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Profiles, sources and potential exposures of parent, chlorinated and brominated polycyclic aromatic hydrocarbons in haze associated atmosphere

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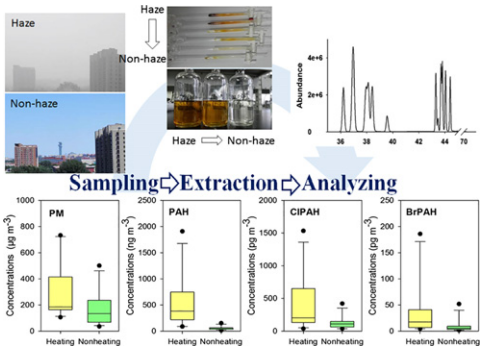
HIGHLIGHTS

- Several congeners of Cl, Br-PAHs in haze air were reported for the first time.
- Cl, Br-PAH levels in heating period were higher than that in non-heating period.
- Coal combustion contributes to the elevated levels of Cl, Br-PAHs in heating period.
- Inhalation of PM was important exposure pathway of Cl, Br-PAHs in haze days.

GRAPHICAL ABSTRACT



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ABSTRACT

Profiles, sources and potential exposures of chlorinated and brominated polycyclic aromatic hydrocarbons (ClPAHs and BrPAHs) in haze associated atmosphere remain unclear. Haze events happened frequently during heating period in Beijing provided a typical urban context to investigate the concentrations, profiles, sources and potential exposures of ClPAHs, BrPAHs and their non-halogenated parent compounds (PAHs) in air samples. Average concentrations of PAHs, ClPAHs and BrPAHs during heating periods (with more frequent haze events) were about 3–9 times higher than during non-heating periods. Concentrations of particulate matter (PM)-associated ClPAHs and BrPAHs were higher in heating period than in non-heating period, while for gas-associated ClPAHs and BrPAHs, this distinction was not significant. Congener patterns and congener profiles indicated that with increasing coal combustion during the heating period, concentrations of PAHs and ClPAHs in air were elevated in comparison to the non-heating period. Inhalation of PM-associated PAHs, ClPAHs and BrPAHs accounted for higher exposure than inhalation of gas phase and dermal contact of both gas phase and particulate phase. In this study we found that the particulate phase is the dominant exposure pathway of atmospheric PAHs, ClPAHs and BrPAHs during haze days, which is different from previous studies.

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1. Introduction

Air pollution in developing countries has attracted increasing public attention as rapid urbanization and industrial development have taken place (Cao et al., 2016; Wang et al., 2014; Zheng et al., 2016). It has been found that air pollution can significantly increase lung cancer risk (Beelen et al., 2008; Pope et al., 2002). In 2010, premature mortality linked to air pollution in China was estimated to be 1357 thousand deaths (Lelieveld et al., 2015). A recent study reported that air pollution might even lead to the occurrence of fine particle matter in the human brain (Maher et al., 2016). Organic matter occurs in both gaseous and particulate fractions of the air, accounting for about 31–48% of fine particulate matter (PM) (Huang et al., 2014b). In spite of their trace occurrence in air, persistent organic pollutants (POPs) are potentially carcinogenic to human health (Van den Berg et al., 2006). POPs also pose a long-term adverse effect on human health because of their persistence and bioaccumulation.

Polycyclic aromatic hydrocarbons (PAHs), as ubiquitous organic pollutants in the atmosphere, have been of public concern for decades (Armstrong and Gibbs, 2009; Zhang et al., 2009). A number of studies have assessed atmospheric PAHs as to their sources, concentrations in air, distributions in particles of different sizes and lung cancer risk (Hong et al., 2016; Jia et al., 2011; Phoothiwut and Junyapoon, 2013; Zhang et al., 2009). PAH derivatives, such as chlorinated or brominated PAHs (ClPAHs or BrPAHs) have attracted attention only recently. The toxicological studies suggested that some ClPAHs and BrPAHs exhibited even higher carcinogenic and mutagenic toxicity than their non-halogenated parent PAHs (Horii et al., 2009; Ohura et al., 2007; Ohura et al., 2009). Typically, the toxicities of most 3–5 ring ClPAHs and BrPAHs are higher than 2-ring compounds (e.g., polychlorinated naphthalenes; PCN) (Noma et al., 2004; Ohura et al., 2007). PCNs have already been added to annexes A and C of the Stockholm Convention on Persistent Organic Pollutants. ClPAHs and BrPAHs also tend to be bound to the Aryl hydrocarbon receptor (AhR), causing them to display a similar toxicity to that of notorious polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). In some specific environmental contexts, ClPAHs contribute much more to the total toxic equivalents (TEQs) than PCDD/Fs (Ma et al., 2009). It was estimated that the toxicity of exposure to ClPAHs, based on their AhR activities, was approximately 30–50 times higher than for dioxins in urban air in Japan (Ohura et al., 2007). To date, studies of the occurrence, sources and health risks of ClPAHs and BrPAHs in air samples are clearly insufficient, compared with their parent PAH compounds. Although a few case studies reported the concentrations, profiles, size distributions and health risks of PM-associated ClPAHs in urban air (Kakimoto et al., 2016; Kitazawa et al., 2006; Ma et al., 2013; Ohura et al., 2016; Ohura et al., 2005; Ohura et al., 2009; Sun et al., 2015; Wang et al., 2012), those for gas-associated ClPAHs are still very limited. No study has yet described the occurrence, sources and health risks of BrPAHs in gaseous and particulate air fractions.

In winter, large amount of coals are combusted to give warm in north China, and this season is normally called heating period. During the heating period, haze events happened frequently. A comparison between heating and non-heating period in Harbin, China suggested that the atmospheric PAH concentrations in heating period were approximately 3–17 fold of those in non-heating period (Ma et al., 2010). Coal combustion was suggested to be the major factors for the elevated PAH concentrations in heating period (Ma et al., 2010). But, whether the coal combustion in heating period would contribute to atmospheric ClPAHs and BrPAHs or not remains unclear.

Haze episodes in Beijing have attracted wide public concern in recent years (Fig. S1) (Huang et al., 2014a; Sun et al., 2016). There were two 'red' haze alarms (the highest grade of alarm for haze pollutions, predicting serious PM pollution for more than three days) and one 'orange' haze alarm (predicting serious PM pollution for three days) between August 2015 and March 2016 in Beijing. The most severe haze episode occurred between November 26 and December 1, 2015 with an hourly maximum $PM_{2.5}$ concentration of up to 626 μg m^{-3}. During these haze events, normal activities of workers and students were severely disrupted. For example, all teaching activities in schools were stopped during the 'red' alarm in Beijing.

The compositions, sources and health risks of haze pollution in Beijing have attracted great attention because of the seriousness of these haze events. Although some studies have addressed composition, sources and health risks of PM in haze episodes (Andersson et al., 2015; Betha et al., 2014; Liu et al., 2014), the occurrences, sources and associated health risks of trace ClPAHs, BrPAHs in particulate and gas fractions have never been studied, due to the requirement of high-volume air samplers and the difficulties in achieving accurate analytical results for ClPAHs and BrPAHs. Previous studies indicate that Beijing has one of the highest atmospheric PAH concentrations in several investigated cities in Asia (Hong et al., 2016; Zhang et al., 2016). Likewise, PM-associated ClPAHs had highest concentrations in air samples from Beijing, compared with the investigated other several Asian cities (Kakimoto et al., 2014). Therefore, it is vital to clarify the levels and sources of ClPAHs, BrPAHs and their parent compounds in Beijing, using haze events from August 2015 to March 2016 as a case study. An evaluation of risks of ClPAHs, BrPAHs and PAHs in haze also is critical to protect the health of Beijing's population.

The accurate quantification of congener specific ClPAHs and BrPAHs remains a challenge. In this study, isotopic dilution high-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC/HRMS) was used for simultaneously analysing 19 ClPAH and 19 BrPAH (3–5 ring) congeners in air samples. Some specific congeners were analysed for the first time in this study. The sources and the exposure risks of these pollutants in haze are discussed. To the best of our knowledge, this is the first study to simultaneously report ClPAHs, BrPAHs and their parent compounds, in both gaseous and particulate fractions during serious haze in Beijing. It provides important data on the adverse effects of trace carcinogenic organic contaminations in haze on human health.

2. Materials and methods

2.1. Abbreviations for the congeners

The 19 PAH congeners determined in this study were listed as follows: naphthalenes (Nap), 2-methynaphthalenes (2-MNap), acenaphthylene (Any), Acenaphthene (Ana), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(*a*)anthracene (BaA), chrysene (Chr), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*e*)pyrene (BeP), benzo(*a*)pyrene (BaP), perylene (Per), indeno(1,2,3-*cd*)pyrene (IcdP), dibenz(*ah*)anthracene (DahA), benzo(*ghi*)perylene (BghiP). The abbreviations of 19 ClPAH and 19 BrPAH congeners were also derived from their PAH skeletons. For example, 9-ClPhe represents the 9-chlorophenanthrene, and 1,2-Br_2Any represents the 1,2-dibromoacenaphthylene. The only exception was 2-BrTriph, which represented the 2-bromotriphenylene. Details about the abbreviations of ClPAH and BrPAH congeners were listed in Table S1.

2.2. Sampling method

Air samples were collected from August 2015 to March 2016 in Beijing from the rooftop of a building (116°12′28″ E, 40°00E, 4 N), around 20 m above ground. Sampling period covered both heating period (from Nov. 7, 2015 to Mar. 15, 2016: including the heating test time) and non-heating period in Beijing. This sampling station is an ecological and environmental monitoring station in Beijing. There are research institutes, residential buildings and local streets around the sampling site, typical of an urban setting. Samples were collected using high-volume samplers (Echo Hi-Vol, Tecora Co., France). The gaseous phase PAHs and halogenated PAHs (HPAHs) were adsorbed onto polyurethane foam (PUF;