Distributions and multiple sources of chlorinated polycyclic aromatic hydrocarbons in the air over Japan

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HIGHLIGHTS

- Spatial distributions of ClPAHs in Japan were reported for the first time.
- Diagnostic ratios using certain ClPAHs are useful tool to identify the sources.
- A heat map analysis using the environmental data permits to visualize the source impacts.
- The sources of ClPAHs are classified into three broad types.

GRAPHICAL ABSTRACT
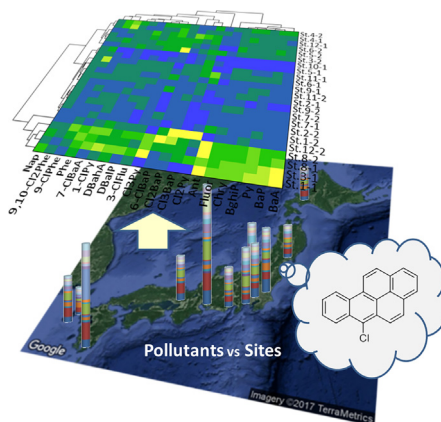
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ABSTRACT

Chlorinated polycyclic aromatic hydrocarbons (ClPAHs) have been detected in the air at discrete sites in Japan, but there is no information on their distributions throughout Japan. This study was a widespread survey of atmospheric concentrations of ClPAHs throughout Japan. The majority of 24 species of ClPAHs were detected in either the gas or particle phase at all sampling sites. The concentrations were weakly related to human population densities. The relationships between total concentrations of ClPAHs and PAHs suggested that atmospheric ClPAHs at ~70% of the sites were derived from common sources of PAHs. A ternary diagram based on diagnostic ratios of 1-chloropyrene, 7-chlorobenz[*a*]anthracene, and 6-chlorobenzo[*a*]pyrene normalized to 3-chlorofluoranthene suggested that waste combustion was the likely source of ClPAHs in summer and that vehicular emissions and coal burning were the likely sources of ClPAHs in winter. A heat map analysis estimated from the concentrations of individual compounds at each site suggested that there were three categories of sources at the sites: i) common sources of ClPAHs and PAHs that had moderate impacts, ii) common sources of ClPAHs and PAHs that had high impacts, and iii) specific sources of ClPAHs.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are recognized as major environmental hazardous factors that influence human health risks because of their mutagenic and carcinogenic potencies (Abbas et al., 2018; Bostrom et al., 2002; Kim et al., 2013; Nisbet and LaGoy, 1992). PAHs in the environment are produced mainly by anthropogenic sources that include incomplete combustion of organic refuse and fossil fuels and by natural sources that include volcanic eruptions and forest fires (Abbas et al., 2018; Lima et al., 2005; Mastral and Callén, 2000; Richter and Howard, 2000). Dispersal of PAHs through the air can lead to environmental pollution. In addition, PAHs have a wide range of reactivity. For example, they react with hydroxyl radicals, nitrate radicals, and ozone, and the products of some of the reactions are more toxic than the reactants (Sasaki et al., 1995). Understanding the behavior of PAHs in the atmosphere could therefore provide important information that might be used to reduce the environmental and biological risks that they pose (Kim et al., 2013).

Chlorinated PAHs (ClPAHs) are PAH derivatives formed by substituting chlorine for hydrogen atoms on PAHs. They are structurally similar to dioxins and polychlorinated biphenyls (PCBs), which are very toxic organochlorine compounds. This structural similarity suggests that ClPAHs are probably mutagenic and carcinogenic, like PAHs and dioxins. Indeed, the ability of most ClPAHs to activate an aryl hydrocarbon receptor could enable them to exert a variety of toxic effects on body tissues (Horii et al., 2009a; Ohura et al., 2007). A number of researchers have carried out studies to clarify the risks to human health related to ClPAH toxicity, including the sources and behavior of ClPAHs in the environment (Ohura, 2007; Sun et al., 2013). Environmental studies of ClPAHs over the past decade have led to their recognition as ubiquitous environmental contaminants (Fan et al., 2017; Horii et al., 2009b; Jin et al., 2017a; Nishimura et al., 2017; Qiao et al., 2017; Wang et al., 2018; Wang et al., 2017). However, the knowledge base is distinctly limited for ClPAHs compared to PAHs, PCBs and dioxins.

Knowledge of the spatial distribution of an air pollutant can aid efforts to control its concentrations and assessments of the risks to human health from exposure to it. Investigations of the spatial distributions of atmospheric PAHs in various cities around the world have shown that their distributions have expanded globally because of increasing anthropogenic activities (Friedman and Selin, 2012; Lammel et al., 2009; Sehili and Lammel, 2007; Shen et al., 2013; Zhang and Tao, 2009). In contrast, only a few studies have reported the spatial distributions of atmospheric ClPAHs (Kakimoto et al., 2014; Ohura et al., 2018; Ohura et al., 2016). Results to date, however, have shown that ClPAHs and PAHs have quite different distributions (Ma et al., 2013; Ohura et al., 2018). The implication is that the dominant sources are different for ClPAHs and PAHs, whereas some reports have indicated that the principal sources of ClPAHs and PAHs are very similar (Kitazawa et al., 2006; Ohura et al., 2013; Ohura et al., 2005). This disagreement suggests that the sources of ClPAHs should be investigated in more detail to evaluate their environmental impacts.

To date, most studies of atmospheric ClPAHs have been conducted at a single site or at a few sites within a limited area over the seasons (Kakimoto et al., 2014; Ma et al., 2013; Ohura et al., 2013; Ohura et al., 2018; Ohura et al., 2016). Although those studies have enhanced understanding of annual and local variations of atmospheric ClPAH concentrations, there is no information on the global distribution of ClPAHs and their composition. The lack of information about the spread of atmospheric ClPAHs may delay implementation of strategies to control and reduce ClPAH concentrations in the future. In this study, we measured atmospheric ClPAH concentrations at 12 sites throughout Japan to provide information that will hopefully become part of a global ClPAH database. We also performed data analyses to estimate the sources and behavior of specific ClPAHs.

2. Materials and methods

2.1. Chemicals

This study targeted 24 species of ClPAHs with three to five aromatic rings. Most of these ClPAHs are synthesized ab initio, and the detailed procedures have been reported previously (Kamiya et al., 2015; Kitazawa et al., 2006; Ohura et al., 2005). In addition, we analyzed 23 other PAHs, including 16 that have been classified as priority pollutants by the U.S. Environmental Protection Agency. PAH standards were purchased from Sigma-Aldrich (Saint Louis, MO, USA). The abbreviations of the 23 PAHs and 24 ClPAHs targeted are listed in Table S2. 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 extractions and cleanups were performed with analytical grade solvents purchased from Wako Pure Chemical (Osaka, Japan) or Kanto Chemical (Tokyo, Japan).

2.2. Sampling sites and procedures

The air samples were collected during two-day intervals in the summer (August 2010) and winter (February 2011). The sites were distributed primarily along the Pacific side of the archipelago and included a wide range of land uses, from agricultural to industrial (Table S1). The sky was either clear or cloudy on each sampling day; mean temperatures were 28.9 °C in summer and 6.9 °C in winter. Table S1 provides more information about the sampling sites. The air was drawn through quartz fiber filters (20.3 × 25.4 cm) to collect particles and then through polyurethane foam plugs to collect compounds present in the vapor phase. The samples were collected with a high-volume air sampler (e.g., HV-700F; Sibata Scientific Technology Ltd., Saitama, Japan) at a constant flow rate of 700 L/h for 23 h. The sampler was placed on the ground level or rooftop of a building. A part of each filter and plug was cut out for analysis and was separately wrapped in aluminum foil, sealed, and stored in a freezer at −30 °C until extraction.

2.3. ClPAH and PAH analyses

Samples collected at a given site and day were treated as a single sample. The samples were extracted, the extracts cleaned, and the concentrations of ClPAHs and PAHs associated with particles determined as previously described (Kamiya et al., 2015). After air sample collection, the quartz fiber filters and polyurethane foam plugs were Soxhlet extracted separately for 16 h in a mixture of n-hexane/dichloromethane (1:3, v/v). Each extract contained 5 ng of fluoranthene-d_{10} and perylene-d_{12} as internal standards. The extracted samples were concentrated to ~1 mL in a rotary evaporator. Each condensed solution was cleaned on a column chromatograph with silica gel (Supelclean LC-Si SPE tube, Sigma-Aldrich Co., St. Louis, MO, USA) and was 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 with 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, the initial oven temperature of 100 °C was held for 2 min. The temperature was then increased at 25 °C/min to 200 °C, increased at 5 °C/min to 300 °C, and then held at 300 °C for 15 min. For the PAH analyses, the initial oven temperature of 70 °C was held for 3 min. The temperature was then increased at 20 °C/min to 240 °C, increased at 5 °C/min to 310 °C, and then held for 20 min. For both the ClPAH and PAH analyses, the