Environmental Pollution 238 (2018) 749–759

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Spatiotemporal variability of polybrominated diphenyl ether concentration in atmospheric fine particles in Shenzhen, China

Jinling Peng [a], Dongting Wu [b], Yousheng Jiang [a, *], Jianqing Zhang [a], Xiaoshi Lin [a], Shaoyou Lu [a], Pengpeng Han [c], Jian Zhou [a], Shengnong Li [a], Yixiong Lei [d, **], Jinsong Chen [c]

[a] Shenzhen Center for Disease Control and Prevention, Shenzhen, 518055, PR China
[b] School of Medicine, Shenzhen University, Shenzhen, Guangdong, 518060, PR China
[c] Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, 518055, PR China
[d] School of Public Health, Guangzhou Medical University, Guangzhou, 510182, PR China

A R T I C L E I N F O

Article history:
Received 10 July 2017
Received in revised form
21 March 2018
Accepted 21 March 2018

Keywords:
Polybrominated diphenyl ethers
Atmospheric fine particles
Meteorological parameters
Inhalation exposure

A B S T R A C T

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants for various products and have become ubiquitous pollutants in environmental media. However, little is known about PBDE levels in Shenzhen, a manufacturing center of electronic products. This study aimed to investigate spatio-temporal variability of PBDE concentration in atmospheric fine particles ($PM_{2.5}$) and to estimate the daily inhalation exposure doses for local residents in Shenzhen, China. A total of 36 samples were collected and 8 PBDE compounds (BDE-28, 47, 99, 100, 153, 154, 183 and 209) were analyzed by isotope dilution high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS). Mean concentrations of Σ_8PBDEs and BDE-209 in $PM_{2.5}$ in Shenzhen were 33.47 pg/m^3 and 24.75 pg/m^3, respectively, which were lower than those for other reported cities from China. The mean concentration of Σ_8PBDEs was higher in the winter + spring than that in summer + autumn, and both concentrations of BDE-28 and BDE-47 in $PM_{2.5}$ were significantly higher in winter + spring than those in summer + autumn. Among the 8 congeners, BDE-209 was predominant, accounting for 73.9% of the Σ_8PBDEs concentrations. Traffic area, industrial area, residential area and discharge of electronic industries had significant positive influences on PBDE concentrations in $PM_{2.5}$. Both vegetation area and water area were significantly negatively correlated with PBDE levels in $PM_{2.5}$. Significantly negative correlation was also found between PBDE concentrations in $PM_{2.5}$ and the relative humidity. The ranking of estimated inhalation exposure doses of PBDEs via $PM_{2.5}$ inhalation were toddlers (1.74 pg/kg b.w./day) > children (1.33 pg/kg b.w./day) > adults (1.26 pg/kg b.w./day) > teenagers (0.64 pg/kg b.w./day), and toddlers had a highest risk to expose to PBDEs by $PM_{2.5}$. To our knowledge, the present study is the first to reveal the spatiotemporal variability of PBDEs in $PM_{2.5}$ of Shenzhen, China.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are extensively used as flame-retardant additives in high-impact plastics, electronic circuitry, television sets, foams and textiles. They are also a class of emerging persistent organic pollutants (POPs) sharing the properties of persistence, long-distance transmission, bioaccumulation and high toxicity and are ubiquitous in the environment. Human exposure to PBDEs has been linked to development neurotoxicity (Chao et al., 2011), adverse birth outcomes (Harley et al., 2011), thyroid dysfunction (Huang et al., 2014; Jacobson et al., 2016; Allen et al., 2016) and reproductive disorders (Chao et al., 2010; Harley et al., 2010). Environmental and health concern have led to a global ban of two commercial mixtures: penta-BDE and octa-BDE (UNEP, 2010) and the last commercial mixture still allowed for use is the deca-BDE at present. As the main component of deca-BDE, BDE-209 was found to be predominated in various environment media (Salvadó et al., 2012; Tu et al., 2012; Wu et al., 2015) even in waters of Arctic Ocean (Salvadó et al., 2016). Growing studies were reported on its potential harm to human health. BDE-

* Corresponding author. Shenzhen Center for Disease Control and Prevention, No. 8 Longyuan Road, Shenzhen, 518055, Guangdong, PR China.
** Corresponding author. School of Public Health, Guangzhou Medical University, No. 59 Jingxiu Road, Guangzhou, 510182, Guangdong, PR China.
E-mail addresses: ysjiang2000@163.com (Y. Jiang), gz-leizeng@163.com (Y. Lei).

https://doi.org/10.1016/j.envpol.2018.03.076

209 can transport across the placenta and accumulate a higher concentration in newborns than in their mothers despite its large size (Vizcaino et al., 2014). It's suggested that prenatal or postnatal exposure to BDE-209 potentially delay the neurological development of infants (Chao et al., 2011). Moreover, environmental concern raised due to the breakdown of BDE-209 into more toxic penta- and octa-like congeners (Ross et al., 2009).

Fine particulate matter ($PM_{2.5}$) refers to atmospheric particles with diameters less than or equal to 2.5 μm. The particle-size distribution of PBDEs featured a distinct enrichment in fine particles (Zhang et al., 2012a; Besis et al., 2015), due to the mechanism of absorption and adsorption (Lyu et al., 2016). Fine particle-bound PBDEs can be inhaled deep into the lungs, reaching the pulmonary alveoli and may pose a great risk to human health (Besis et al., 2015). Numerous studies have reported that human exposure to high levels of $PM_{2.5}$ can lead to cardiovascular diseases (Qiu et al., 2013; Lin et al., 2017), respiratory damage (Gaviria et al., 2011; Loftus et al., 2015) and lung cancer (Chiang et al., 2014; Fu et al., 2015). Without chemical bond, PBDEs can easily release from consumer products and highly absorb onto fine particles. Limited data were published on concentration as well as spatiotemporal variability of $PM_{2.5}$-bound PBDEs worldwide. Higher PBDE levels in $PM_{2.5}$ were strongly associated with unregulated dismantling of electric-waste (e-waste) (Deng et al., 2007; Han et al., 2009) and emission from the surfaces of household PBDE-contained products (Chao et al., 2016). In addition, concentrations of PBDEs in $PM_{2.5}$ varied between different types of industrial areas (Dong et al., 2015). However, spatiotemporal variability of polybrominated diphenyl ethers in atmospheric fine particles in China esp. from a electronics industry production base has never been reported.

China has been one of the main recipient of e-waste from developed countries because of increasing domestic market demand of PBDEs (Ni and Zeng, 2009). Up to 261000 tons of e-wastes containing PBDEs were imported into Guangdong Province in 2002 in scrap electronic devices, which was 3–5 times the global production of PBDEs in 1999 (She et al., 2010). It is well known that Shenzhen of Guangdong has been a globally important electronics industry production base since the 1980s. Gross output value of manufacture of communication equipment, computers and other electronic equipment accounted for 59.02% of the total gross output of the whole city in 2016 (Shenzhen Statistics Bureau, 2017). By December 2016, the total number of motor vehicles in the city reached 3.23 million (Shenzhen Statistics Bureau, 2017) and the vehicle density was the highest in the whole country. All the above may increase a relatively higher exposure of PBDEs for local residents in Shenzhen. However, little is known about PBDE levels in $PM_{2.5}$ in Shenzhen. According to several previous reports, PBDE levels in breast milk in primiparas from Shenzhen were higher than those from the other cities of mainland China and other countries of Asia and European (Zhang et al., 2012b). Moreover, the mean levels of PBDEs in soil of Shenzhen were higher than that of other areas in the Pearl River Delta (PRD) of Guangdong (Qin et al., 2011). However, relatively lower levels of PBDEs in retail foods were also reported for Shenzhen (Jiang et al., 2010; Liu et al., 2011). Therefore, it's necessary to conduct surveys on the levels as well as spatiotemporal variability of PBDEs in $PM_{2.5}$ in Shenzhen, which is important and helpful for future surveillance and trend analysis.

Although there were a few reports on the levels of PBDEs in fine particles, the influences of emission sources especially for land use and meteorological factors on PBDEs in $PM_{2.5}$ have not been comprehensively studied. The study aimed to investigate the concentrations, profiles, spatial distributions, and seasonal variations of PBDEs in $PM_{2.5}$ as well as to estimate the daily inhalation doses for local residents in Shenzhen, China. Factors influencing the PBDE levels such as emission sources and meteorological parameters were also explored.

2. Materials and methods

2.1. Chemical reagents and standard solutions

Organic solvents for trace residual analysis (toluene, n-hexane, dichloromethane, ethyl acetate and acetone) were purchased from Merck (Darmstadt, Germany). Calibration standard solutions (EO-5279), ^{13}C-labeled surrogate standards (EO-5277), cleanup standards (EO-5276) and injection standards (EO-5275) specified in US EPA Method 1614A (US EPA, 2010) for PBDE analysis were purchased from Cambridge Isotope Laboratories Co. (Andover, MA, USA).

2.2. Sampling procedures

Twelve sampling sites with different surrounding circumstances were chosen from the environmental monitoring stations, covering 6 administrative regions and 2 functional divisions of Shenzhen. Their locations are showed in Fig. 1. $PM_{2.5}$ samples were collected on quartz fiber filters (20 cm × 25 cm, Whatman, UK) using high volume air samplers (Tianhong Intelligent Instrument Plant, Wuhan, China) at the flow rate of 1.05 m^3/min. The air samplers of TH-1000 series are equipped with $PM_{2.5}$ cutters and can exclusively collect atmospheric particles with diameters less than or equal to 2.5 μm. It is recommended the ideal instrument for sampling particle matters in the atmosphere by the State Environmental Protection Department and the National Environmental Monitoring Station. Each sample was collected continuously for 24 h, yielding a total sampling volume of about 1436 m^3. Following the US EPA Compendium Method TO-9A (US EPA, 1999), a total of 36 samples with 1–3 for each site were collected from December 2014 to March 2015. In addition, Shenzhen belongs to a subtropical monsoon climate and the four seasons are unclear, only with the cent of the rainy and dry seasons. To better represent the meteorology and climatology during the entire study period, the sampling period was further divided into 2 periods, the winter + spring period (February to April in 2014 and January to March in 2015) and the summer + autumn period (June 2014 to October 2014). Prior to sampling, quartz fiber filters were baked at 550 °C for 5 h to remove any organic impurities. After sampling, the quartz fiber filters were retrieved and stored at 4 °C until extraction.

2.3. Source and meteorological parameters

In the present study, a total of 12 parameters including 7 source parameters and 5 meteorological parameters were studied. Based on Landsat OLI satellite image data, the land use information and classification (residential, industrial land, traffic, vegetation and water) within the radius of 3 km around sampling points was obtained by object-oriented method, accomplished by Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences. Electronic factories were reported as an important source of PBDEs. Since there are large amount of electronics factories in Shenzhen, China, we marked electronics factories with a annual discharge (including solid waste, waste water, and air emissions) of more than 1000 tons at the map (Fig. 1) according to the unpublished data from Environmental Monitoring Station of Shenzhen Municipality. Electronics factories at a distance ≤10 km (based on the diffusion distance of pollutant model) to the sampling sites were further picked out and the ratio of the annual discharge amount to the distance from these electronic factories was computed and the cumulative sum for each site was taken as one of the parameters. The traffic flow of each sampling site within a radius of 1 km was