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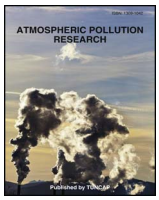

Original Article

Spatial distribution and source apportionment of atmospheric polycyclic aromatic hydrocarbons in the Pearl River Delta, China

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ABSTRACT

Air samples were collected using polyurethane foam passive samplers from 26 air-monitoring stations located in the Pearl River Delta, China and two in Shaoguan City in Guangdong Province in 2015 to investigate the occurrence and distribution of priority polycyclic aromatic hydrocarbons (PAHs). Sixteen PAHs were identified and 15 of them (except for naphthalene) were quantified at a total concentration (Σ_{15}PAHs) that varied from 3.56 ng/m^3 to 37.2 ng/m^3 (average value 19.8 ± 9.69 ng/m^3). The results indicated that PAHs with 3–4 benzene rings accounted for approximately 80% of all PAH compounds, among which phenanthrene and fluoranthene were the predominant components. Diagnostic parameters suggested that the possible sources of PAHs in the Delta region were mixed of petrogenic and pyrogenic sources from fuel/biomass/coal combustion. Based on the measured PAHs concentrations, the Carcinogenic Potency Risk (BaP_{eq}) and Inhalation Cancer Risk (ICR) were assessed, and indicated that two air samples from Guangzhou and one from Foshan exceeded the BaP_{eq} limit (1 ng/m^3), whereas all samples from the 28 sampling locations exceeded the health-based guideline concentration for ICR. The results of this research suggest that a potential human health risk exists from PAHs in the study area via the respiration and inhalation pathway.

1. Introduction

The Pearl River Delta (PRD), located in the downstream reach of the Pearl River, is one of the most developed areas of China. Previous studies have revealed severe pollution of the region's central cities by polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers, organochlorine pesticides and other persistent organic pollutants (Gao et al., 2012; Huang et al., 2014; Liu et al., 2010; Pan et al., 2011; Zhang et al., 2009) due to the rapid economic development and high level of anthropisation (Gao et al., 2012; Li et al., 2007).

The PAHs are a group of persistent organic pollutants with two or more benzene rings, and among these chemicals 16 congeners have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA) due to their persistence, bioaccumulation potential and toxicities. Extensive studies have reported that PAHs are ubiquitous in every part of the environment, such as water (Zhang et al., 2012), soil (Liu et al., 2011; Wang et al., 2012), air (Evci et al., 2016; Motelay-Massei et al., 2005) and sediment (Barakat et al., 2011; Zhang et al., 2011). Previous studies have found that pollution by PAHs in the PRD mainly originated from vehicular emissions and biomass/coal combustion (Gao et al., 2012; Wang et al., 2015; Yu et al., 2016). After emission, these compounds can undergo long-range atmospheric transportation and be back to terrestrial and aquatic ecosystems via dry/wet deposition (Galarneau, 2008; Klánová et al., 2008). During transportation, PAHs with more than four rings tend to be present in particulate phase, while those with two and three rings have relatively low octanol-air partition coefficients and are mainly associated with the gaseous phase (Gao et al., 2015).

Until now, insufficient data was available for assessing local airborne PAHs pollution in the PRD, because the sampling sites selected for monitoring in the aforementioned studies were limited and the data obtained was somewhat site-specific (Gao et al., 2012; Huang et al., 2014; Liu et al., 2010). In addition, several years have elapsed since these studies were conducted, and it is unknown whether levels of PAHs changed with the population increase and resultant energy demand increase, as well as due to the stricter vehicular emission standards (National Standard IV) which have been put in force in July 1st, 2013. Therefore, it is necessary to monitor the regional atmospheric PAHs simultaneously from different locations in the PRD.

In recent years, the passive sampling technique has been adopted by

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an increasing number of researchers using semipermeable membrane devices, polyurethane foam (PUF), and other types of filters (Liu et al., 2011; Markovic et al., 2015; Niu et al., 2017; Pozo et al., 2015). The passive sampling technique enables monitoring of air pollution in many locations simultaneously and independent of electrical supply. The resulting data facilitate determining the time-weighted average concentrations of persistent organic pollutants during long-time exposure (several days to months), thus obtaining local information about airborne PAHs occurrence and profile patterns, as well as spatiotemporal characterization simultaneously (Niu et al., 2017; Peverly et al., 2015). The objectives of this study were to 1) assess regional air pollution from PAHs based on measured airborne PAHs concentrations at 28 air-monitoring stations located in nine cities in the PRD, as well as Shaoguan City in Guangdong Province, 2) identify the main sources of PAHs, and 3) assess the potential cancer risk and inhalation cancer risk arising from the PAHs.

2. Materials and methods

2.1. Sampling area

The PRD is one of the most populated and industrialized areas in China, and is composed of nine cities (Guangzhou, Shenzhen, Foshan, Dongguan, Zhaoqing, Zhuhai, Huizhou, Jiangmen and Zhongshan) covering an area of nearly 42,000 km^2 (Tian et al., 2008) with a total permanent population of more than 57 million at the end of 2014 (GPBS, 2015). As shown in Fig. 1, 26 air-monitoring stations were selected as sampling sites in nine cities in the PRD, covering urban areas, suburban areas, industrial areas and residential areas (Li et al., 2018). In addition, two air-monitoring stations in Shaoguan (identified as TJS and ZGK) were selected as background stations far away from densely inhabited areas. In these selected sampling sites, passive air quality samplers were operated from February to April 2015. As aids in calculating the sampling rate of the passive samplers, active samplers were simultaneously used at three of the passive sampling sites (designated DHS, TH and TY) (Evci et al., 2016; He and Balasubramanian, 2010).

2.2. Chemicals and materials

The 16 mixed PAH standards specified in USEPA Method 610 were obtained from Supelco (Bellefonte, PA, USA): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), indeno[1,2,3-cd]pyrene (InP), and benzo[g,h,i]perylene (BghiP). The detailed information was listed in Table S1. Five deuterated PAHs also were obtained from Supelco and used as surrogate standards: Nap-d8, Ace-d10, Phe-d10, Chr-d12 and perylene-d12 (Per-d12). An internal standard, hexamethylbenzene (HMB), was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All solvents and reagents used were pesticide grade. Envi-Florisil® SPE columns (1 g/6 mL) also were purchased from Supelco.

PUF disks (14 mm diameter, 1.35 cm thickness) and PUF plugs (63 mm diameter, 80 mm length) used in samplers were pre-cleaned with dichloromethane (DCM) by Soxhlet extraction for 48 h and dried in a vacuum oven operated in vacuum environment at 1 mbar and ambient temperature (VT 6025, Thermo Scientific). Teflon® filters (203 × 254 mm, Munktell, Sweden) were ultrasonically cleaned in a mixture of acetone and *n*-Hexane (1:1 v/v) for more than 30 min. All filter materials were sealed in aluminum foil envelopes and stored at −20 °C prior to use in sampling.

2.3. Sample collection and extraction

The PRD is located in the subtropics, and has an annual average temperature of 25 °C (monthly average temperature of 14–30 °C) with relative humidity in the range of 60–90%. The monthly average temperature in spring (February to April) varied in the range of 16–23 °C with moderate relative humidity about 80%, and less sunshine hours (about 150–250 h out of annual total 2300 h). Consequently, we carried out field sampling in spring for assessment the occurrence, and distribution of PAHs avoiding potential photochemical reaction under high temperature and long sunshine. In the present study, passive atmosphere samplers were assembled at the sampling sites using steel sheltered chambers and PUF disks (see Jaward et al., 2004 for details) and then placed at each air-monitoring station for approximately two months (February to April 2015). Simultaneously, active atmosphere samplers were set at three sites (DHS, TH and TY), each consisting of a high-volume sampler (model TH-1000C, Tianhong Instruments (China) Co. Ltd., Wuhan) that collected 24-h samples weekly at a flow rate of 300 L/min during the same sampling period as the passive samplers. Particles were retained on Teflon® filters and gaseous contaminants were collected in the PUF plugs. In total, eight particulate samples and eight gaseous samples were obtained at each active sampling site. In all, 28 passive air samples and 48 active air samples (gaseous and particulate) were obtained for analysis. All samples (PUF disks, PUF plugs and Teflon® filters) were stored in a freezer at −20 °C until they were analyzed.

2.4. Analytical procedure

Each sample was spiked with 200 ng deuterated PAHs as surrogate standards and Soxhlet extracted with 250 mL DCM for 72 h. The extracts were reduced to approximately 2 mL by rotary evaporation, after which the solvent was exchanged into *n*-Hexane and concentrated to 1 mL again. The resulting extract was passed through an Envi-Florisil® SPE cartridge for further separation. The cartridge was conditioned continuously with 5 mL ethyl acetate, 5 mL *n*-Hexane/dichloromethane (8:2 v/v) and 8 mL *n*-Hexane, and the analytes were eluted with 10 mL *n*-Hexane/dichloromethane (8:2 v/v). The collected fraction was concentrated by evaporation under a gentle nitrogen stream to 200 μL. As an internal standard, 200 ng HMB was added to the samples prior to analysis. Detailed information about pretreatment procedure has been reported previously (Liu, 2015).

Determination and quantification of PAHs were accomplished using a gas chromatograph mass spectrometer (model QP 2010, Shimadzu (Japan) Co. Ltd., Kyoto) equipped with a J & W Scientific DB-5MS column (30 m × 0.25 mm × 0.25 μm, Agilent Technologies, Santa Clara, CA, USA). The column temperature was initiated at 70 °C, then programmed to increase at 3 °C/min to 285 °C (holding for 5 min). The ion source temperature was 250 °C and the mass spectra were recorded using selected ion monitoring mode. To begin the analysis, a 1-μL sample was injected in splitless mode with a solvent delay of 7.5 min. The monitored ions used for quantification as well as their limit of detection (LOD) were listed in Table S1.

2.5. Quality assurance/quality control (QA/QC)

Seven PUF disks as well as six Teflon® filters and six PUF plugs, sealed individually in aluminum foil envelopes and taken to sampling sites without exposure to the atmosphere, were set as field blanks. All field blanks and six method blanks (solvent) were analyzed as real samples to determine any background contamination. The target compounds (Flu, Phe, Fla and Pyr) were found below the LOD in all method blanks and field blanks, and the other PAHs were not detected in any blanks.

Surrogate compounds were added to samples so that procedural performance and matrix effects could be monitored. The recoveries of the five surrogate standards in samples were 61.5 ± 6.89% (Nap-d8), 73.0 ± 4.28% (Ace-d10), 80.4 ± 7.45% (Phe-d10), 86.2 ± 9.81% (Chr-d12) and 76.2 ± 7.45% (Per-d12). The concentrations of

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