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Analysis of Halogenated Polycyclic Aromatic Hydrocarbons in the Air

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1. Introduction

CIPAHs are a class of compounds with one or more chlorines attached to the aromatic rings of a PAH. In studies of CIPAHs in the environment, naphthalenes with four to eight chlorines attached—polychlorinated naphthalenes (PCNs)—have been comparatively well investigated [1-4]. Technical PCN mixtures known as Halowax and Nibren wax have physical and chemical properties similar to those of polychlorinated biphenyls (PCBs), so that they have been widely used flame retardant as alternative material of PCBs. In addition to their emission as byproducts of product manufacture, PCNs are released to the environment from waste incineration processes, in slag residues from copper ore smelters, and from some chloro-alkali processes [5-8]. PCNs are also present as impurities in PCB mixtures [9]. In contrast, because there have been only limited environmental studies of the larger (>3-ring) CIPAHs, the environmental occurrence of these compounds has not yet been fully investigated. One of the reasons is that reference substances for almost all the larger CIPAHs are not generally available commercially. Therefore, researchers who want to investigate the environmental occurrence and properties of the CIPAHs have to synthesize their own reference substances. Nevertheless, some energetic researchers have performed environmental studies of the CIPAHs. Recently, Ohura et al. succeeded to synthesize a variety of CIPAHs with 3 to 5 ring as analytical standards (Figure 1) [10-12]. It has been advanced the studies on not only environmental behaviors but also biological effects of CIPAHs. Indeed, the AhR-mediated activities of CIPAHs have been determined by using yeast and CULUX assay systems [13, 14]. Although the activities were observed for all the 3- to 5-ring CIPAHs, which were at levels considerably lower (>80-times) than that of TCDD. Also, the intensities of activities depended on the molecular size: relatively high molecular weight CIPAHs (> 4-ring) were lower than those of the parent compounds, for the relatively

low molecular weight CIPAHs, the activity tended to increase with increasing chlorine substitution [13]. For mutagenicity of some CIPAHs, there were some reports in which the toxicities were carried out with *Salmonella typhimurium* TA98 and TA100 in the presence or absence of S9 activation enzyme system [15-17]. In addition, certain CIPAHs are reported to have other toxic effects, such as tumorigenicity and oncogene activation, as reviewed by Fu et al. [18]. Here we describe the analytical and environmental studies on 3- to 5-ring Cl-/Br-PAHs.

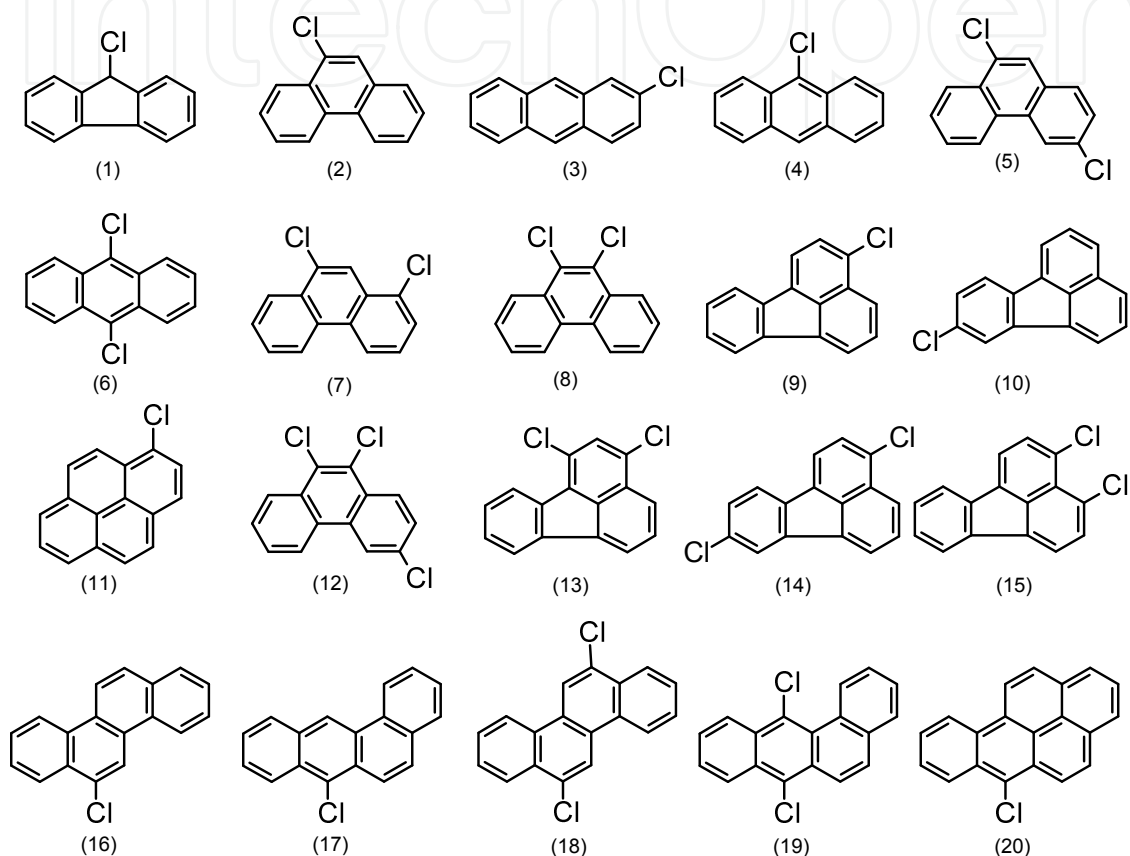


Figure 1. Structures of CIPAHs. The number noted is corresponded to Table 1.

2. Analytical methods of HPAHs

Comparing halogenated aromatics such as PCB and dioxins, there are fewer reports in regard to HPAHs in the environment. In the late 1970s to 1980s, Oyler et al. identified various chlorinated PAHs with 2~4-ring as the products of aqueous chlorination reactions of PAHs using reversed phase HPLC with UV detector, GC equipped with photoionization detector, and GC/MS [19, 20]. The study would be first report that CIPAHs were detected from environmental sample, whereas that would be artificial environment of water-treatment including chlorination reaction of PAHs.

Nilsson and Colmsjo investigated in detail the analytical methods of not only chloro-substituted PAHs, here defined as CIPAHs, but also chloro-added PAHs using normal

phase HPLC [21, 22]. In the study, three stationary phases, i.e. aminopropylsilica, cyanopropyltrimethylsilica and silica were used, resulting that CIPAHs among congeners showed similar retention behaviors among these columns. On the other hand, the retention behaviors of chloro-added PAHs showed stronger than CIPAHs. It was dismissed as due to the differences of steric hindrance caused by the large chlorine atoms.

For analysis of ambient halogenated PAHs, authors developed the methods for CIPAHs and BrPAHs using GC/qMS and HRGC/HRMS. We investigated the analytical method of 20 and 11 species of CIPAHs and BrPAHs, respectively, and applied to the surveys in the air. As GC methods, those conditions relatively adapt to those of PAH methods such as EPA method 8275A. The usage of non-polar GC column such as DB-5 could achieve good separation of HPAHs. Figure 2 and 3 shows the GC/qMS chromatographs of 20 species of CIPAHs and 11 species of BrPAHs standard mixtures, respectively. The common conditions are as follows: the HPAHs were analyzed on 7890A gas chromatograph (Agilent) coupled to a JMS-Q1000GC mass selective detector (JEOL) operated in selective ion monitoring mode. The column used was a 30 m x 0.25 mm i.d. Inertcap-5MS/NP capillary column with a film thickness of 0.25 μm (GL Sciences). Helium was used as the carrier gas and the flow rate of 1.0 ml/min at constant. The injection volume was 2.0 μl and was a pulsed splitless injection at 300 $^{\circ}\text{C}$. The temperature program began at 100 $^{\circ}\text{C}$, held for 1min, increased 200 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C}/\text{min}$, finally increased to 300 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$, and was held for 5 min (total 30 min). The MSD system was run in the electron impact mode. The ion source temperature was 300 $^{\circ}\text{C}$, and the ionization energy and current was 70 eV and 200 μA , respectively. Table 1 and 2 show the retention time (RT) and monitored ions of individual CIPAH and BrPAH targeted, respectively.

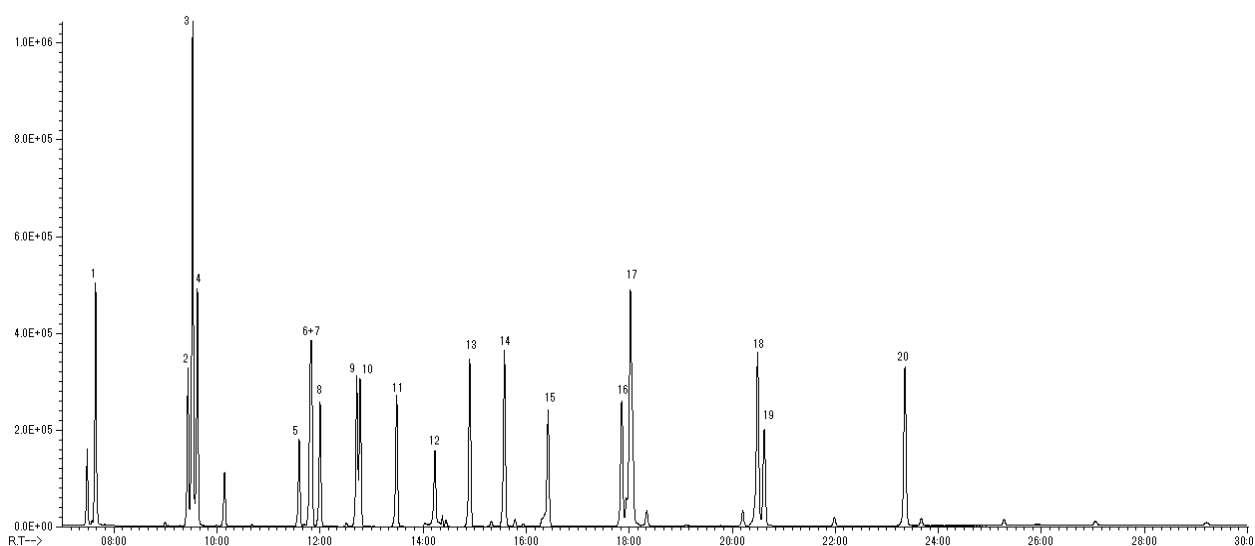


Figure 2. GC/qMS chromatogram of 20 CIPAHs. The number noted in chromatogram is corresponded to Table 1.

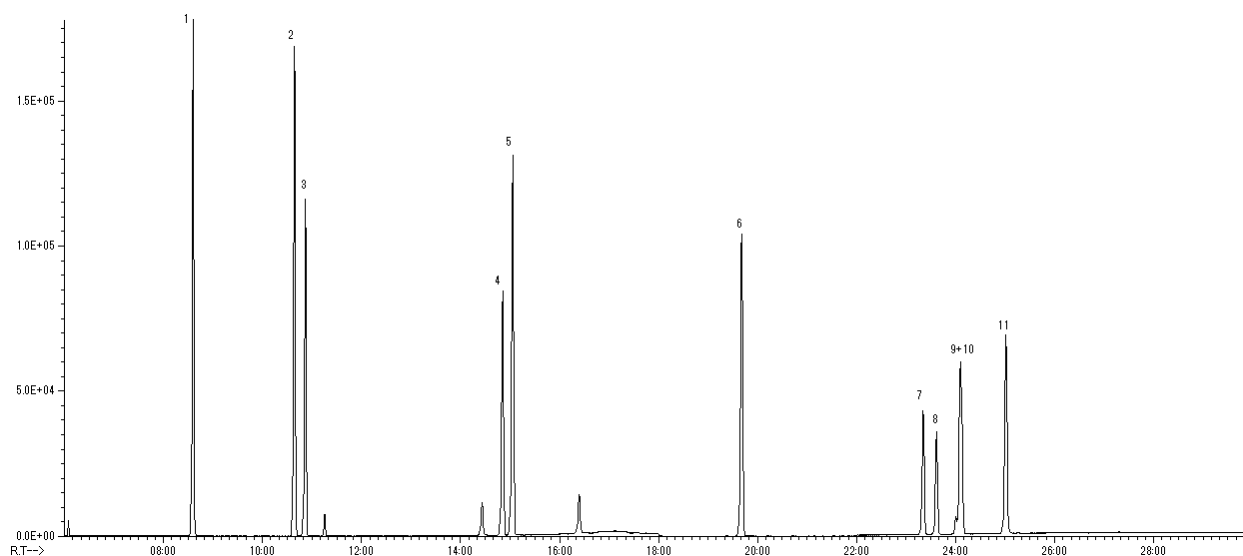


Figure 3. GC/qMS chromatogram of 11 BrPAHs. The number noted in chromatogram is corresponded to Table 2.

No	CIPAH	Abbrev.	RT ^a (h:m:s)	Ions monitored	
1	9-chlorofluorene	9-ClFlu	0:07:45	200	202
2	9-chlorophenanthrene	9-ClPhe	0:09:35	212	214
3	2-chloroanthracene	2-ClAnt	0:09:40	212	214
4	9-chloroanthracene	9-ClAnt	0:09:46	212	214
5	3,9-dichlorophenanthrene	3,9-Cl ₂ Phe	0:11:46	246	248
6	9,10-dichloroanthracene	9,10-Cl ₂ Ant	0:12:01	246	248
7	1,9-dichlorophenanthrene	1,9-Cl ₂ Phe	0:12:01	246	248
8	9,10-dichlorophenanthrene	9,10-Cl ₂ Phe	0:12:11	246	248
9	3-chlorofluoranthene	3-ClFluor	0:12:54	236	238
10	8-chlorofluoranthene	8-ClFluor	0:12:58	236	238
11	1-chloropyrene	1-ClPy	0:13:41	236	238
12	3,9,10-trichlorophenanthrene	3,9,10-Cl ₃ Phe	0:14:26	280	282
13	1,3-dichlorofluoranthene	1,3-Cl ₂ Fluor	0:15:07	270	272
14	3,8-dichlorofluoranthene	3,8- Cl ₂ Fluor	0:15:47	270	272
15	3,4-dichlorofluoranthene	3,4- Cl ₂ Fluor	0:16:39	270	272
16	6-chlorochrysene	6-ClChry	0:18:05	262	264
17	7-chlorabenz[<i>a</i>]anthracene	7-ClBaA	0:18:15	262	264
18	6,12-dichlorochrysene	6,12-Cl ₂ Chry	0:20:44	296	298
19	7,12dichlorobenz[<i>a</i>]anthracene	7,12-Cl ₂ BaA	0:20:52	296	298
20	6-chlorobenzo[<i>a</i>]pyrene	6-ClBaP	0:23:36	286	288

^a RT: retention time.

Table 1. Abbreviations of CIPAH standard and analytical performance of GC/qMS

No	BrPAH	Abbrev.	RT ^a (h:m:s)	Ions monitored	
1	2-bromofluorene	2-BrFlu	0:08:36	244	246
2	9-bromophenanthrene	9-BrPhe	0:10:40	256	258
3	9-bromoanthracene	9-BrAnt	0:10:52	256	258
4	9,10-bromoanthracene	9,10-Br2Ant	0:14:51	336	338
5	1-bromopyrene	1-BrPy	0:15:04	280	282
6	7-bromobenz[<i>a</i>]anthracene	7-BrBaA	0:19:41	306	308
7	7,11-dibromobenz[<i>a</i>]anthracene	7,11-Br2BaA	0:23:21	386	388
8	7,12-dibromobenz[<i>a</i>]anthracene	7,12--Br2BaA	0:23:37	386	388
9	5,7-dibromobenz[<i>a</i>]anthracene	5,7-Br2BaA	0:24:06	386	388
10	4,7-dibromobenz[<i>a</i>]anthracene	4,7-Br2BaA	0:24:06	386	388
11	6-bromobenzo[<i>a</i>]pyrene	6-BrBaP	0:25:01	330	332

^a RT: retention time.

Table 2. Abbreviations of BrPAH standard and analytical performance of GC/qMS

Air sample collection for HPAHs might be generally performed using high volume air sampler, which is fundamentally similar to the case of PAHs and dioxins in the air. The differences of sampling efficiency between quartz fiber filters and glass fiber filters for HPAHs analysis have been not confirmed. The extraction process is also fundamentally same to the case of PAHs. Dichloromethane will be useful solvent in the Soxhlet extraction because of the solubility and handling ability. In the case of toluene as the solvent, it requires attention such as protection from light because toluene has highly reactivity compared to dichloromethane. Also, authors have adopted a ultrasonic extraction (20 min) in the case of small size of sampling because the method was also obtained suitable recovery rates.

Concerning pretreatment of CIPAH analysis from suspended particle matters, Nilsson and Ostman investigated the cleanup method and revealed that the behaviors of chloro-added PAHs showed the different from chloro-substituted PAHs in detail [23]. It represents that after silica cleanup, treatment using HPLC back-flush elution with cyanopropyldimethylsilica was effective method to separate chloro-added PAHs from chloro-substituted PAHs, parent PAHs, and aliphatics. For the extraction process, artifact formation of CIPAHs was also investigated from comparison of extraction solvents, dichloromethane and benzene. It shows that no artifact formation of CIPAHs takes place by using chlorine-involving solvent, dichloromethane. Note that the cleanup process after extraction should use the column packing material appropriated for PAHs but not dioxins because the usage of such sulfate treatment column for elimination of organic compounds could lead to disappearance of HPAHs. We believe that the cleanup could successfully satisfy by using only silica gel column. Furthermore, the possibility of artifact formation to the difference of sampling filters, glass fiber filters and Teflon filters, were also investigated, showing that there was no difference between the two types of filter. In short, required information from sampling to analysis of CIPAHs in the air could be based on those of PAHs.

Recently, Ieda et al. reported environmental analysis of HPAHs using comprehensive two-dimensional GC coupled to high-resolution time-of-flight mass spectrometry (GC × GC-HRTOF-MS) [24]. The GC × GC-HRTOF-MS method allowed highly selective group type analysis in the two-dimensional (2D) mass chromatograms with a very narrow mass window, accurate mass measurements for the full mass range (m/z 35-600) in GC × GC mode, and the calculation of the elemental composition for the detected HPAHs congeners in the real-world sample. This tool combines high sensitivity and selectivity for organic compounds including HPAHs detection by which higher chlorinated PAHs (penta, hexa and hepta substitution) will be possible to be detected in the environmental samples.

3. HPAHs in the air

First report concerning ClPAHs in the air was achieved by Nilsson and Östman, which were performed as long ago as 1990s [23]. Firstly, they synthesized some standard compounds of ClPAH. At that time, the environmental study on ClPAHs had been behind compared to the cases of PAHs and dioxins. That is, one of the top priorities for study on HPAHs could be difficult to get the standard compounds. Despite of such problems, they detected nine species of ClPAHs from urban air and road tunnel (Table 3). The concentrations in urban air ranged from 0.4 pg/m^3 for 7-chlorobenz[*a*]anthracene (7-ClBaA) to 10.4 pg/m^3 for 1,6- and 1,8-dichloropyrene (1,6-/1,8-Cl₂Py) in particle phase, and from <0.3 pg/m^3 for 7-ClBaA and 6-chlorobenzo[*a*]pyrene (6-ClBaP) to 17.5 pg/m^3 for 1,6-/1,8-Cl₂Py in gas phase. In addition, the concentrations in road tunnel ranged from 2.0 pg/m^3 for 1,3-dichloropyrene to 19.1 pg/m^3 for 4-chloropyrene (4-ClPy) in particle phase, and from <0.3 pg/m^3 for 7-ClBaA and 6-chlorobenzo[*a*]pyrene to 30.7 pg/m^3 for 4-ClPy in gas phase.

From the 2000's, Ohura and co-workers have been investigated the occurrences and behaviors of ClPAHs and BrPAHs in the air [10-12, 25]. Of the detected ClPAHs, the concentrations are summarized in Table 3. The magnitudes of ClPAHs concentrations were extent of ~100 pg/m^3 , which were middle range between dioxins and PAHs (Figure 4). The concentrations of almost ClPAHs in the air showed typical seasonal variation that were elevated in winter and decreased in summer, observed in the case of PAHs. Also, the characteristics of gas/particle partitioning of ClPAHs in the air showed the similar trends of PAHs: highly gaseous contents of relatively low-molecular weights ClPAHs and highly particulate contents of relatively high-molecular weights ClPAHs. It indicates that the partitioning could be significantly affected by the characteristics of corresponding parent PAHs even if being high molecular weights by substitution of chlorine. On the other hand, the concentration of 6-ClBaP was relatively high (<3.2 ~ 137 pg/m^3) in compared to other ClPAHs and showed a characteristic trend: elevated suddenly in summer. The level was significantly different from the early work that was performed by Nilsson and Östman [23]. Currently, there is no data that account nicely for the mysterious phenomenon. We have suggested that the trend, elevated in summer, of 6-ClBaP might be due to secondary formation of BaP and activated chlorine in the particles. Kitazawa et al. have investigated temporal trends of particulate ClPAHs in an urban air, and relationships to the parent PAHs are also investigated [11]. Over the study period, the concentrations of the ClPAHs, except

6-ClBaP, remained almost constant, whereas the parent PAH concentrations declined moderately. In addition there was significant correlation between the concentrations of the CIPAHs, except 3,9- and 9,10-Cl₂Phe, and the concentrations of the corresponding parent PAHs. This finding could indicate that the formation of CIPAHs associated with particles proceeds via that of PAHs, which provide clues as to the underlying emission sources and environmental behaviors. To unravel the occurrences, behaviors, and sources of CIPAHs in the air, it will need to investigate in various sites to clarify the concentrations.

Site/source	Air				Product				
	urban street	road tunnel	urban air	urban air	flue gas	fly ash	bottom ash	PVC	PVDC
9-ClFlu	na	na	na	0.62	na	nd	nd	na	na
2-ClAnt	na	na	na	1	1.2	nd~15	nd~0.68	140	58
9-ClAnt	na	na	na	9.9	13	nd~230	nd~1.0	700	29
9-ClPhe	na	na	3.5	19	67	nd~240	nd~16	9,600	31
3,9-Cl ₂ Phe	na	na	2.7	1.4	2.8	nd~46	nd~3.1	na	nd
9,10-Cl ₂ Phe/Ant	5.6	na	5.1	2.9	7.2	nd~290	nd~17	1,200	7.9
3-ClFluor	4.6	19.1	4.5	11	26	nd~1,000	nd~4.0	960	2.3
8-ClFluor	1.3	8.6	nd	3	6.4	nd~110	nd~1.1	na	nd
1-ClPy	11.8	39.6	7.5	13	310	nd~1,100	nd~2.6	1,100	nd
4-ClPy	8.1	49.8	na	na	na	na	na	4,500	na
1,3-Cl ₂ Py	5.6	4	na	na	na	na	na	na	na
1,6/1,8-Cl ₂ Py	27.9	42.7	na	na	na	na	na	na	na
6-ClChry	na	na	na	1.9	6.8	nd~1,200	nd~7.9	na	nd
6,12-Cl ₂ Chry	na	na	na	2.1	2.7	nd~870	nd~2.5	na	nd
7-ClBaA	0.4	2.3	2.4	5.6	16	nd~870	nd~0.92	na	nd
7,12-Cl ₂ BaA	na	na	na	14	2.8	nd~1,100	nd~2.9	na	nd
6-ClBaP	1.9	6.1	5.6	7.1	120	nd~5,300	nd~0.68	na	nd
unit	pg/m ³	pg/m ³	pg/m ³	pg/m ³	ng/Nm ³	ng/g	ng/g	ng/g	ng/g
Material	G, P	G, P	P	G, P	G	S	S	G, P	G, P
Reference	[23]	[23]	[10]	[12]	[28]	[26]	[26]	[30]	[29]

^a na: not analyzed, nd: not detected. ^b air samples released from combustion (800°C) of polyvinylchloride (PVC). ^c G: gas-phase, P: particle matters, R: residues

Table 3. CIPAH concentrations in the air and emission sources^a

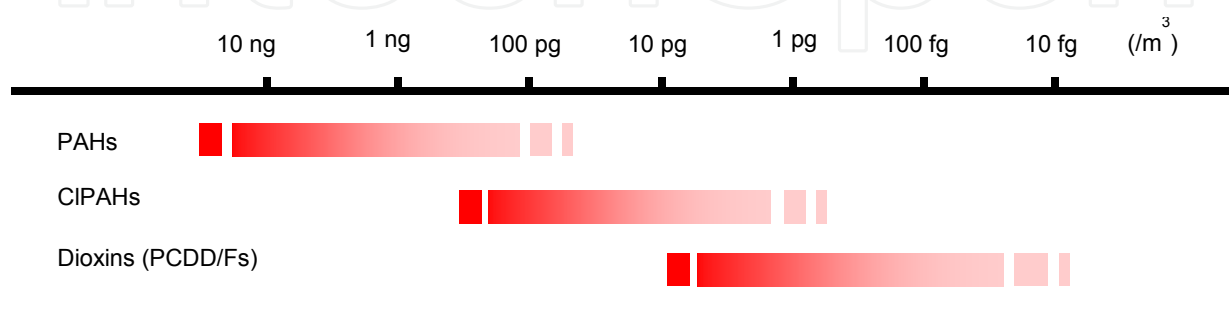


Figure 4. Concentration levels of PAHs, CIPAHs, and dioxins in the air.

Based on the findings of ClPAHs, brominated PAHs (BrPAHs) were expected to be present in the environment. There was, however, no the study at all. Ohura et al. tried to synthesis BrPAHs with 3- to 5-ring as standard compounds, which were newly detected from the urban air samples in Japan [25]. Of the BrPAHs detected, 5,7-Br2BaA was most abundant (mean concentration, 8.7 pg/m³), followed by 7,12-Br2BaA (6.3 pg/m³) and 6-BrBaP (3.3 pg/m³). The mean concentrations of total BrPAHs, ClPAHs, and PAHs detected were 8.6 pg/m³, 15.2 pg/m³, and 1.2 ng/m³, respectively, which showed that concentrations of such HPAHs tended to be approximately 100-fold lower than PAHs. For the moment, this study is only report in which BrPAHs were investigated in the air. Besides the environmental analysis, the occurrence and profiles of BrPAHs in waste incinerators were investigated by Horii et al. [26]. 1-Brominated pyrene was predominant in the fly ash sample among BrPAHs targeted. The reports regarding environmental surveys of BrPAHs have been limited rather than those of ClPAHs, so that the environmental behaviors and sources remain unclear.

4. Emission sources of ambient HPAHs

In light of the production mechanisms established by studies of PAHs and dioxins, it is no wonder that the principal sources of ClPAHs in the air are traffic and incineration facilities. In a previous study by Nilsson and Östman, it was suggested that dichloroethane as a scavenger contained in leaded gasoline may be the source of chlorine in ClPAHs [23]. Indeed, some ClPAHs have been detected from not only urban air but also in snow and vehicle exhaust gas, although they have not been quantified [27].

The air and residues samples emitted from incinerators were also investigated to evaluate the occurrences of HPAHs [26, 28]. For flue gas samples collected in actual operating incinerators, a number of ClPAHs were detected at extremely high levels compared to the air samples (Table 3). Dioxins were also detected from the flue gas samples, levels of which showed significant correlations to the certain ClPAHs levels. These findings show that ClPAHs in air are possible to emit from incinerators, and could be indicator of dioxins production. Horii et al. have, as described in above, investigated the occurrences of ClPAHs rather than BrPAHs in fly ash and bottom ash from waste incinerators [26]. The total concentrations of ClPAHs in ash samples ranged from <0.06 to 7000 ng/g, in which 6-ClBaP and 1-ClPy were dominant compounds.

Studies of the production of ClPAHs in other combustion processes have investigated emissions from the combustion of chlorine-containing materials. Wang et al. investigated the mechanism of formation of ClPAHs in the polyvinylchloride combustion process by a laboratory-scale tube-type furnace with electric heating [29]. At the temperature range of 600-900 °C, about 18 Cl-PAHs were determined, most of which were monochlorinated derivatives of naphthalene, biphenyl, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. Only two dichlorophenanthrenes or anthracenes were identified. As the other experiment, ClPAHs emissions were also investigated by polyvinylidene chloride plastic wrap over a flame of the gas burner [30]. Only seven of 27 target ClPAHs were detected,

which were all relatively low molecular weight CIPAHs with 2~4-ring. As the other interesting emission sources,

Considering the concentrations of individual CIPAHs, there were significant correlations among them, suggesting that these compounds might be emitted from common sources [10-12]. Also, factor analysis based on the experimental data of CIPAHs and PAHs in air suggest that the emission sources for CIPAHs except for 6-ClBaP may be similar to the sources of the parent PAHs [11]. As is suggested by the above discussions, the production of CIPAHs and dioxins through the combustion of organic materials requires chlorine. The occurrence of CIPAHs and dioxins simultaneously should be investigated further to give us more information on their production processes in the environment and their possible sources.

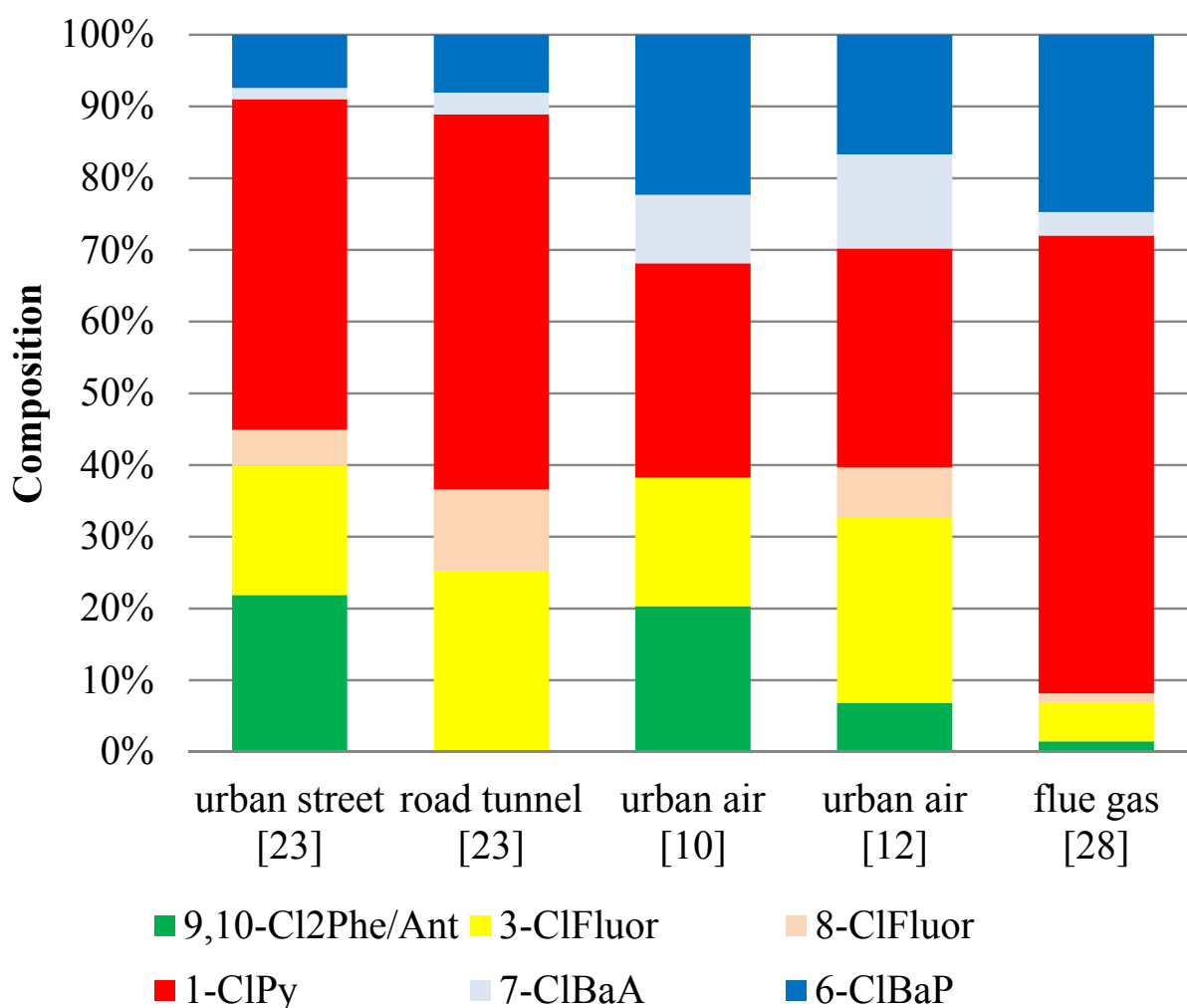


Figure 5. Profiles of typical CIPAH concentrations in the air and flue gas samples.

Comparing the compositions of targeted compounds in among the different samples could be useful technique to understand the origins and behaviors in the environment. Here we compared the profiles of typical ClPAH (9,10-Cl₂Phe/Ant, 3-ClFluor, 8-ClFluor, 1-ClPy, 7-ClBaA, and 6-ClBaP) concentrations in among the samples from air and flue gas from incinerators (Figure 5). 1-ClPy was most abundant among the group of ClPAHs. The profiles were somewhat same between samples between urban street and road tunnel, suggested that the ClPAHs detected in urban air could be significantly contributed to traffic sources. The profiles obtained from air samples collected in Japan were also similar ones, whereas those sampling date were different. This suggests remaining unchanged of the emission sources for long periods of time in the area. On the other hand, the characteristic profile of flue gas sample was observed that the contribution of 1-ClPy was much larger than those of air samples. These findings suggest the diversity of emission sources of ClPAHs in the air.

5. Photoreaction of HPAHs

Atmospheric behaviors of organic pollutants are affected by various factors: climate conditions and chemical/physical properties of own organic pollutants. In the case of PAHs, the significant factors fall into two broad categories: (i) heterogeneous processes involving particle-associated compounds such as photolysis/photooxidation and gas-particle interactions; and (ii) homogeneous gas-phase reactions of volatile 2- and 3-ring PAHs and semivolatile 4-ring PAHs, initiated by OH (daytime) and NO₃ (night-time) radicals and ozone. Here we focus on photoreactivities of HPAHs, which model on the photoreaction (photodegradation) on particle surfaces using irradiation system.

Ohura et al. have investigated the photoreaction of ClPAHs in some organic solvents under high-pressure Hg lamp irradiation (450 W) [10]. The photolysis rates of all of the ClPAHs fitted the pseudo-first-order reaction model. The order of decay rates of mono chloro-substituted PAHs such as 1-ClPy, 7-ClBaA, 6-ClBaP, etc. were somewhat consistent with that of the corresponding parent PAHs. In the case of polychlorinated PAHs (Cl_nPAH, n>2), the decay rates decreased with increasing extent of chlorination of the PAHs whereas the trend has been observed in only chlorinated phenanthrenes. It suggests that chlorination of PAH may be more photostable compared to parent PAHs. The photoproducts of the photolytic reactions were also tentatively identified [10]. The photolyses of ClPhe and 7-ClBaA were confirmed to proceed by initial abstraction of chlorine, followed by oxidative degradation. Although it is not clear whether the oxidized byproducts of ClPAHs are ubiquitous in the environment or body tissues, the toxicities of the byproducts should also be determined.

Concerning BrPAHs, the photolysis rates were relatively faster than the corresponding ClPAHs [25]. This is could be due to weak bond energy of C-Br (276 kJ/mol) than that of C-Cl (330 kJ/mol). Comparing the ambient profiles among the PAH congeners suggested that ambient BrPAHs that came from the specific local emission sources differed from ClPAHs and PAHs, and/or could be driven by various seasonal factors, including photodecay processes.

6. Conclusion

The study on halogenated PAHs in the environment could be at the beginning stage. Here we note mainly about the analytical methods and environmental data of HPAHs that are still insufficiency in comparison of PAHs and dioxins. Therefore, the hazardous contributions of HPAHs in the environment have yet to be revealed. The concentrations of HPAHs in the air were middle range between dioxins and PAHs. Because the structures of HPAHs are combination of those of dioxins and PAHs, the production mechanism of HPAHs may be also follow to the characteristics of them. The ambient levels of HPAHs, therefore, could be middle range of them. This finding may be useful characteristic for environmental and risk monitoring of such hazardous aromatic compounds. That is, monitoring HPAHs in the environment may provide the levels of both dioxins and PAHs. The attempt may be also capable of adapting to the risk assessment.

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