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Halogenated flame retardants (HFRs) and water-soluble ions (WSIs) in fine particulate matter ($PM_{2.5}$) in three regions of South China☆

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ABSTRACT

Halogenated flame retardants (HFRs) and water-soluble ions (WSIs) were investigated in fine particulate matter ($PM_{2.5}$) collected from an urban site, a rural e-waste recycling (e-waste) site, and a background site in South China. Generally, the WSI concentrations were highest at the e-waste site and comparable at the other sites and secondary species (SO_4^{2-}, NH_4^+, and NO_3^-) were dominant components at the three sites. The compositions and seasonal variations of WSIs at the e-waste site were distinct from those in the urban and background areas suggesting significant influence of e-waste recycling on $PM_{2.5}$ components. Polybrominated diphenyl ethers (PBDEs) dominated the HFRs in $PM_{2.5}$ from the e-waste site, and their concentrations (median = 883 pg/m^3) were significantly higher than those at the urban (375 pg/m^3) and background site (52.4 pg/m^3). However, novel decabromodiphenyl ethane (DBDPE) was the primary HFRs in the urban air, with noticeably elevated concentrations (median = 356 pg/m^3) compared to those in the other two areas (medians = 62.3 and 5.09 pg/m^3). The composition profiles of HFRs in the background air followed those in the e-waste areas, with substantial contributions of legacy chemicals. This was explained by the prevailing NE wind, which favored atmospheric transport of HFRs from the e-waste recycling area to the background area. Correlation analysis showed that most HFRs in the urban air are associated with Cl^-, implying an industrial emission sources. In the e-waste area, HFRs are associated with organic and elemental carbons (OC and EC) and K^+, confirming a common source of e-waste recycling. Significant correlations between HFRs and EC and Cl^- in the background air suggest that their occurrence in this region was attributed to both the e-waste and urban areas.

1. Introduction

Halogenated flame retardants (HFRs), usually containing chlorine or bromine bonded to carbon, are a class of organic compounds that are added to many consumer products (such as electronic products, textiles, and furniture) to delay the spread of fire after ignition (Venier et al., 2015). Most of these chemicals are not covalently bound to the polymers of the products, and can be released to the environment during usage and disposal of the HFRs-containing products (Alaee, 2003). A class of HFRs known as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and Dechlorane Plus (DP) have become a topic of great concern because of their persistence, widespread occurrence in the environment, and potential adverse effects on humans and wildlife (Cetin and Odabasi, 2007; Qiu et al., 2007; Harrad et al., 2009; Covaci et al., 2011; Ali et al., 2012).

Pollution of fine particulate matter with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) is a prominent environmental issue in recent decades because of the substantial adverse impacts for human health, visibility, and climate (He et al., 2011; Xu et al., 2016). $PM_{2.5}$ may originate from primary emissions (e.g., from fuel combustion, industrial emissions, and biomass burning) or secondary aerosol formation (including new particle formation and particle growth). Therefore, $PM_{2.5}$ has various chemical components such as mineral dust, water-soluble ionic species (WSIs), and carbonaceous material because of the natures of the sources. Ions such as NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, K^+, Ca^{2+} Na^+, and Mg^{2+} are significant

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water-soluble components of aerosols. NH_4^+, SO_4^{2-}, and NO_3^- are main secondary species that are formed largely through heterogeneous or homogeneous reaction (Tian et al., 2016). Organic carbon (OC) and elemental carbon (EC) are also major components of $PM_{2.5}$ aerosols, accounting for 10–45% of the mass (Wang et al., 2015). OC may emit directly through various combustion sources or formed through atmospheric oxidation of gaseous organic precursors; while EC is produced from incomplete combustion processes such as biomass burning, vehicle exhaust, and coal combustion (Arhami et al., 2017; Zhang et al., 2017b).

HFRs in the environment originate largely from primary sources, such as HFR-containing products by volatilization or abrasion, industrial emissions, and combustion sources (e.g., waste incinerators, metallurgical processes, and power-heating systems) (Ceradini et al., 2011; Odabasi et al., 2009; Wang et al., 2010b). Because of their properties of lipophilicity and lower vapor pressure, many HFRs tend to closely bind to PM, especially particles with small size and abundant organic matter (Li et al., 2015; Okonski et al., 2014; Qi et al., 2014), which exerts important influence on the environmental fate of HFRs. Raff and Hites (2007) found that PBDEs bonded to urban particles may be more resistant to photo-degradation because of the shield effect of carbonaceous aerosols (Raff and Hites, 2007). HFRs associated with small size particle have ability to transport at long distances to remote regions (Hoh and Hites, 2005; Ma et al., 2017; Tian et al., 2011). Chemical components of WSIs and carbonaceous material have been used to identify and quantify the sources of PM based on receptor models in many studies (Jeong et al., 2017; Lee et al., 2008; Liu et al., 2017a; Xu et al., 2017). Thus, a combined analysis these components and HFRs is conducive to understanding the sources of HFRs in air due to the close association of HFRs with $PM_{2.5}$.

In this study, year-round $PM_{2.5}$ was collected from three sites in an industrialized megacity, a rural electronic waste recycling (e-waste) area, and a background forest area in South China, respectively. Components of OC and EC, WSI, and HFRs were measured in the $PM_{2.5}$. We aim to investigate the concentrations and compositions of these pollutants in the three regions and to examine their spatial and temporal variations in South China. The main objective is to explore the associations of HFRs and other components to understand the atmospheric sources and processes of HFRs in the $PM_{2.5}$.

2. Materials and methods

Information on the materials and methods was given in detail in the Supplementary Material and was described briefly here.

2.1. Sample information

Sampling was conducted at three sites in South China (Fig. 1). The urban site is representative of the residential areas in a megacity (Guangzhou). The e-waste site is in a rural e-waste recycling area covering an area of about 330 km^2). The background site is located in Dinghushan Mountain National Nature Reserve (with an area of 11.33 km^2). $PM_{2.5}$ samples were collected using a high-volume air sampler (TE-6001-2.5-I, Tisch Environment Inc., USA) operated at 1.03 m^3/min, which was set on a building rooftop approximately 9–12 m above ground level. The samples were obtained in 6-consecutive days in every month from March 2013 to February 2014. Each sample was collected for 24 h by drawing air through Whatman quartz microfiber filters. In total, 72 $PM_{2.5}$ samples were obtained at each site. After sampling, the filters were wrapped in aluminum foil, and stored at −20 °C until analysis.

2.2. Chemical analysis

$PM_{2.5}$ samples for HFR analysis were spiked with BDE77, BDE181, BDE205, ^{13}C-BDE209 and ^{13}C-α-, β-, γ-HBCDs as surrogate standards to determine the procedural recoveries and Soxhlet extracted with a mixture of hexane and acetone (1:1) for 48 h. The extracts were concentrated to 1–2 mL and then were purified and fractionated through a florisil solid phase extraction (SPE) column (Supelclean ENVI-Florisil, 3 mL, 500 mg). BDE118 and BDE128 and d_{18}-α-, β-, γ-HBCDs were added as internal standards before instrumental analysis. The majority of the target compounds including PBDEs, decabromodiphenyl ethane (DBDPE), BTBPE, DPs, pentabromotoluene (PBT), and hexabromobezene (HBB) were analyzed using a gas chromatograph coupled to a mass spectrometer in electron capture negative ionization mode (GC-ECNI-MS). HBCDs were measured using a reversed-phase liquid chromatography (LC)/MS-MS in electrospray negative ionization (ESI) mode. For the WSIs, a punch (5.06 cm^2) of the filters was extracted twice with 10 mL ultrapure Milli-Q water using an ultrasonic ice-water bath. The ions were analyzed with an ion-chromatography (IC) system (Metrohm, 883 Basic IC plus). OC and EC were measured using a thermal/optical reflectance method (DRI Model 2001 OC/EC analyzer, Atmoslytic Inc., US).

2.3. Quality control

Field blanks were routinely processed in each sampling session, they and laboratory blanks were analyzed with the field samples. Trace amounts of BDE47, 206, 207, 208, and 209 were detected in the field blanks. Accordingly, the reported concentrations in the samples were blank corrected. The average surrogate recoveries were 98.3 ± 16.5% for BDE77, 109 ± 22.3% for BDE181, 107 ± 39.4% for BDE205, and 107% ± 32.8% for ^{13}C-BDE209, respectively and the recoveries for ^{13}C-α-, β-, and γ-HBCD were 105% ± 27.1%, 86.8% ± 27.6%, and 95.2% ± 46.9%, respectively. Sample concentrations were not surrogate recovery corrected. The method detection limits (MDLs) were assigned as the average values of the field blanks plus 3 times the standard deviation. When compounds were not found in the field blanks, the MDLs were calculated as a signal five times the noise level. The MDL for PBDEs and non-BDE flame retardants ranged from 0.015 to 0.53 pg/m^3 and from <0.01 to 0.90 pg/m^3, respectively. The MDL for water soluble inorganic compounds ranged from 0.015 to 0.15 μg/m^3.

3. Results and discussion

3.1. Concentrations and seasonal variations of $PM_{2.5}$, OC, EC, and WSIs

The average $PM_{2.5}$ concentrations in the air during the sampling period at the e-waste site (182 ± 62.0 μg/m^3) were significantly higher than those at the urban (73.0 ± 31.0 μg/m^3) and background (80.8 ± 31.7 μg/m^3) sites ($p < 0.001$) (Table S1 in the Supplementary Material), suggesting that e-waste recycling activities may be a significant source of $PM_{2.5}$ surrounding the e-waste site. However, there is no significant difference in the concentrations between the urban and background sites. The average levels in the study region all exceeded the National Ambient Air Quality Standards of China-Grade II (35 μg/m^3 for annual $PM_{2.5}$ concentration). $PM_{2.5}$ concentrations were higher in winter (from DEC to FEB) and fall (from SEP to NOV) at the three sites (Fig. S1).

OC and EC are important carbonaceous components of aerosol and play a significant role in the behaviors of semi-volatile organic compounds in the atmosphere. The median concentrations of OC and EC at the urban, e-waste, and background sites were 7.69, 12.9,