



Atmospheric chlorinated polycyclic aromatic hydrocarbons in East Asia



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HIGHLIGHTS

- Among six cities, atmospheric CIPAHs were highest in the samples from Beijing China.
- In Kanazawa and Busan, concentrations of CIPAHs were correlated with PAHs.
- Among 19 CIPAHs, 1-chloropyrene and 6-chlorobenzo[a]pyrene were abundant in this study.

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ABSTRACT

This study estimates atmospheric concentrations of chlorinated polycyclic aromatic hydrocarbons (CIPAHs) and polycyclic aromatic hydrocarbons (PAHs) in East Asia using a Gas Chromatograph with High Resolution Mass Spectrometer (GC-HRMS). CIPAHs are ubiquitously generated from PAHs through substitution, and some CIPAHs show higher aryl hydrocarbon receptor (AhR)-mediated activities than their parent PAHs. Atmospheric particles were collected using a high-volume air sampler equipped with a quartz-fiber filter. We determined the CIPAH concentrations of atmospheric particles collected in Japan (Sapporo, Sagami-hara, Kanazawa, and Kitakyushu), Korea (Busan), and China (Beijing). The concentrations of CIPAHs were highest in the winter Beijing sample, where the total mean concentration was approximately 15–70 times higher than in the winter samples from Japan and Korea. The concentrations of $\Sigma 19$ CIPAHs and $\Sigma 9$ PAHs were significantly correlated in the Kanazawa and the Busan samples. This indicates that within those cities CIPAHs and PAHs share the same origin, implying direct chlorination of parent PAHs. Toxic equivalent concentrations (TEQs) of the total CIPAHs and PAHs were lowest in Kanazawa in the summer, reaching 1.18 and 2610 fg-TEQ m⁻³ respectively, and highest in Beijing in the winter, reaching 627 and 4240 000 fg-TEQ m⁻³ respectively.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are environmental carcinogens and mutagens (IARC, 2013), which are distributed in the environment through combustion, discharge of fossil fuels, and automobile emissions (Lee et al., 1995; Takasuga et al., 2007; Pinedo et al., 2013). Humans are exposed to PAHs from various sources, including certain occupational environments, dietary sources, cigarette smoking, and fossil fuels (Lodovici et al., 1995; Hoffmann and Hoffmann, 1997; Liu et al., 2001). In recent decades, the detection of chlorinated PAHs (CIPAHs) in the environment,

including in tap water, road tunnels, and soil (Shiraishi et al., 1985; Nilsson and Öestman, 1993; Sugiyama et al., 1999; Ishaq et al., 2003) has attracted considerable interest. The structure of CIPAHs is similar to polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs). PAHs generated from the combustion of organic compounds can lead to concurrent production of CIPAHs (Takasuga et al., 2007), and Horii et al. (2008) reported a mechanism of direct chlorination of parent PAHs during incineration of wastes. In addition, the combustion of polyvinylchloride (PVC) and plastic wrapping made from polyvinylidene chloride (PVDC) results in the production of CIPAHs (Fujima et al., 2006). The evidence suggests that the combustion of organic materials in combination with the chlorine source, or of organic materials containing chlorine, is a possible source of environmental CIPAH pollution. There are concerns that

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CIPAHs have adverse effects on humans, based on reports that some CIPAHs exhibited mutagenic potential in *Salmonella typhimurium* strains TA98 and TA100 (Colmsjö et al., 1984; Bhatia et al., 1987), and showed stronger aryl hydrocarbon receptor (AhR)-mediated activities than those of the parent PAHs in yeast assays (Ohura et al., 2007). Owing to the lack of authentic CIPAH analytical standards, their environmental chemistry has not yet been examined in detail. In this study, we compare levels of atmospheric CIPAH contamination across East Asian countries. Atmospheric particles were collected using a high-volume air sampler equipped with a quartz-fiber filter, and we determined CIPAHs using a gas chromatograph with a high-resolution mass spectrometer (GC-HRMS).

2. Materials and methods

2.1. Sample collection

Samples were collected in six cities in Japan, Korea, and China in 2010. Detailed information about the sampling sites and times is presented in Table 1 and Fig. 1. Sapporo is located in the northern part of Japan and is the fourth-largest city in Japan. Sagami-hara is a suburban city located in the area around Tokyo, Kanazawa is a suburban city located on the Sea of Japan side of the archipelago, and Kitakyushu is a suburban city located in southern Japan. Busan is the second-largest city in Korea, and is located in southern part of the country. Beijing is the largest city in China, located in the northeast of the country. Atmospheric samples were collected at a flow rate of 1.0 m³ min⁻¹. The quartz-fiber filter was replaced daily. After sampling, the filters were packaged in aluminum foil and stored in a freezer until analysis.

2.2. Chemicals

A non-labeled 19CIPAH solution mix was provided by Ohura et al. (2005). A non-labeled PAH solution mix was purchased from Accu Standard (CT, USA). Deuterium-labeled standards (phenanthrene-*d*₁₀, chrysene-*d*₁₂, and perylene-*d*₁₂) were purchased from Wako Pure Chemicals (Osaka, Japan), and pyrene-*d*₁₀ was purchased from Cambridge Isotope Laboratories (MA, USA). Organic solvents of pesticide-analysis grade were used for the extraction and cleanup of samples, and a silica gel of dioxin analysis grade was purchased from Wako Pure Chemicals. The nineteen different CIPAHs analyzed in this study are abbreviated as follows: 9-chlorophenanthrene (9-CIPhe), 2-chloroanthracene (2-ClAnt), 9-chloroanthracene (9-ClAnt), 3,9-dichlorophenanthrene (3,9-diClPhe), 9,10-dichloroanthracene (9,10-diClAnt), 1,9-dichlorophenanthrene (1,9-diClPhe), 9,10-dichlorophenanthrene (9,10-diClPhe), 3-chlorofluoranthene (3-ClFluor), 8-chlorofluoranthene (8-ClFluor), 1-chloropyrene (1-ClPy), 3,9,10-trichlorophenanthrene (3,9,10-triClPhe),

1,3-dichlorofluoranthene (1,3-diClFluor), 3,8-dichlorofluoranthene (3,8-diClFluor), 3,4-dichlorofluoranthene (3,4-diClFluor), 6-chlorochrysene (6-ClChry), 7-chlorobenz[a]anthracene (7-ClBaA), 6,12-dichlorochrysene (6,12-diClChry), 7,12-dichlorobenz[a]anthracene (7,12-diClBaA), and 6-chlorobenzo[a]pyrene (6-ClBaP). The PAHs used in this study are abbreviated as follows: phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), chrysene (Chry), benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), and perylene (Pery).

2.3. Extraction and cleanup

The treatments for the atmospheric particle samples followed almost the same method used by Kitazawa et al. (2006); briefly: the filters were ultrasonically treated for 30 min with 50 mL of dichloromethane containing a stable isotope standard mixture (phenanthrene-*d*₁₀, pyrene-*d*₁₀, chrysene-*d*₁₂, and perylene-*d*₁₂; 5 ng each). After centrifugation, the supernatant was concentrated to approximately 1 mL. The solution was cleaned using a silica gel column (0.5 g). Then 10 mL of a hexane-dichloromethane mixture (9:1, v/v) was used as an eluent, 0.5 mL of nonane was added to this solution, after which it was evaporated until the hexane was completely removed. Finally, 1 μL of the sample solution was used for analysis by GC-HRMS.

2.4. GC/MS conditions

GC-HRMS analyses used a gas chromatograph (6890 series, Agilent Technologies, CA, USA) coupled with a high-resolution mass spectrometer (JMS-800D, JOEL, Tokyo, Japan). The GC conditions were as follows: column, capillary column (DB-5MS, 30 m, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, CA, USA); column temperature program: 100 °C (held for 1 min) to 200 °C at 25 °C min⁻¹, then to 310 °C (held for 5 min) at 5 °C min⁻¹; carrier gas, helium; column head pressure, 10 psi; injection temperature, 270 °C; injection mode, splitless (splitless time, 1.5 min). The MS conditions were as follows: electron ionization mode; electron energy, 38 eV; filament current, 500 μA; ion source temperature, 270 °C; resolution, 10000 (10% valley definition). The monitoring ions for each target compound are shown in Supplementary information (Table S1).

2.5. Quality assurance and quality control

The filters were spiked with the working solution, which includes all 19 CIPAHs and 9 PAHs, then extracted and analyzed by the same method used for the samples. Recoveries of each CIPAH and PAH in the filter samples (*n* = 5) all exceeded 90%, and the relative standard deviations of the recoveries of each CIPAH and PAH were less than 16.8% (spiking amounts: CIPAHs, 2–4.4 ng; PAHs,

Table 1
Sampling information.

Location	Population (million)	Season	Period	Temperature (°C)
Sapporo, Japan (latitude 43°04' 54.998", longitude 141°20' 00.366")	2	Summer (<i>n</i> = 7) Winter (<i>n</i> = 7)	9–15, August 12–18, February	25 –5
Sagami-hara, Japan (latitude 35°34' 41.675", longitude 139°23' 21.415")	0.7	Summer (<i>n</i> = 7) Winter (<i>n</i> = 6)	7–13, August 12–17, February	27 3
Kanazawa, Japan (latitude 36°32' 51.997", longitude 136°42' 33.188")	0.5	Summer (<i>n</i> = 7) Winter (<i>n</i> = 7)	9–16, August 11–24, February	29 3
Kitakyushu, Japan (latitude 33°53' 43.018", longitude 130°49' 45.753")	1	Summer (<i>n</i> = 7) Winter (<i>n</i> = 7)	9–22, August 13–19, February	29 5
Busan, Korea (latitude 35°15' 16.53", longitude 129°5' 1.114")	3.6	Summer (<i>n</i> = 7) Winter (<i>n</i> = 7)	9–15, August 12–20, February	27 5
Beijing, China (latitude 40°24' 50.94", longitude 116°43' 3.695")	20	Summer (<i>n</i> = 7) Winter (<i>n</i> = 7)	9–16, August 25–31, January	26 –1

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