Occurrences and Characteristics of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons in Stack Gas of Waste Incinerators

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Introduction

The ubiquitous chlorinated and brominated polycyclic aromatic hydrocarbons (ClPAHs and BrPAHs) are halogenated derivatives of PAHs. In some matrices, the toxic equivalents of ClPAHs are even higher than polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs).[1] ClPAHs and BrPAHs are unintentional produced chemicals, but the data that reported about the sources of ClPAHs and BrPAHs is limited. Analysis on the sources of ClPAHs and BrPAHs could provide information on their emission characteristics, and help for their further control.

Waste incineration was not only an important industry for waste management, but also a significant source for many persistent organic pollutants (POPs).[2] During the combustion of the polyvinyl chloride (PVC), which was the common component of wastes, the ClPAHs have been identified to form. Therefore, ClPAHs and BrPAHs could be formed during the combustion of waste. Actually, previous studies have reported the occurrences and profiles of some ClPAH and BrPAH congeners in the fly ash and bottom ash of waste incinerators.[3] The content of the halogen contained materials, such as PVC, vary among different types of wastes. For example, the medical waste contained higher content of halogens than municipal solid wastes. Whether the formation of ClPAHs and BrPAHs would be affected by different types of wastes or not remain unclear.

In this study, stack gas samples collected from five waste incinerators, including two municipal solid waste incinerators (MSWI), one medical waste incinerator (MWI) and one hazardous waste incinerator (HWI) were analyzed for 19 PAHs, 19 ClPAHs and 19 BrPAHs by isotopic dilution gas chromatography coupled with high resolution mass spectrum (GC-HRMS).

Materials and Methods

Stack gas samples were collected by automatic isokinetic sampling system (TCR TERORA, Italy). The stack gas samples were spiked by six isotopic internal standards: $^{13}C_6$-9-chlorophenanthrene (9-ClPhe), $^{13}C_6$-2-

chloroanthracene (2-ClAnt), $^{13}C_6$-1-chloropyrene (1-ClPyr), $^{13}C_6$-7-chlorobenz[a]anthracene (7-ClBaA), $^{13}C_6$-7-bromobenz[a]anthracene (7-BrBaA) and d_9-9-bromophenanthracene (9-BrPhe) before Soxhlet extracted. The extracts were then concentrated, and cleaned by an active silica gel column, and finally concentrated into about 50 μL before injected by injection standard $^{13}C_6$-7,12-dibromobenz[a]anthracene (7,12-Cl_2BaA), and analyzed by GC-HRMS. Separation was conducted on a DB-5 MS capillary column (60 m × 0.25 mm × 0.25 μm, Agilent Technologies). HRMS was operated at a resolution of above 10000.

Results and Discussion

Average concentrations of PAHs, ClPAHs and BrPAHs were 18.0 μg m^{-3}, 78.0 ng m^{-3}, and 34.2 ng m^{-3} respectively in stack gas from MSWI, 13.5 μg m^{-3}, 3.48 ng m^{-3}, and 0.65 ng m^{-3} respectively in stack gas from HWI, and 45.4 μg m^{-3}, 135 ng m^{-3}, and 47.6 ng m^{-3} respectively in stack gas from MWI. Average BaP equivalent (BaP_{eq}) concentrations of PAHs, ClPAHs and BrPAHs were 0.32 BaP_{eq} μg m^{-3}, 8.85 BaP_{eq} ng m^{-3}, and 1.29 BaP_{eq} ng m^{-3} respectively in the MSWI, 0.32 BaP_{eq} μg m^{-3}, 0.89 BaP_{eq} ng m^{-3}, and 0.11 BaP_{eq} ng m^{-3} respectively in the HWI, and 0.87 BaP_{eq} μg m^{-3}, 13.6 BaP_{eq} ng m^{-3}, and 1.56 BaP_{eq} ng m^{-3} respectively in the MWI. Both mass concentrations and BaP_{eq} concentrations of PAHs, ClPAHs and BrPAHs in MWI were obviously higher than those from MSWI and HWI. One of the possible reason could be the high content of halogen contained materials in the medical wastes, which provided more halogen for formation of ClPAHs and BrPAHs during the thermal processes in MWI than in MSWI and HWI.

Congener distributions could provide important information for source tracing. In this study, the congener distributions of ClPAHs and BrPAHs in the different waste incinerators were similar (Figure 1). Naphthalene (NaP) was the major PAH congener, followed by phenanthrene (Phe) and fluoranthene (Flu). For ClPAHs, 1-chloropyrene (1-ClPyr) was the major congener, followed by 9-chlorophenanthrene (9-ClPhe)/ 2-chlorophenanthene (2-ClPhe). For BrPAHs, 1-bromopyrene (1-BrPyr) (>48%) was the major congener, followed by 7-bromobenz[a]anthracene (7-BrBaA) and 1,6-dibromopyrene (1,6-Br_2Pyr). Congener distributions of ClPAHs were different from previous studies about the fly ash from waste incinerators, which reported the dominance of 6-chlorobenzo[a]pyrene (6-ClBaP), 1-ClPyr, 3-chlorofluoranthene (3-ClFlu) and 7-chlorobenz[a]anthracene (7-ClBaA) for ClPAHs. But congener distributions of BrPAHs were similar with fly ash from waste incinerators, which also dominated by 1-BrPyr and 7-BrBaA.[3] Besides that, benz[a]anthracene (BaA), Chrysene (Chr) and benzo[a]pyrene (BaP) were the major contributors for BaP_{eq} concentrations of PAHs, 3,8-dichlorofluoranthene (3,8-Cl_2Flu) and 7-chlorobenz[a]anthracene (7-ClBaA) were the major congeners contributed to BaP_{eq} concentrations of ClPAHs, and 1-BrPyr and 7-BrBaA were the major congeners contributed to BaP_{eq} concentrations of BrPAHs.

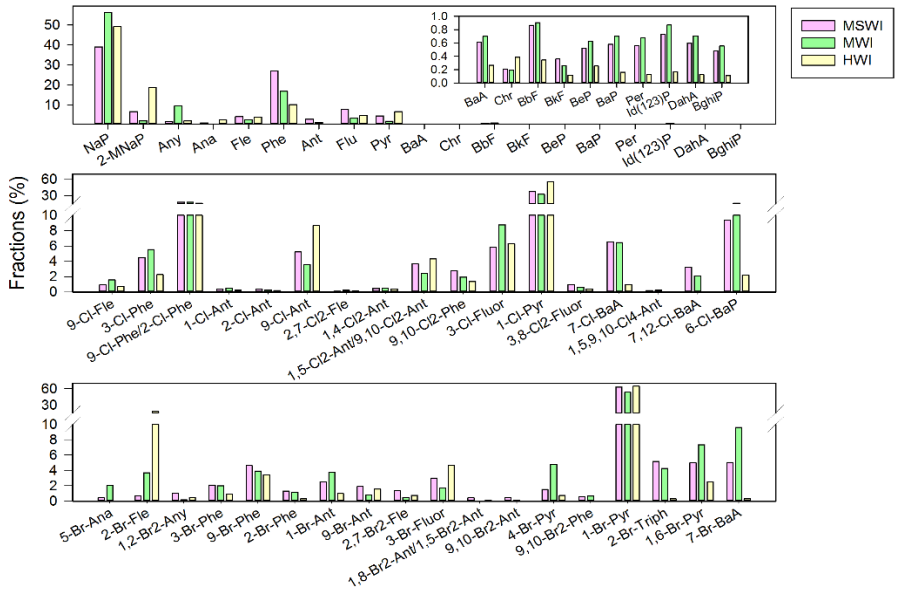

Figure 1. Congener distributions of PAHs, ClPAHs and BrPAHs in stack gas of waste incinerators.

Congener ratios were always used for sources apportionment in previous studies. The ratios of 6-chlorobenzo[a]pyrene (6-ClBaP)/ 1-ClPyr, 3-chlorofluoranthene (3-ClFlu)/1-ClPyr, 7-ClBaA/1-ClPyr, 6-ClBaP/3-ClFlu, 1-ClPyr /3-ClFlu, and 7-ClBaA/3-ClFlu were always used to trace the sources of ClPAHs. And the ratios of 7-BrBaA/1-BrPyr, 3-bromofluoranthene (3-BrFlu)/1-BrPyr, 9-bromophenanthrene (9-BrPhe)/1-BrPyr, 7-BrBaA/3-BrFlu, 1-BrPyr/3-BrFlu and 9-BrPhe/3-BrFlu were used to trace the sources of BrPAHs.[3] In this study, these ratios were listed in Table 1. Ratios of congeners in stack gases from different types of waste incinerators were similar, but different from those in fly ash from waste incinerators and dust from e-waste dismantling processes.[3,4]

Table 1. Average congener ratios in stack gas of different waste incinerators

	MSWI	MWI	HWI		MSWI	MWI	HWI
6-ClBaP/1-ClBaP	0.27	0.48	0.04	7-BrBaA/1-BrPyr	0.08	0.18	0.00
3-ClFlu/1-ClPyr	0.16	0.27	0.11	3-BrFlu/1-BrPyr	0.05	0.03	0.07
7-ClBaA/1-ClPyr	0.19	0.20	0.02	9-BrPhe/1-BrPyr	0.09	0.07	0.05
6-ClBaP/3-ClFlu	1.66	1.77	0.35	7-BrBaA/3-BrFlu	2.21	5.51	0.06
1-ClPyr/3-ClFlu	7.02	3.70	8.94	1-BrPyr/3-BrFlu	25.08	30.70	13.80
7-ClBaA/1-ClPyr	1.28	0.74	0.15	9-BrPhe/3-BrFlu	1.31	2.25	0.74

Correlations between the Cl-/BrPAH congeners and their parent PAH congeners were also calculated (Table 2). As shown in the table, for most of the Cl-/BrPAH congeners, the correlations were not significant. This indicated that chlorination from their parent PAH congeners maight not be the major formation pathways for these ClPAH and BrPAH congeners. Further studies needed to be done to further study on the formation mechanisms of ClPAHs and BrPAHs during the combustion of waste.

Table 2. Pearson correlations between Cl-/BrPAH congeners and their PAH congeners.

ClPAHs		BrPAHs	
9-ClFle	0.906*	5-BrAna	−0.150
3-ClPhe	0.986**	2-BrFle	0.765
9-ClPhe/2-ClPhe	0.840*	1,2-Br_2Any	0.103
1-ClAnt	0.143	3-BrPhe	0.572
2-ClAnt	0.281	9-BrPhe	0.623
9-ClAnt	0.870*	2-BrPhe	0.656
2,7-Cl_2Fle	0.808	1-BrAnt	0.510
1,4-Cl_2Ant	0.378	9-BrAnt	0.879*
1,5-Cl_2Ant/9,10-Cl_2Ant	0.908*	2,7-Br_2Fle	0.799
9,10-Cl_2Phe	0.692	3-BrFlu	0.956**
3-ClFlu	0.996**	1,8-Br_2Ant/1,5-Br_2Ant	0.203
1-ClPyr	0.686	9,10-Br_2Ant	−0.131
3,8-Cl_2Flu	0.948**	4-BrPyr	0.969**
7-ClBaA	−0.753	9,10-Br_2Phe	0.167
1,5,9,10-Cl_4Ant	0.971**	1-BrPyr	0.406
7,12-ClBaA	−0.776	1,6-BrPyr	0.266
6-ClBaP	−0.807	7-BrBaA	−0.762

References

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