Spatial distribution and exposure risks of ambient chlorinated polycyclic aromatic hydrocarbons in Tokyo Bay area and network approach to source impacts☆

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ABSTRACT

Chlorinated polycyclic aromatic hydrocarbons (ClPAHs) receive increasing attention as hazardous pollutants in terms of the high environmental persistence and toxicities. Ambient concentrations of 24 ClPAHs and 24 PAHs were investigated at 14 sites in the Tokyo Bay area of Japan. Twelve of 18 ClPAH species were detected in air samples, in spite of small sampling volumes. Mean concentrations of total PAHs in gas and particle phases were 5400 and 1400 pg/m^3, and mean concentrations of total ClPAHs in gas and particle phases were 40 and 14 pg/m^3, respectively. The spatial distributions of both total ClPAH and PAH concentrations indicated heavy pollution at sites in industrial activity areas. Principal component analysis suggested that the dominant sources of gaseous and particulate ClPAHs differed substantially from each other. In particular, gaseous ClPAHs could be produced by specific sources different from those of particulate ClPAHs. However, the dominant sources of particulate ClPAHs could be the same as those of particulate PAHs, including industrial activities such as steel and gas-production plants and natural gas-fired power plants. The influences of spatial relationships among sampling sites were represented using a network analysis. The constructed network showed that ambient ClPAHs and PAHs were dominated by local rather than regional pollution, because there were weaker relationships among nearby sites. Finally, exposure risks for ClPAHs were dominated by 7-chlorobenz[a]anthracene, followed by 9-chlorophenanthrene and 6-chlorobenzo[a]pyrene, and total risk was ~1/200 that of PAHs.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been known as emblematic environmental carcinogens, which are mainly produced by incomplete combustion of organic materials (Abdel-Shafy and Mansour, 2016; Baek et al., 1991; Bostrom et al., 2002; Kim et al., 2013; Lima et al., 2005). The generated PAHs initially disperse into the atmosphere, followed by wet/dry-deposition onto environmental media such as water, soil and plants, and are ultimately incorporated into the human body. Thus, investigation of the atmospheric incidence and possible sources of PAHs is important to evaluate exposure risks.

Regarding PAHs, it has been known that their atmospheric incidence is strongly driven by various external and internal factors in an area, such as meteorological and industrial (Burkart et al., 2013; Genualdi et al., 2009; Van Drooge et al., 2010). In particular, many studies have indicated definite relationships between human activities (population, industry, national gross domestic product, and others) and regional atmospheric PAH concentrations (Hafner et al., 2005; Leroyer et al., 2010; Shen et al., 2013; Zhang et al., 2016; Zhang and Tao, 2009). These findings suggest that the atmospheric PAH concentration is proportional to local anthropogenic energy consumption. Therefore, surveys of ambient PAHs in a local area are important to evaluate the exposure risks of residents in the vicinity of their potential sources.

Chlorinated polycyclic aromatic hydrocarbons (ClPAHs) are a group of PAH derivatives, some of which have carcinogenicity and mutagenicity as biological toxicities (Ohura, 2007; Sun et al., 2013).

Recently, 2-ring polychlorinated naphthalenes were included the ClPAH category, were listed in Annexes A and C of the Stockholm Convention on Persistent Organic Pollutants. Such ClPAHs have been detected in various environments worldwide, such as air, water and sediment, and are ubiquitous hazardous contaminants (Jin et al., 2017; Ohura, 2007; Ohura et al., 2014, 2016; Qiao et al., 2017; Sun et al., 2013). However, knowledge of sources of 3-ring ClPAHs is considerably limited compared with that of PAHs. Kamiya et al. (2016) investigated possible sources of ClPAHs associated with particles using positive matrix factorization analysis, showing that the primary source of ClPAHs was different from that of PAHs. Such different behaviors between ClPAHs and PAHs have been observed in our previous studies. For example, the composition ratios of individual PAHs in the atmosphere are relatively constant seasonally, whereas profiles of ClPAHs showed seasonal variation (Kamiya et al., 2016; Kitazawa et al., 2006). These findings demonstrate that sources and atmospheric behaviors of ClPAHs have little correspondence with those of PAHs. In addition, the photostabilities of many ClPAHs tend to be larger compared with those of their corresponding parent PAHs (Ohura et al., 2008a). These characteristics indicate that their atmospheric behaviors differ from PAHs.

Surveys of ClPAHs and PAHs at the same time at multiple sites are needed to demonstrate the different behaviors of ClPAHs, but no such surveys have been conducted. Therefore, we conducted simultaneous surveys of ambient ClPAHs and PAHs at various sites in the Tokyo Bay area, which is the most intensive industrial area in Japan. Spatial relationships of atmospheric ClPAHs and PAHs among the sites were evaluated using network analysis. We also estimated exposure risks of the compounds. This study provides the first data on the spatial distribution of ClPAHs and a new approach using network analysis for evaluation of that distribution.

2. Material and methods

2.1. Sampling procedure and site characteristics

The area along the shore of Tokyo Bay is the largest industrial zone in Japan, and has a number of steel, oil, and chemical plants. Therefore, air pollution from such plants has been a problem for some time in the area. In the present study, we took at air samples at 14 sites in the area within consecutive 4 days in 8–11 April 2004, among which 12 and 2 sites were on Tokyo Bay area and inland, respectively (Fig. S1 of Supplementary Material). The mean temperature and humidity at the sites were 18.2 ± 4.1 °C and 66.8 ± 11.1%, respectively.

Air samples were collected using a high-volume air sampler (HV-1000F; Sibata Scientific Technology Ltd., Tokyo, Japan) operated at a constant flow rate of 1.0 m^3/min for 1 h (total air volume ~60 m^3) at each site at ground level. The air was drawn through quartz fiber filters (QFFs; 20.3 × 25.4 cm) to collect particles, and then through polyurethane foam (PUF) plugs to collect compounds present in vapor phase. The QFF and PUF plugs were separately wrapped in aluminum foil, sealed, and stored in a freezer at −30 °C until extraction.

2.2. Chemicals

The target compounds were 18 ClPAHs. Detailed procedures for synthesizing 16 of these have been described previously (Kitazawa et al., 2006; Ohura et al., 2005). In addition, 22 PAHs, including 16 that have been classed as priority pollutants by the US Environmental Protection Agency, were analyzed. Standards of the PAHs were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Three deuterated PAHs (phenanthrene-d_{10}, fluoranthene-d_{10}, and

perylene-d_{12}), purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA), were used as internal standards. The solvents used in extraction and cleanup were of pesticide analysis grade, purchased from Wako Pure Chemical (Osaka, Japan) or Kanto Chemical (Tokyo, Japan). The 18 ClPAHs analyzed were the following: 9-chlorophenanthrene (9-ClPhe), 1,9-dichlorophenanthrene (1,9-Cl2Phe), 3,9-dichlorophenanthrene (3,9-Cl2Phe), 9,10-dichlorophenanthrene (9,10-Cl2Phe), 3,9,10-trichlorophenanthrene (3,9,10-Cl3Phe), 2-chloroanthracene (2-ClAnt), 9-chloroanthracene (9-ClAnt), 9,10-dichloroanthracene (9,10-Cl2Ant), 3-chlorofluoranthene (3-ClFluor), 8-chlorofluoranthene (8-ClFluor), 3,4-dichlorofluoranthene (3,4-Cl2Fluor), 3,8-dichlorofluoranthene (3,8-Cl2Fluor), 1-chloropyrene (1-ClPy), 6-chlorochrysene (6-ClChry), 6,12-dichlorochrysene (6,12-Cl2Chry), 7-chlorobenz[*a*]anthracene (7-ClBaA), 7,12-dichlorobenz[*a*]anthracene (7,12-Cl2BaA), and 6-chlorobenzo[*a*]pyrene (6-ClBaP). The 22 PAHs analyzed were as follows: naphthalene (Nap), acenaphthylene (Acl), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluor), pyrene (Py), benzo[*c*]phenanthrene (BcP), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*j*]fluoranthene (BjF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), benzo[ghi]perylene (BghiP), dibenzo[a,h]anthracene (DBahA), indeno[1,2,3-*cd*]pyrene (IP), dibenzo[a,h]pyrene (DBahP), dibenzo[a,i]pyrene (DBaiP), and dibenzo[a,l]pyrene (DBalP).

2.3. ClPAH and PAH analyses

The samples were extracted and the extracts cleaned, and the mass conditions using a method that has been described previously, allowing the concentrations of ClPAHs and PAHs associated with particles to be determined (Kamiya et al., 2015). Indeed, after air sample collection, the QFFs and PUF plugs were Soxhlet extracted separately for 16 h, in a mixture of *n*-hexane/dichloromethane (1:3, v/v) containing each 5 ng of fluoranthene-d_{10} and perylene-d_{12} as internal standards. The extracted samples were concentrated to ~1 mL by rotary evaporator. Each condensed solution was cleaned on a column chromatography with silica gel (Supelclean™ LC-Si SPE tube, Sigma-Aldrich Co. Ltd, St Louis, MO), and were eluted with 10 ml of 10% dichloromethane in *n*-hexane. The eluate was concentrated to ~500 μl under a gentle stream of N_2 at 45 °C. Prior to injection, phenanthrene-d_{10} (5 ng) was added to the residue as a recovery standard. During these operations, the solutions were protected from light to prevent photochemical degradation of the analytes. The extracts were analyzed using a JMS-Q1000GC quadrupole mass spectrometer (JEOL, Tokyo, Japan) equipped with a 7890A gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) fitted with an InertCap 5MS/NP capillary column (30-m long, 0.25-mm i.d., 0.25-μm film thickness; GL Science Inc., Tokyo, Japan). Helium was used as the carrier gas, at a flow rate of 1.0 mL/min. For the ClPAH analyses, oven temperature began at 100 °C and was held for 2 min. It was then increased at 25 °C/min to 200 °C and then increased at 5 °C/min to 300 °C, and held for 15 min. For the PAH analyses, oven temperature began at 70 °C and was held for 3 min. It was then increased at 20 °C/min to 240 °C and then increased at 5 °C/min to 310 °C, and held for 20 min. In both the ClPAH and PAH analyses, injector temperature was 300 °C and the transfer line temperature was 280 °C. The mass spectrometer was operated in selected ion monitoring and electron impact ionization modes. A constant ion current of 200 μA was used, and the electron energy was 70 eV.

2.4. Quality assurance

The purities of the compounds were determined by gas