to other toxic chemicals (including flame retardants, dioxins, and heavy metals).⁴¹ Furthermore, the BaP_{eq} concentrations for all of the days sampled, at both sites, exceeded the European Union's annual average BaP_{eq} standard (1 ng/m^3)⁴² and the WHO guideline level (1 ng/m^3).⁴³

Zhang et al. estimated the average BaP_{eq} concentration of sixteen parent PAHs in ambient air in China at 2.43 ng/m^3 based on a high-resolution PAH emission inventory.⁴⁴ This estimated concentration is lower than the $\Sigma PAH_{12-BaP_{eq}}$ concentrations we measured at the e-waste (11.3 ng/m^3) and urban sites (7.31 ng/m^3) in South China and is consistent with the high PAH emission density for the PRD region as compared to the rest of China.¹⁶ Hu et al. measured the BaP_{eq} concentrations at a different site in Guangzhou using a toxic equivalency factor (TEF) approach.³⁹ During 2004–2005, the BaP_{eq} concentrations for 12 priority pollutant parent PAHs on $PM_{2.5}$ ranged from 1.31 ng/m^3 in summer to 10.8 ng/m^3 in winter, with an average of 5.39 ng/m^3 . The BaP_{eq} concentrations for 16 priority pollutant parent PAHs on TSP collected from Guiyu, a different e-waste area in South China, varied greatly from 136 ng/m^3 in the incineration field during the day to 5.12 ng/m^3 in the e-waste dismantling workshop at night.⁴⁵ Wei et al. measured the BaP_{eq} concentration of 7 priority pollutant parent PAHs and 4 MW 302 PAHs in $PM_{2.5}$ samples from an industrial area and e-waste area in Qingyuan, Guangdong province.³² The BaP_{eq} concentration in the industrial area (12.8 ng/m^3) was higher than the e-waste area (6.38 ng/m^3). Our estimated BaP_{eq} concentrations, based on

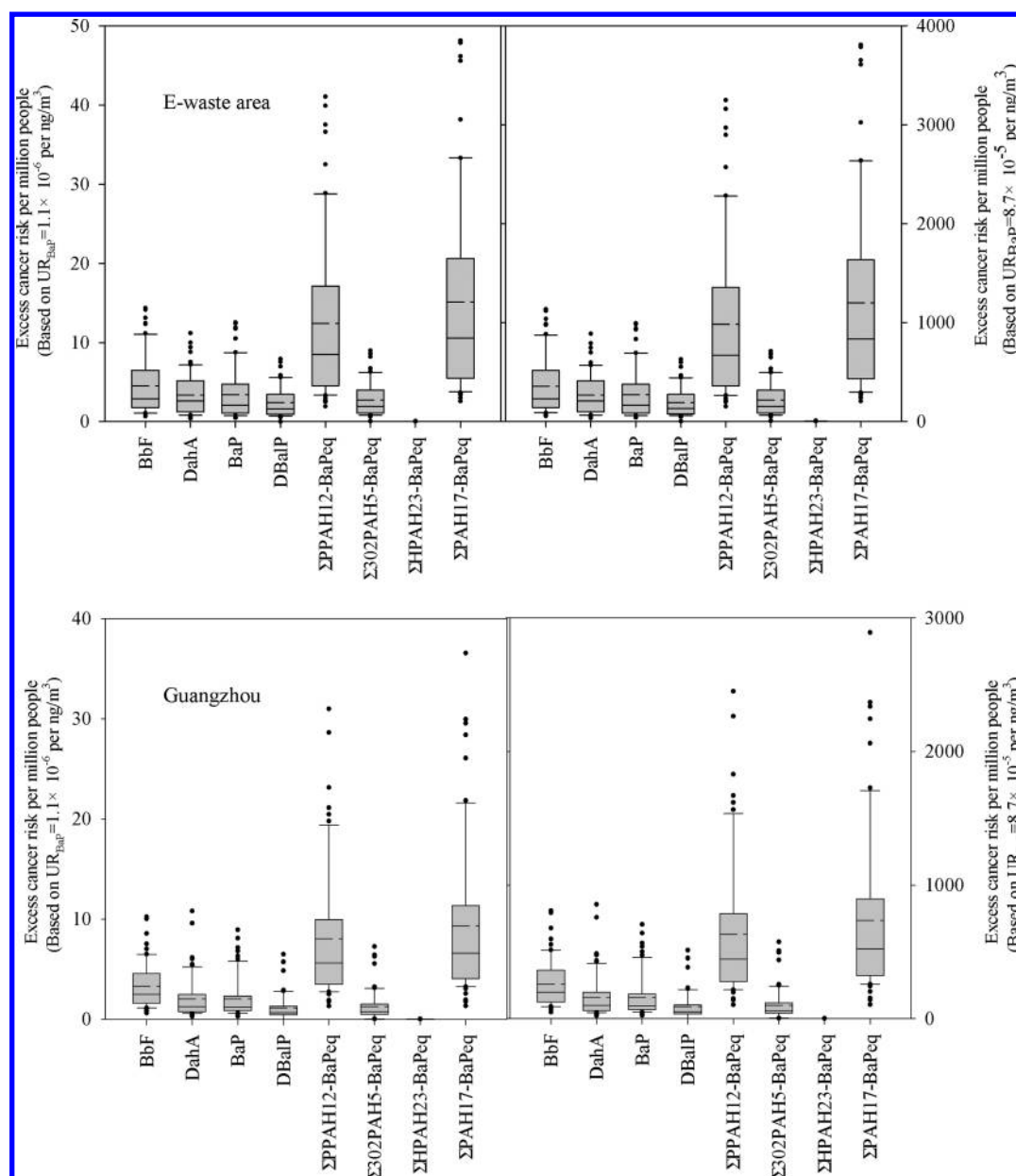


Figure 3. Estimated number of excess inhalation cancer cases per million people for selected PAHs measured on TSP in the e-waste and urban areas. The left y-axes based on a UR_{BaP} value of 1.1×10^{-6} per ng/m^3 from a rodent study (OEHHA 1993); right y-axes based on a UR_{BaP} value of 8.7×10^{-5} per ng/m^3 from an epidemiology study (WHO 2000). The boxes represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles, and the short dash and solid lines within the boxes represent the mean and median, respectively.

the most recently recommended RPF approach, are comparable to, or lower than, these concentrations in South China.

Because we have made the first measurements of HPAHs in ambient air in China, we cannot compare our measured HPAH air concentrations to other studies in China. However, Ohura et al. measured the $\Sigma HPAH_{BaPeq}$ concentrations for Cl-PAHs and Br-PAHs on particulate matter collected from Shizuoka, Japan, with mean concentrations of 2.6 and 1.7 pg/m^3 , respectively.¹² The Cl-PAH concentrations were higher at our sampling sites in China (5.8 pg/m^3 in the e-waste area and 3.5 pg/m^3 in the urban area) compared to the study in Shizuoka, Japan, while the Br-PAH concentrations were lower at our sampling sites (0.7 pg/m^3 in the e-waste area and 0.4 pg/m^3 in the urban area). This difference in the relative abundance of Cl-PAH and Br-PAH concentrations in Chinese air as compared to Japanese

air suggests that there may be different HPAH sources in the two countries.

It is important to note that the MW 302 PAHs made a significant contribution to the total BaP_{eq} concentrations at both sites (Figure 1). At the e-waste site, the percentage contribution of $\Sigma 302PAH_{5-BaPeq}$ to the total BaP_{eq} concentration ranged from 1.34 to 36.0% (mean of $18.7 \pm 5.4\%$) throughout the year, while the contribution ranged from 0.35 to 25.6% (mean of $12.3 \pm 6.0\%$) at the urban site throughout the year. These results suggest that exposure to MW 302 PAHs, in addition to traditionally measured parent PAHs, are of concern in both areas and that combustion of e-waste is a potentially important source of MW 302 PAHs.

The mean BaP_{eq} concentration profiles of the individual PAHs and total HPAHs at the two sites, in the different

seasons, are shown in Figure 2, while Figures S1 and S2 show the mean concentration profiles at the two sites. Some individual PAHs had significant differences ($p < 0.01$) in their relative proportions in the e-waste and urban PAH profiles. However, BaA, BghiP, DahA, IcdP, BaP, and total HPAHs did not show a difference in the profiles between the two sites. The percentage contribution of individual PAHs varied seasonally, with relative standard deviations from 5% to 110% at the two sites, with greater variation in the PAH profiles at the e-waste site compared to the urban site. The greater variation in the PAH profiles at the e-waste site may be because the PAH sources in the e-waste area (including the processing and burning of e-waste) are more variable than the PAH sources in the urban area. BbF, DahA, BaP, and DBaP were the four major individual PAH contributors to the total BaP_{eq} concentrations at both sites, accounting for 29.9%, 22.3%, 22.7%, and 15.8%, respectively, at the e-waste site and 35.1%, 21.6%, 21.7%, and 11.9%, respectively, at the urban site, on average, for the entire year.

Estimation of Inhalation Cancer Risk. Figure 3 shows the estimated lifetime excess inhalation cancer risk per million people due to PAH exposure in the e-waste and urban areas. Based on an average lifetime of 70 years and the UR_{BaP} value of 1.1×10^{-6} per ng/m³, the mean estimated excess inhalation cancer risk associated with Σ PPAH_{12-BaP_{eq}}, Σ 302PAH_{5-BaP_{eq}}, and Σ HPAH_{23-BaP_{eq}} exposure was 15.1 cancer cases per million people in the e-waste area, with 2.7 cases attributed to exposure to MW 302 PAHs, and 9.3 cancer cases per million people in the urban area, with 1.3 cases attributed to exposure to MW 302 PAHs. The excess inhalation cancer risk associated with exposure to HPAHs was less than 0.01 cases per million people in both areas. When an UR_{BaP} value of 8.7×10^{-5} per ng/m³ was used, the mean estimated excess inhalation risk associated with exposure to these PAHs was 1198 cancer cases per million people in the e-waste area, with 214 cases resulting from exposure to MW 302 PAHs, and 737 cancer case per million people in the urban area, with 100 cases resulting from exposure to MW 302 PAHs. The cancer risk associated with HPAHs was less than 1 case per million people in both areas.

People living in the e-waste area have a greater inhalation cancer risk due to PAH exposure than people living in the urban area. In addition, MW 302 PAHs make a significant contribution to the total inhalation cancer risk, while HPAHs do not. If all age groups are assumed to have the same inhalation cancer risk, the annual inhalation cancer cases (the number of lifetime excess inhalation cancer cases divided by the assumed lifetime of 70 years) caused by inhalation of PAH mixtures in Guangzhou would be 0.1–10.5 per million people. In 2003, the annual incidence of lung cancer in Guangzhou was 540 cases per million people,⁴⁴ so the contribution of PAH mixture inhalation to the total lung cancer cases in Guangzhou would be approximately 0.02–1.94%. This percentage is relatively low compared to cigarette smoking, which accounts for 50% and 35% of male and female deaths due to lung cancer in China, respectively.⁴⁶ However, inhalation exposure from ambient air is inevitable for the entire population living in these areas. In addition, cigarette smoking would likely increase the lung cancer risk for people in the e-waste area (smoking rate of 23.3%) compared to the urban area (smoking rate of 20.7%).⁴⁷

Jia et al. estimated the inhalation cancer risk of 12 parent PAHs and 5 MW 302 PAHs during different source control periods of the Beijing Olympic Games from July to October in 2008.²⁰ The estimated lifetime excess inhalation cancer risk

ranged from 12.2 to 964 per million people during nonsource control period in Beijing, which is slightly higher than our estimates for the e-waste and urban areas of South China. The mean contribution of MW 302 PAHs in Beijing was 15.5% of the total inhalation cancer risk attributable to the measured PAH mixture, which is slightly higher than our estimate of 13.6% for Guangzhou. In addition, Beijing has significantly higher air PAH concentrations in winter than in other seasons because of coal combustion for heating^{36,48} and three times as many cars are on the road compared to Guangzhou. As a result, the inhalation cancer risk from PAH exposure in Beijing would be higher than in Guangzhou if winter PAH concentrations are taken into consideration.

The relative contribution of the four major PAH contributors to the total inhalation cancer risk over the entire year was BbF > DahA ~ BaP > DBaP at both sites. However, their relative order varied season to season. In the e-waste area, DahA was the largest contributor to inhalation cancer risk in summer, while BbF was the largest contributor in other seasons. In the urban area, BbF was the largest contributor in all seasons, followed by DahA in summer and spring and BaP in autumn and winter. The relative contribution of individual PAHs to the inhalation cancer risk in the e-waste and urban areas we studied was different from the relative contribution found in Beijing where the order was DahA > BbF > DBaP > BaP.²⁰ This suggests that there are different relative contributions of PAHs to the inhalation cancer risk in southern China and northern China. The seasonal inhalation cancer risk associated with these four PAHs followed the order winter > spring > summer > fall in the e-waste area and winter > spring > fall > summer in the urban area. The exception was DBaP in e-waste area, which had a higher cancer risk in fall than in summer.

In order to decrease the inhalation cancer risk in the studied areas, the emissions of BbF, DahA, BaP, and DBaP would need to be reduced. Because these PAHs are bound to particulate matter, this reduction could be achieved through general reductions in particulate matter emissions from combustion sources in China. In addition, biomass combustion and power plant emissions are major sources of BbF and DahA, respectively.^{32,49} The sources of DBaP include coal combustion and vehicle emission and the sources of BaP in our sampling area may include industrial oil burning, firewood combustion, and cooking fuel.^{32,49} All of these sources are related to energy consumption, suggesting that the use of green energy would likely significantly reduce the inhalation cancer risk due to PAH exposure. Our results also suggest that e-waste burning for recycling is also an important source of PAHs to ambient air.

This assessment of inhalation cancer risk has several uncertainties and limitations. First, the sampling sites used may not be representative of the entire e-waste and urban areas evaluated. Second, the point-estimate approach used assumes additive cancer risk. Different PAH isomers, in conjunction with other pollutants (including metals) may increase or decrease the toxicity of PAHs. Third, the use of UR_{BaP} value of 8.7×10^{-5} per ng/m³ based on an epidemiology study on coke-oven workers may overestimate the inhalation cancer risk.³³

However, even with these uncertainties, our assessment gives a general evaluation of the inhalation cancer risk associated with PAH exposure and how e-waste dismantling activities affect cancer risk for the residents.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed sample preparation procedural, information on chemicals included in risk assessment, and mean monthly BaP_{eq} concentrations of individual parent PAHs and MW 302 PAHs from the e-waste area and the urban area are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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