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Gas–particle phase partitioning and particle size distribution of chlorinated and brominated polycyclic aromatic hydrocarbons in haze[☆]

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ABSTRACT

Chlorinated and brominated polycyclic aromatic hydrocarbons (Cl/Br-PAHs) are emerging semi-volatile organic pollutants in haze-associated particulate matter (PM). Their gas–particle phase partitioning and distribution among PM fractions have not been clarified. Clarification would increase understanding of atmospheric behavior and health risks of Cl/Br-PAHs. In this study, samples of the gas phase and 4 PM phases (aerodynamic diameters (d_{ae}) > 10 μm, 2.5–10 μm, 1.0–2.5 μm, and <1.0 μm) were collected simultaneously during haze events in Beijing and analyzed. Normalized histogram distribution indicated that the Cl/Br-PAHs tended to adhere to fine particles. Over 80% of the Cl-PAHs and 70% of the Br-PAHs were associated with fine PM ($d_{ae} < 2.5$ μm). The gas–particle phase partitioning and PM distribution of Cl/Br-PAHs when heating of buildings was required, which was associated with haze events, were obviously different from those when heating was not required. The relationship between the logarithmic geometric mean diameters of the Cl/Br-PAH congeners and reciprocal of the temperature ($1/T$) suggested that low air temperatures during the heating period could lead to high proportions of Cl/Br-PAHs in the fine particles. Increased coal burning during the heating period also contributed to high Cl/Br-PAH loads in the fine particles.

1. Introduction

Chlorinated and brominated polycyclic aromatic hydrocarbons (Cl/Br-PAHs, three-to-five rings) are halogenated derivatives of polycyclic aromatic hydrocarbons (PAHs). The Cl/Br-PAH congeners can induce aryl hydrocarbon receptor-mediated toxic responses, and the mutagenicities of some Cl/Br-PAH congeners are higher than those of their parent PAH congeners (Horii et al., 2009; Ohura et al., 2007, 2009). The potencies of Cl/Br-PAH congeners to induce aryl hydrocarbon receptor activities relative to the potency of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxins (2,3,7,8-TCDD) have also been determined (Horii et al., 2009; Ohura et al., 2007). Therefore, the occurrence, characteristics, and gas–particle phase partitioning of Cl/Br-PAHs in the atmosphere are of great concern.

Cl/Br-PAHs are semi-volatile organic compounds (SVOCs) that partition between the gaseous and particulate phases of the atmosphere. In previous study about Cl-PAHs in atmosphere of Japan, Cl-PAHs were thought to exist mainly in the gas phase, with about 81% of Cl-PAHs in this phase (Ohura et al., 2008). We found that the fraction of Cl-PAHs associated with particulate matter (PM) obviously increased with higher PM concentrations in the air, especially during haze events, which occur frequently during the period when heating of buildings is required in northern China (referred to as the heating period) (Jin et al., 2017a). This proportion of Cl-PAHs associated with PM was 67% on hazy days in Beijing, China. Therefore, in addition to the gas phase, the PM phase is an important exposure source to atmospheric Cl/Br-PAHs, especially on hazy days. There is no study on the gas–particle

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phase partitioning of brominated PAHs (Br-PAHs). Because gas–particle phase partitioning affects the atmospheric behavior and fate of Cl-PAHs and Br-PAHs, further studies on gas–particle phase partitioning and the factors that influence this partitioning are needed.

Particles with different sizes may undergo different atmospheric transport or deposition processes (Barmpadimos et al., 2012; Bidleman, 1988). In addition, the mechanisms of adsorption and absorption of PM-associated SVOCs, such as Cl-PAHs and Br-PAHs, vary with the particle size. Therefore, particle size affects environmental behavior of SVOCs, such as long-range transport (Barmpadimos et al., 2012; Lammel et al., 2017), atmospheric dry and wet deposition (Bidleman, 1988; Luo et al., 2014), and inhalation and penetration into organs (Brunekreef and Forsberg, 2005; Haddrell et al., 2015; Li et al., 2017). Intensive studies by Ohura et al. have investigated the occurrences and profiles of Cl-PAHs and Br-PAHs in total airborne PM (Ohura et al., 2008, 2016, 2009). However, studies focusing on the distribution of both Cl-PAHs and Br-PAHs in different particle size fractions are lacking. Moreover, there are many congeners of Cl-PAHs and Br-PAHs with different parent rings and halogen substitution numbers and positions. Therefore, there are large variations in the physiochemical properties, such as vapor pressure and molecular weight, among many Cl-PAH and Br-PAH congeners, and these differences could affect their particle size distribution (Sun et al., 2013a). To date, the differences among Cl-PAH and Br-PAH congeners have not been investigated, and the factors that affect the distribution of Cl-PAH and Br-PAH congeners in PM fractions remain unclear. Therefore, studies on the PM distribution of Cl-PAH and Br-PAH congeners are required for better understanding of their atmospheric behavior, fate, and risks for human health.

Beijing, located in northern China, has suffered from haze events in recent years (Du and Li, 2016; Wang et al., 2014; Zheng et al., 2016). Coal combustion is commonly used for heating buildings during the cold seasons in North China (heating period). Over this period, hazy days occur much more frequently than over the period when heating is not required (non-heating period). In our previous studies, we found that the concentrations of Cl/Br-PAHs were three to nine times higher in the heating period than those in the non-heating period in Beijing (Jin et al., 2017a). A comparison among Asian cities for PM associated Cl-PAHs showed that the highest concentrations were found in winter (heating period) in Beijing (Kakimoto et al., 2014). However, differences in gas–particle phase partitioning and the PM distribution of Cl/Br-PAHs between hazy and non-hazy days have not been investigated, and the mechanisms influencing the partitioning and distribution remain unknown.

The present study aimed to clarify the gas–particle phase partitioning and PM distribution of emerging Cl/Br-PAHs under various atmospheric conditions with different PM concentrations. Gas phase and size-fractionated PM samples were collected during the heating and non-heating periods in Beijing on days with severe haze and no haze. The PM samples had aerodynamic diameters (d_{ae}) of >10 μm, 2.5–10 μm, 1.0–2.5 μm, and <1.0 μm. Thirty-seven Cl/Br-PAHs congeners in the gas phase and four particle phases were identified and quantified by isotope dilution high resolution gas chromatography combined with high resolution mass spectrometry. Air samples with different PM concentrations ($PM_{2.5}$ range = 54.1–216 μg m^{-3}) were collected, analyzed, and compared for the gas–particle phase partitioning and PM distribution of Cl/Br-PAHs. The results were used to examine potential factors and mechanisms contributing to the gas–particle phase partitioning and PM distribution of Cl/Br-PAHs in the atmosphere during haze events.

2. Materials and methods

2.1. Chemicals

Nineteen Cl-PAH congeners and eighteen Br-PAH congeners were analyzed in PM in this study. Standards, isotope labeled internal standards of the Cl/Br-PAHs were purchased commercially as reported in our previous study (Jin et al., 2017b). The mono-to tetrachlorinated PAH congeners used in this study were chlorofluorene (ClFle), chloroanthracene (ClAnt), chlorophenanthrene (ClPhe), chlorofluoranthene (ClFlu), chloropyrene (ClPyr), chlorobenz[*a*]anthracene (ClAnt), and chlorobenzo[*a*]pyrene (ClPyr). The mono-to dibrominated PAH congeners used in this study were bromofluorene (BrFle), bromoacenaphthene (BrAna), bromoanthracene (BrAnt), bromophenanthrene (BrPhe), bromofluoranthene (BrFlu), bromopyrene (BrPyr), and bromobenz[*a*]anthracene (BrBaA). The specific Cl-PAH and Br-PAH congeners analyzed in this study and their abbreviations are detailed in the Supporting Information (Table S1). $^{13}C_6$ labeled 9-chlorophenanthrene ($^{13}C_6$-9-ClPhe), 2-chloroanthracene ($^{13}C_6$-2-ClAnt), 1-chloropyrene ($^{13}C_6$-1-ClPyr), 7-chlorobenz[*a*]anthracene ($^{13}C_6$-7-ClBaA), 7-bromobenz[*a*]anthracene ($^{13}C_6$-7-BrBaA), and d-labeled bromophenanthrene (d_9-9-BrPhe) were used as the internal standards, $^{13}C_6$ labeled 7,12-dichlorobenz[*a*]anthracene ($^{13}C_6$-7,12-Cl2BaA) was used as recovery standard.

2.2. Simultaneous collection of gas and particle phase samples

Ambient air samples were collected from March 2016 to January 2017 in Beijing using a high-volume cascade impactor (KS303 p.m. 10/2.5/1.0 sampler, Kálmán System, Hungary) with size-selective inlets. Samplers were placed on the roof of a building (approximately 12 m above the ground), with no obviously industrial source within 4 km. Each sample was collected continuously for 3–6 d, with a constant flow rate of 24 m^3 h^{-1}. Each sample set included a gas phase sample and PM samples of four different sizes. Six samples were collected during the heating period, and six samples during the non-heating period. Sampling dates and average temperatures are provided in the Supporting Information (Table S2).

The gas phase was adsorbed onto a polyurethane foam filter (ø 63 mm and length 76 mm; Tisch Environmental, USA), which was put in a glass cartridge in the sampler. Before use, the polyurethane foam filters were extracted by accelerated solvent extraction (Thermo Fisher Scientific, USA) with acetone, and then by a 1:1 mixture of dichloromethane and hexane. Four quartz fiber filters (QFFs; Ahlstrom Munktell, Sweden), were used to capture the particles with d_{ae} of >10 μm, 2.5–10 μm, 1.0–2.5 μm, and <1.0 μm. Before sampling, the QFFs were baked at 450 °C for more than 6.5 h to remove any organic contaminants. The QFFs were dried and weighed before and after sampling to determine the mass of each PM fraction collected. Details for operation of the sampler are provided in our previous study (Zhu et al., 2016). All samples were transported to the laboratory and stored at −18 °C until required for analysis.

2.3. Sample extraction and analysis

Cl-PAHs and Br-PAHs were analyzed by using isotope dilution high resolution gas chromatography combined with high resolution mass spectrometry as described in our previous studies (Jin et al., 2017a, 2017b). The samples were spiked with 1 ng of ^{13}C-labeled Cl/Br-PAH or deuterium-labeled Br-PAH internal standards before extraction by accelerated solvent extraction with dichloromethane and hexane (1:1, *v*:*v*). The extracts were then cleaned using an active silica gel column, and concentrated to

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