

RELATIONSHIPS BETWEEN CHLORINATED POLYCYCLIC AROMATIC HYDROCARBONS AND DIOXINS IN URBAN AIR AND INCINERATORS

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Abstract

Chlorinated polycyclic aromatic hydrocarbons (CIPAHs) are ubiquitous contaminants in the environment. Seasonal concentrations of 12 CIPAHs with 3- to 5-ring associated with particles in urban air in Shizuoka, Japan were investigated from 1998 to 2002. Among the seven target CIPAHs that were detected in the air samples, which ranged from 1.97 pg/m³ (3,9-dichlorophenanthrene) to 13.21 pg/m³ (6-chlorobenzo[*a*]pyrene). In the near-source air samples, dioxins were also detected with range of 0.06 to 0.54 pg-TEQ/m³. There were no significant correlations of the concentrations between each particulate CIPAH and dioxins in the air. For flue gas samples collected in actual operating incinerators, a number of CIPAHs were detected at extremely high levels compared to the air samples. Dioxins were also detected from the flue gas samples, levels of which showed significant correlations to the certain CIPAHs levels. Consequently, these findings show that CIPAHs in air are possible to emit from incinerators, and could be indicator of dioxins production.

Introduction

Chlorinated organic compounds such as polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/DFs) and polychlorinated biphenyls (PCBs) are a serious problem because of their toxicity and the associated adverse effects on health^{1,2}. These compounds have many congeners, the toxicity of which depends on both the number and the position of the chlorine substituents. PCDDs/DFs are released into the environment by various sources, such as waste incineration, industrial activities, and vehicle emissions^{3,4}. PCBs are also released into the environment not only by the use and disposal of PCB products but also as byproducts of waste incineration^{5,6}. They are widespread environmental pollutants. In addition to PCDDs/DFs and PCBs, chlorinated polycyclic aromatic hydrocarbons (CIPAHs) in various environments have also been studied in recent years⁷.

CIPAHs contain two or more aromatic rings and one or more chlorine atoms attached to the ring system. They have many congeners, and the occurrences and toxicities of the congeners differ, as is the case for PCDDs/DFs. For example, 75 polychlorinated naphthalene (PCN) congeners contain 1 to 8 chlorine atoms. Several PCN congeners have dioxin-like toxicity, and the toxicity depends on the molecular structure⁸. Recently, CIPAHs with more than two rings were detected in some environmental samples, such as road tunnel air, exhaust gas from a municipal waste incinerator, and the pulp, effluent, and biosludge from bleached Kraft mills⁷. Several reports on the emission sources of CIPAHs have been published. Eklund et al.⁹ detected 12 species of CIPAHs in flue gas from a municipal waste incinerator and a coal fire boiler, at concentrations ranging from 0.01 to 23 µg/m³. Haglund et al. analyzed snow samples collected at various distances from a motorway and suggested that one possible major source for CIPAHs is car exhaust because CIPAH concentrations decreased with increasing distance from the road. The source of the halogen atoms is the halogen scavengers contained in leaded gasoline¹⁰.

Interest has been focused on the detection of CIPAHs in environmental samples, and we recently reported on seasonal trends in the concentrations of CIPAHs associated with particles in urban air^{11,12,13}. However, the occurrences of CIPAH in the air and the relationships to other chlorinated pollutants, dioxins, are not clear. In this study, we investigated long-term trends (1998–2002) in particulate concentrations of CIPAHs, followed by comparison to the corresponding dioxin levels. The aim of the study is to evaluate the traceability of CIPAHs to environmental dioxin.

Materials and Methods

Target CIPAHs.

As target, 12 species of CIPAHs with 3 to 5-ring and 25 species of CIPAHs with 2 to 5-ring were selected in the surveys of ambient particles and domestic combustion emissions, respectively (Fig. 1). Those CIPAHs were synthesized to use as the standard as described in elsewhere¹².

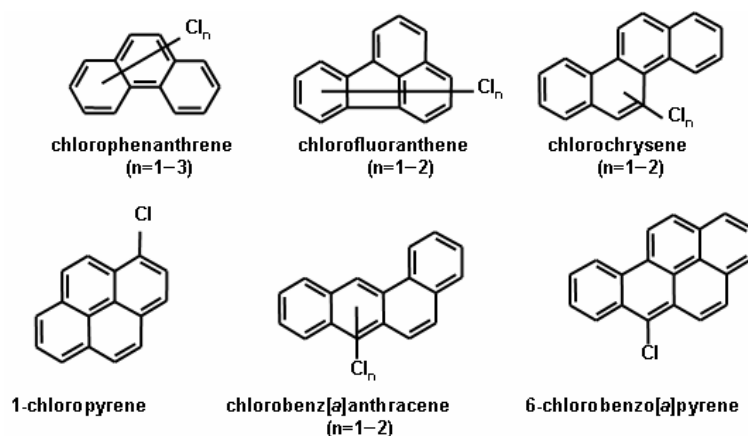


Figure 1. Structures of CIPAHs

Sample Collection.

Atmospheric suspended particle matter was collected approximately 25 m above ground level on the University of Shizuoka campus (latitude 34°59N, longitude 138°27E), which is located 6 km northeast of the center of the city of Shizuoka. To the north, the campus is surrounded by a residential area, and a national road, a prefectural road, and an expressway are located ca. 0.7 km from the campus. A semi-industrial area is also located ca. 1.3 km north of the campus. To the south of the campus are a mountainous area and then the Pacific Ocean; the area south of the campus is considered to be a background area. For the most part, the campus is influenced by wind from the Pacific Ocean in the summer and from the residential area in the winter. Therefore, traffic in the residential area and manufacturing plants in the semi-industrial area are the main sources of atmospheric pollutants around the campus. Sample collection was carried out for 24 h on a glass fiber filter (20.3 × 25.4 cm, type A/E, Gelman Science Inc., Ann Arbor, MI) with a high-volume air sampler (Sibata Scientific Technology Co., Tokyo, Japan) at a flow rate of about 1 m³/min. A sample was collected during the first week of every month from 1992 to 2002. After sample collection, the filters were wrapped in aluminum foil, placed in a vinyl bag, and stored in a freezer at -45 °C until extraction. Each 1-week sample was counted as a single sample. Samples of flue gas emissions were collected in actual operating incinerators (n=54) in Japan. The sampling was conducted with JIS K0311.

Procedure for Analysis of CIPAHs.

CIPAHs were extracted for 20 min with sonication in 50 mL of dichloromethane containing phenanthrene-*d*₁₀ (63 ng) and perylene-*d*₁₂ (155 ng) as internal standards. After centrifugal separation (10 min, 2000 rpm), 40 mL of the supernatant liquid was used as the sample solution. The liquid was concentrated to about 5 mL in a rotary evaporator and then blown down to about 1 mL under a gentle stream of nitrogen at 30 °C. The residue was cleaned up with a glass solid-phase extraction column (Supelco) packed with silica (500 mg; particle size, 40 μm; surface area, 520 m²/g; Supelco), which was eluted with 10 mL of a mixed solvent of *n*-hexane and dichloromethane (9:1, v/v). The eluate was concentrated to about 300 μL under a gentle stream of nitrogen at 30 °C for GC/MS analysis.

To analyze completely isomers of certain CIPAHs used, we here carried out the analysis using an HP 6890 GC/HP 5972A MSD (mass selective detector) system. The GC/MSD instrument was equipped with an automated sample introduction system and a splitless injector. A DB-5 capillary column was used (5% phenylmethylpolysiloxane, 60 m × 0.320 mm × 0.25 μm, J&W Scientific). Helium was used as a carrier gas at a flow rate of 1 mL/min. The oven temperature was kept at 80 °C for 2 min, increased from 80 to 300 °C at a rate of 5 °C min⁻¹, and then kept at 300 °C for 20 min. The temperature of the injector and the GC/MS transfer line was kept at 300 °C. The MSD was run in electron impact ionization mode, and the electron energy was 70 eV. Qualification of CIPAHs was performed in selected-ion monitoring (SIM) mode. The CIPAHs were identified by their specific retention times and their chlorine isotope ratios. The average recoveries (n = 6) of the target CIPAHs ranged from 90.1% ± 2.1% (3,9,10-Cl₃Phe) to 104.1% ± 2.5% (3,9-Cl₂Phe). The method detection

limits (MDL) were defined as 3 times the standard deviation of the low-concentrated standard solution ($S/N < 15$). The MDLs ranged from 0.34 ng (1-CIPy) to 1.9 ng (3,9,10-Cl₃Phe). To determine the reproducibility of the analytical method, we carried out double measurements; the reproducibility was within 15%.

Results and Discussion

CIPAH levels in ambient air.

The annual mean concentration ranges of detected CIPAHs and dioxins from 1998 to 2002 are summarized in Table 1. During the study period, 7 of 12 target CIPAHs were detected. The occurrences of 1-CIPy and 6-ClBaP remained at relatively high levels in the CIPAHs. The annual levels of total CIPAHs (Σ CIPAHs) generally continue to be flat during the period, whereas those of dioxins varied. The seasonal levels of CIPAHs showed typical trends, i.e. higher in cold season and lower in warm season (Fig.2). On the other hand, the trend of dioxins in the air, that was not shown such typical seasonal behavior. Indeed, there were no significant

Table 1. Annual mean concentrations of CIPAHs (pg/m³) and dioxins (pg-TEQ/m³) in the air

Compounds	1998	1999	2000	2001	2002
9-ClPhe	4.16	2.48	3.33	3.24	3.50
3,9-Cl ₂ Phe	< 0.82	< 0.82	< 0.82	1.97	2.74
9,10-Cl ₂ Phe	< 1.1	< 1.1	4.37	5.1	5.13
3-ClFluor	6.35	3.94	4.19	4.92	4.45
1-CIPy	6.50	3.94	6.99	5.59	7.5
7-ClBaA	4.73	3.38	3.38	3.02	3.08
6-ClBaP	13.2	9.61	8.49	7.12	6.47
Σ CIPAHs	32.6	22.8	30.6	30.7	31.4
Dioxin	0.54	0.10	0.29	0.17	0.06

correlations between each CIPAH and dioxins levels. In the previous study, however, we suggested that the predominant sources of CIPAHs associated particles collected in the same area could be incineration based on factor analysis. Therefore the disagreement of levels between two would be due to the reasons as follows: (1) the CIPAHs were measured in only particles in the air, whereas the dioxins were determined from gaseous and particles, (2) the difference of photostabilities between CIPAHs and dioxins, (3) difference of the potent emission sources between CIPAHs and dioxins, (4) difference of the production process in the certain sources between CIPAHs and dioxins. To reveal the relationship between CIPAHs and dioxin levels in air, it will need to investigate the occurrences of not only the particulate but also the gaseous CIPAHs.

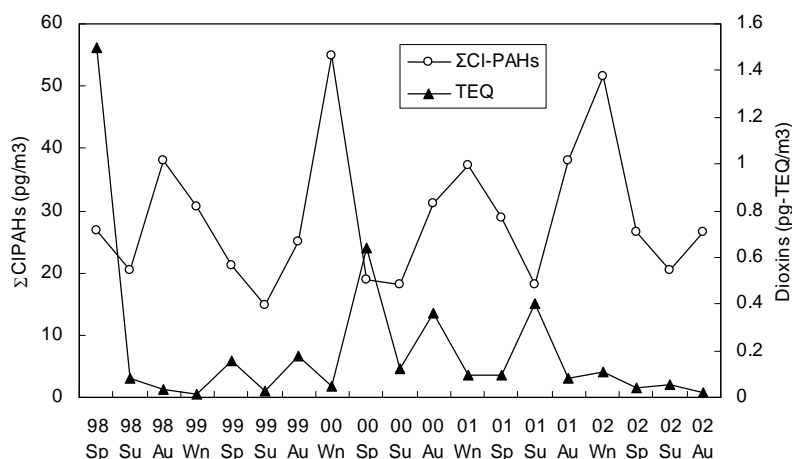


Figure 2. Seasonal trends of concentrations of CIPAHs (pg/m³) and dioxins (pg-TEQ/m³) in the air (1998-2002).

CIPAH levels in incinerators.

Further aim in the study is to investigate the levels of the chlorinated aromatics in flue gas emissions. The 22 of 25-targeted CIPAHs were observed in the flue gas emissions ($n=54$), mean concentrations of which ranged from 0.34 ng/Nm³ (5,7-dichlorofluoranthene) to 308 ng/Nm³ (1-chloropyrene), and that of Σ CIPAHs was 605 ng/Nm³ (Table 2). Those levels were extremely (ca. 350~60,000 times) higher than those in ambient particles, indicated that various CIPAHs were emitted from incinerators at high levels. Then, in the same samples, the levels of dioxins ranged from 0.00002 to 14 ng/m³-TEQ, although which trend to be totally lower than those of CIPAHs (Table 2). Comparison of the levels showed significant correlations between certain CIPAHs and Σ CIPAHs, and dioxin levels (data not shown). To observe the relationships among them, it may be due to detection of gaseous CIPAHs from the flue gas emissions. Although the environmental fates of CIPAHs emitted remained unclear, we can here suggest that CIPAHs could be produced via combustion process as well as dioxins, levels of which are possible to indicator of dioxins production.

Acknowledgements

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Table 2. Mean concentrations and range of CIPAHs (ng/Nm³) and dioxins (ng-TEQ/m³) in flue gas

No.	Compound	Mean conc. (range)
1	1,2,3,4-Cl ₄ Nap	3.8 (< 0.046-47)
2	1,3,5,7-Cl ₄ Nap	7.2 (< 0.084-237)
3	1,2,3,5,7-Cl ₅ Nap	3.2 (< 0.32-34)
4	1,2,3,5,6,7-Cl ₆ Nap	1.7 (< 0.50-15)
5	1,2,3,4,5,6,7-Cl ₇ Nap	1.1 (< 0.82-16)
6	9-ClPhe	67 (< 0.30-889)
7	3,9-Cl ₂ Phe	2.8 (< 1.0-89)
8	9,10-Cl ₂ Phe	0.67 (< 0.36-12)
9	2-ClAnt	1.2 (< 0.42-49)
10	9-ClAnt	13 (< 0.50-268)
11	9,10-Cl ₂ Ant+1,9-Cl ₂ Phe	6.5 (< 0.56-141)
12	3-ClFluor	26 (< 0.42-305)
13	8-ClFluor	6.4 (< 0.56-53)
14	3,4-Cl ₂ Fluor	2.5 (< 1.5-29)
15	3,8-Cl ₂ Fluor	3.2 (< 0.64-65)
16	5,7-Cl ₂ Fluor	0.34 (< 0.42-1.3)
17	1-ClPy	308 (< 0.36-7262)
18	6-ClChry	6.8 (< 0.50-129)
19	6,12-Cl ₂ Chry	2.7 (< 0.36-63)
20	7-ClBaA	16 (< 0.42-277)
21	7,12-Cl ₂ BaA	2.8 (< 0.46-44)
22	6-ClBaP	122 (< 0.92-3073)
23	Σ CIPAHs	605 (< 5.8-8783)
24	Dioxins	1.15 (0.00002-14)