PROFILES AND DISTRIBUTION OF HALOGENATED POLYCYCLIC AROMATIC HYDROCARBONS FROM WASTE INCINERATORS

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are typical carcinogens in the air. Chlorinated or brominated PAHs (halogenated PAHs; XPAHs) were compounds whose one to several hydrogen atoms are substituted to chlorine or bromine atoms of parent PAHs. A number of XPAHs were reported to have same carcinogenicity or mutagenicity as those of parent PAHs. Horii *et al.* have showed that several ClPAHs and BrPAHs elicit dioxin-like activity with potencies comparable to those of several mono-ortho polychlorinated biphenyl (PCB) congeners[1]. In general, the persistency of these compounds in the environment increases as the number of the halogen atoms increase[2,3]. Thus, XPAHs are potential candidates of the persistent organic pollutants (POPs). There is little information about generation and/or degradation mechanisms in waste incinerators though they are reported to be detected in the exhaust and fly ash from the waste incinerators[4].

In this study, we have determined the concentrations of XPAHs in flue gas, fly ash, and bottom ash from four waste incinerators and an aluminum recycling facility. We have also investigated profiles and phase distributions of these XPAHs. Incinerators handled waste sludge, oil, wood, paper, municipal solid waste and so on. XPAHs were detected from all factories.

Materials and methods

Materials and Samples. The standard compounds of 24 chlorinated PAHs (ClPAHs) and 9 brominated PAHs (BrPAHs) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), Sigma-Aldrich (St. Louis, MO, USA) or prepared by ourselves. Target 33 XPAHs include 24 ClPAHs and 9 BrPAHs are listed in Table 1. Isotope labeled $^{13}C_6$-fluoranthene, $^{13}C_6$-chrysene, and $^{13}C_4$-benzo[a]pyrene as internal standards were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). d_{12}-Chrysene and d_{12}-benzo[a]pyrene as recovery standard were purchased from AccuStandard (New Haven, CT). The solvents for extraction and cleanup such as toluene, nonane, dichloromethane, and hexane were residual pesticide analysis grade obtained from Wako Chemicals. The highest grade reduced copper for clean-up of sulfer was bought from Wako Chemicals.

Table 1 List of target chemicals

ClPAHs 24				*BrPAHs 9*	
Compound	***Abbreviation***	***Compound***	***Abbreviation***	***Compound***	***Abbreviation***
9-chlorofluorene	9-ClFle	1,5,9-trichloroanthracene	1,5,9-Cl3Ant	9-bromophenanthrene	9-BrPhe
9-chlorophenanthrene	9-ClPhe	3,8-dichlorofluoranthene	3,8-Cl2Flu	1-bromoanthracene	1-BrAnt
2-chloroanthracene	2-ClAnt	3,4-dichlorofluoranthene	3,4-Cl2Flu	2-bromoanthracene	2-BrAnt
9-chloroanthracene	9-ClAnt	dichloropyrene-1	Cl2Pyr-1	9-bromoanthracene	9-BrAnt
3,9-dichlorophenanthrene	3,9-Cl2Phe	dichloropyrene-2	Cl2Pyr-2	1,5-dibromoanthracene	1,5-Br2Ant
1,9-dichlorophenanthrene	1,9-Cl2Phe	6-chlorochrysene	6-ClChr	9,10-dibromoanthracene	9,10-Br2Ant
9,10-dichloroanthracene	9,10-Cl2Ant	7-chlorobenzo[a]anthracene	7-ClBaA	2,6-dibromoanthracene	2,6-Br2Ant
9,10-dichlorophenanthrene	9,10-Cl2Phe	trichloropyrene	Cl3-Pyr	1-bromopyrene	1-BrPyr
3-chlorofluoranthene	3-ClFlu	6,12-dichlorochrysene	6,12-Cl2Chr	7-bromobenz[a]anthracene	7-BrBaA
8-chlorofluoranthene	8-ClFlu	7,12-dichlorobenz[a]anthracene	7,12-Cl2BaA		
1-chloropyrene	1-ClPyr	tetrachloropyrene	Cl4Pyr		
3,9,10-trichlorophenanthrene	3,9,10-Cl3Phe	6-chlorobenzo[a]pyrene	6-ClBaP		

Target chemicals 33

Flue gas, fly ash, and bottom ash samples from three industrial waste incinerators (IWI), a municipal solid waste incinerator (MSWI), and an aluminum recycling facility from Japan collected in 2012 were analyzed. The detail of waste incinerators are given in Table 2. Sampling method of the samples was based on a modified standard method for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs) (JIS K 0311)[5].

Table 2 The detail of waste incinerators

	Waste type	Incinerator type	Feed type	Capacity (kg/h)
#1	sludge, oil, wood, paper	fixed grate	batch	546
#2	paper	fluid bed	continuous	2000
#3	waste solvent	fluid bed	continuous	2000
#4	MSW	stoker	continuous	3750
#5	aluminum recycling	electric furnace	unknown	unknown

Analytical procedures. The determinations of XPAHs were performed according to an established method[4,5]. Briefly, samples were extracted using a liquid-liquid extraction method or a soxhlet extraction method for all samples, after spiking 2.5 nanograms each of internal standards. The solutions were purified, and fractionated using active carbon cartridge column (Carboxene 1016, 200 mg, Supelco, St. Louis, MO, USA) connected with silica gel cartridge column (Supelclean LC-Si, 2 g, Supelco) on the top. The cartridge columns were eluted with 20 mL of 10% dichloromethane/hexane. The silica gel cartridge was removed and the active carbon cartridge was reversed, then eluted with 120 mL of toluene. The toluene fraction that contained XPAHs was concentrated and 2.5 ng of recovery standards were spiked.

Concentrations of XPAHs were determined by gas chromatography-high resolution mass spectrometry (GC/HRMS; JMS-800D, JEOL, Tokyo, Japan). Gas chromatographic separation was accomplished by a 60-m DB-5ms fused silica capillary column (0.25 mm i.d., 0.25 µm film thickness; Agilent Technologies, Foster City, CA, USA). Two microliters of the aliquot were injected in splitless mode at 280°C. The column oven temperature was programmed from 80°C (1 min) to 170°C at a rate of 20°C/min, to 260°C at 4°C/min, and to 270°C at 1°C, then to 320°C at 8°C/min; this was held for 10 min for XPAH analysis. The MS was operated in an electron impact selected ion monitoring (SIM) at resolution R>10,000 (10% valley). Peaks were identified by comparison of the retention times of samples to standards if the signal-to-noise (S/N) ratio was >3, and were quantified if target/qualifier ion ratios were within 15% of the theoretical values.

Results and discussion

Total concentrations of XPAHs in flue gas, fly ash, and bottom ash. Total concentrations of XPAHs in flue gas, fly ash, and bottom ash of the 5 facilities ranged from 2.16 to 601 ng·m$^{-3}_{\mathrm{N}}$, 2.49 to 12,000 ng·g^{-1}, and 0.225 to 1.88 ng·g^{-1}, respectively (Table 3). The concentration ranges in flue gas, fly ash, and bottom ash measured in this study were comparable to the ranges reported previously (0.29-5,200 ng·m$^{-3}_{\mathrm{N}}$, < 0.14-7,400 ng·g^{-1}, and < 0.14-69 ng·g^{-1}, respectively)[4,6]. All of the highest concentrations of XPAHs were found in the samples collected from facility #1, which is combusting sludge, waste oil, wood chips, and paper waste in fixed grate incinerator and has the lowest capacity of treatment (546 kg·hr^{-1}) among the tested facilities.

Table 3 Total Concentrations of ClPAHs, BrPAHs, and XPAHs in flue gas, fly ash ,and bottom ash

		flue gas ($\mathrm{ng/m^3{}_N}$)	**fly ash (ng/g)**	**bottom ash (ng/g)**
#1	*Cl-PAHs*	413	8720	1.75
	Br-PAHs	188	3270	0.127
	total	601	12000	1.88
#2	*Cl-PAHs*	7.22	5.14	-
	Br-PAHs	1.18	0.409	-
	total	8.39	5.55	-
#3	*Cl-PAHs*	33.9	469	0.215
	Br-PAHs	12.2	58.5	0.0108
	total	46.1	528	0.225
#4	*Cl-PAHs*	1.59	24.2	0.698
	Br-PAHs	0.572	2.65	0.0228
	total	2.16	26.8	0.721
#5	*Cl-PAHs*	3.53	2.43	1.25
	Br-PAHs	0.508	0.0606	0.0296
	total	4.03	2.49	1.28

The lowest concentrations of total XPAHs in flue gas and fly ash from facility #1 to #4, which are combusting common solid waste, were detected at facility #4 and facility #2, respectively. These concentrations in flue gas and fly ash were about 280 and 2200 times lower than the respective concentrations in facility #1. This result could be due to the continuous combustion and incinerator type (fluid bed and stoker type), having higher combustion stability than fixed grate incinerator.

Concentrations of individual XPAHs in flue gas, fly ash, and bottom ash. Concentrations of individual compounds found in facility #1, which emitted XPAHs at the highest concentration, were shown in Figure 1. A total of 31 XPAHs were measured in the flue gas from facility #1. Among target XPAHs, 9-ClPhe occurred at the highest concentration (255 $ng{\cdot}m^{-3}{}_N$). The concentrations of 9-BrPhe (144 $ng{\cdot}m^{-3}{}_N$), 9,10-Cl_2Ant (61 $ng{\cdot}m^{-3}{}_N$), 3-ClFlu (40 $ng{\cdot}m^{-3}{}_N$), and 1-BrAnt (31 $ng{\cdot}m^{-3}{}_N$) were the second- to fifth-highest. All of these compounds were 3-ring XPAHs except for 3-ClFlu. The concentrations of 3 dichlorophenanthrenes, which were 15.6 $ng{\cdot}m^{-3}{}_N$ for 3,9-Cl_2Phe, 6.54 $ng{\cdot}m^{-3}{}_N$ for 9,10-Cl_2Phe, and 3.90 $ng{\cdot}m^{-3}{}_N$ for 1,9-Cl_2Phe, were significantly lower than that of monochlorophenanthlene (9-ClPhe). On the contrary, the concentration of dichloroanthracene (9,10-Cl_2Ant) were significantly higher than those of monochloroanthraces. This suggests that the generation mechanism of phenanthrene derivatives was different from that of anthracene derivatives. Among BrPAHs, the concentrations of monobromo-compounds were high. The concentrations of 4- and 5-ring XPAHs were negligible compared to 9-ClPhe in flue gas.

The concentrations of 3-ClFlu and 1-BrPyr, are 4-ring XPAHs, were the highest (1890 $ng{\cdot}g^{-1}$) and second-highest (1220 $ng{\cdot}g^{-1}$) in the fly ash, respectively. The concentrations of 9-ClPhe (957 $ng{\cdot}g^{-1}$) and 9-BrPhe (934 $ng{\cdot}g^{-1}$), are 3-ring XPAHs, were one half of the concentration of 3-ClFlu. The concentrations of 4- and 5-ring XPAH such as Cl_nPyr, 7-ClBaA, 6-ClBaP, 1-BrPyr, and 7-BrBaA, were not negligible compared to the highest concentration (3-ClFlu). As for Cl_nPyr, 1-ClPyr concentration was 361 $ng{\cdot}g^{-1}$, which was lower than sum concentration of dichloropyrenes (477 $ng{\cdot}g^{-1}$). The concentrations of trichloro- (486 $ng{\cdot}g^{-1}$) and tetrachloro-pyrene (875 $ng{\cdot}g^{-1}$) were higher than those of mono- and di-chloropyrenes. This suggests that pyrene would be easy to generate the highly-chlorinated isomers.

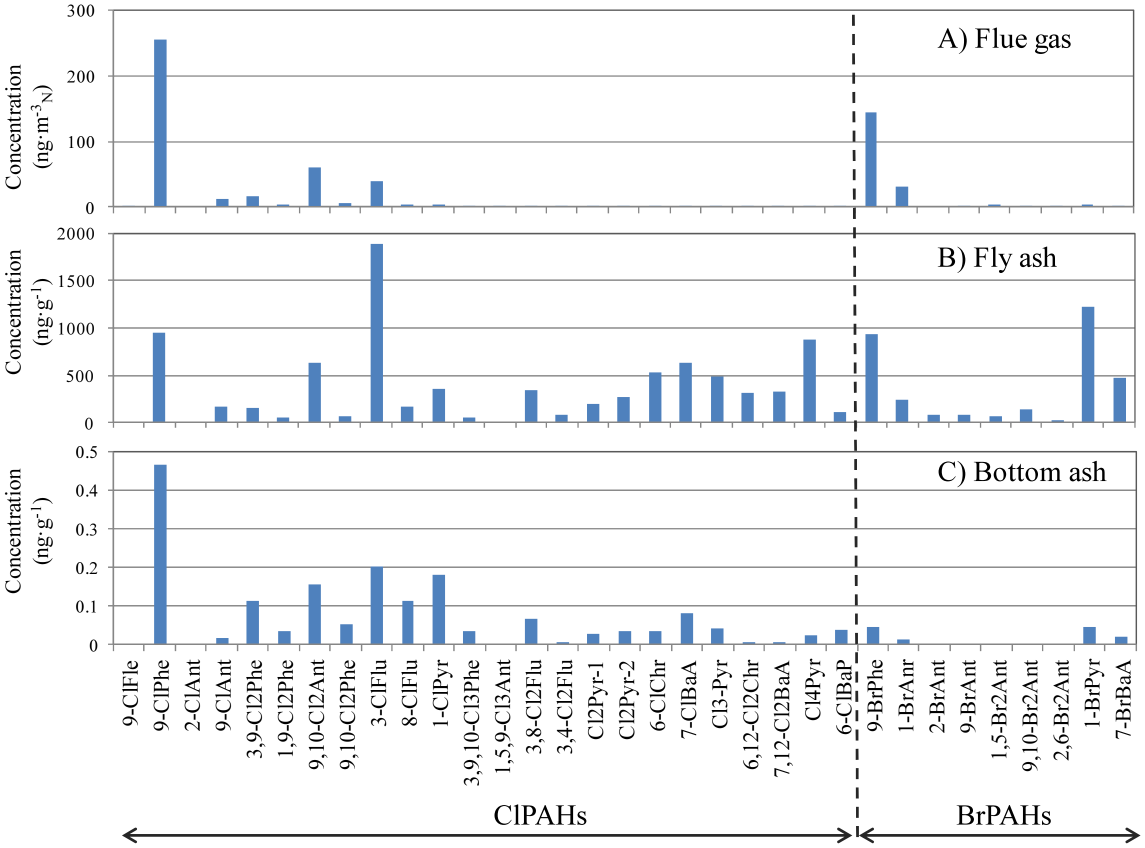

Figure 1. Concentrations of individual XPAHs in flue gas, bottom ash, and fly ash (facility #1)

A total of 26 XPAHs were detected in the bottom ash from facility #1. However, the concentrations of XPAHs were considerably low. For example, the maximum concentration was 0.465 $ng{\cdot}g^{-1}$ for 9-ClPhe.

Ohura *et al.* reported that the concentrations of 1-ClPyr and 6-ClBaP were high in the air in Shizuoka[2,3]. However, these two compounds were not the major component from the waste incinerator in this study. This variation may be due to the incinerator type or the type of the waste materials incinerated.

Distribution of individual XPAHs in flue gas, bottom ash, and fly ash. We calculated total amounts of XPAHs ($g\cdot yr^{-1}$) contained in flue gas, fly ash, and bottom ash emitted from the facility #1. The total amounts of XPAHs calculated from the flow rate of the exhaust gas (9670 $m^3{}_N\cdot hr^{-1}$), emission rate of fly ash (0.124 $kg\cdot hr^{-1}$), and emission rate of bottom ash (16.4 $kg\cdot hr^{-1}$) were 12.1 $g\cdot yr^{-1}$ in flue gas, 13.1 $g\cdot yr^{-1}$ in fly ash, and 0.0640 $g\cdot yr^{-1}$ in bottom ash. The total amount of XPAHs emitted from the facility #1 was 25.2 $g\cdot yr^{-1}$. The distribution of total XPAHs among flue gas, fly ash, and bottom ash were 47.9%, 51.8%, and 0.3%, respectively.

Distributions of 33 XPAHs among flue gas, fly ash and bottom ash were shown in Figure 2. The distributions of 2-ClAnt were deleted because concentration in flue gas or fly ash was under detection limit. The distribution of XPAHs in bottom ash were negligible for all target compounds. We can find phase distributions of XPAHs between gaseous phase and particle phase (fly ash). 9-ClFle and 9-ClPhe, 3-ring XPAHs, were mainly distributed in the gaseous phase. The distributions in particle phase increased with increasing the number of ring and halogenations of XPAHs. For example, the distributions of 3-ring XPAHs in gaseous phase were 19.2-98.7%; whereas those of 4-ring were 0-27.9%. The distribution of monochloro-phenanthrene (82.9%) or anthracene (57.3%) in gaseous phase was higher than those of dichloro-phenanthlenes (55.2-64.8%) or trichloro-anthracene (31.6%). For 4-ring XPAHs, the distributions of monochloropyrene (18.6%) in gaseous phase were higher than those of dichloropyrenes (6.98-7.72%) and trichloropyrenes (3.03%).

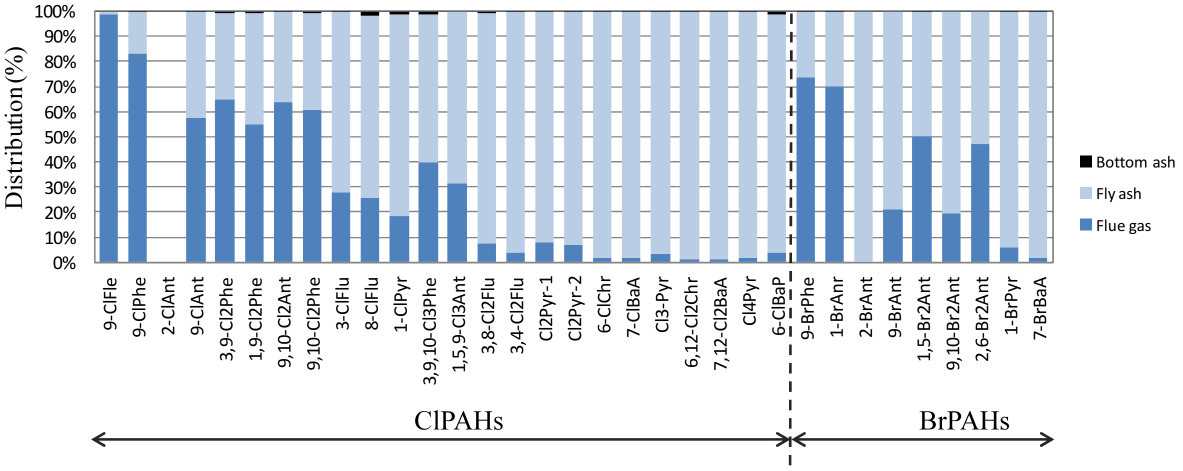

Figure 2. Distribution of individual XPAHs among flue gas, fly ash, and bottom ash (facility #1)

Acknowledgements

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