REVIEW PAPER

Chlorinated and brominated polycyclic aromatic hydrocarbons in ambient air: seasonal variation, profiles, potential sources, and size distribution

Quang Tran Vuong · Phan Quang Thang · Takeshi Ohura · Sung-Deuk Choi

Abstract Chlorinated and brominated polycyclic aromatic hydrocarbons (ClPAHs and BrPAHs, respectively) are a new derivative group of PAHs. These halogenated PAHs (Halo-PAHs) have been reported to be carcinogenic and are considered emerging persistent organic pollutants. Gaining a clear understanding of the distribution and behavior of these ubiquitous organic pollutants is essential for the control and mitigation of their emission into the environment. However, research into the characteristics of Halo-PAHs in the atmosphere has been somewhat limited. This review paper thus aims to provide an overview of the seasonal patterns, profiles, potential sources, and particle-size distributions of atmospheric ClPAHs and BrPAHs with 3–5 rings. Most previous studies have focused on particulate Halo-PAHs and reported that their levels are higher during the cold season than during the warm season, with this seasonal variation more apparent for ClPAHs than for BrPAHs. In terms of their phase distribution, ClPAHs and BrPAHs share a similar trend, with their gaseous concentrations highest in summer and lowest in winter and their particulate concentrations exhibiting the opposite trend. Halo-PAH profiles have been shown to differ between sampling locations, possibly reflecting differences in the potential sources present at these sites, e.g., coal burning, traffic emissions, and industrial activity. The majority of Halo-PAHs tend to accumulate as ultrafine particles with an aerodynamic diameter of less than 1.0 μm. Overall, a detailed understanding of the characteristics of Halo-PAHs in the atmosphere has yet to be achieved; hence, further research on atmospheric Halo-PAHs is necessary.

Q. T. Vuong · P. Q. Thang · S.-D. Choi (✉)
School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea
e-mail: sdchoi@unist.ac.kr

P. Q. Thang
Institute of Environmental Technology (IET), Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet Street, Nghia Do, Cau Giay, Hanoi, Vietnam

T. Ohura
Faculty of Agriculture, Meijo University, Nagoya 468-8502, Japan

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are notorious organic pollutants commonly found in ambient air that have been reported to have serious adverse effects on human health (Abdel-Shafy and Mansour 2016; Armstrong and Gibbs 2009; Menzie et al. 1992). As such, the distribution and behavior of atmospheric

Table 1 Abbreviation, toxicity, and physicochemical properties (at 25 °C) of Halo-PAHs

Compound	Abbreviation	N_R^a	Mass (g/mol)	REP_{BaP}^b	$\log P_L$ (Pa)[c]	$\log K_{OA}^c$	ΔH_L (kJ/mol)[c]	ΔU_{OA} (kJ/mol)[c]
ClPAHs								
9-chlorophenanthrene	9-ClPhe	3	212.5	0.03	− 2.51, − 2.21[d]	8.41	− 82.23	70.24
1,9-dichlorophenanthrene	1,9-Cl₂Phe	3	247.0	0.12	− 3.44	9.25	− 92.34	79.30
3,9-dichlorophenanthrene	3,9-Cl₂Phe	3	247.0	0.32	− 3.43	9.24	− 92.51	79.45
9,10-dichlorophenanthrene	9,10-Cl₂Phe	3	247.0	0.20	− 3.49	9.30	− 92.89	79.79
3,9,10-trichlorophenanthrene	3,9,10-Cl₃Phe	3	281.5	0.77	− 4.25	9.98	− 100.84	86.91
1-chloroanthracene	1-ClAnt	3	212.5	0.04	− 1.68[e]	8.19[f]	_[g]	–
2-chloroanthracene	2-ClAnt	3	212.5	0.10	− 2.57	8.47	− 82.92	70.87
9-chloroanthracene	9-ClAnt	3	212.5	0.03	− 2.57	8.47	− 82.89	70.84
9,10-dichloroanthracene	9,10-Cl₂Ant	3	247.0	0.20	− 3.44	9.25	− 92.34	79.30
3-chlorofluoranthene	3-ClFlt	4	236.5	0.17	− 3.76	9.54	− 95.73	82.33
8-chlorofluoranthene	8-ClFlt	4	236.5	0.18	− 3.81	9.58	− 96.28	82.83
1,3-dichlorofluoranthene	1,3-Cl₂Flt	4	271.0	–	− 4.39	10.11	− 102.00	87.95
3,4-dichlorofluoranthene	3,4-Cl₂Flt	4	271.0	–	− 4.82	10.48	− 105.97	91.50
3,8-dichlorofluoranthene	3,8-Cl₂Flt	4	271.0	5.70	− 4.64	10.32	− 104.53	90.21
1-chloropyrene	1-ClPyr	4	236.5	0.10	− 3.95, − 4.06[d]	9.71	− 97.36	83.79
Dichloropyrene	Cl₂Pyr	4	271.0	–	− 4.74	10.42	− 105.09	90.72
Trichloropyrene	Cl₃Pyr	4	305.5	–	− 5.96	11.51	− 119.27	103.41
1,3,6,8-tetrachloropyrene	1,3,6,8-Cl₄Pyr	4	340.0	–	− 6.66	12.13	− 126.28	109.69
7-chlorobenz[a]anthracene	7-ClBaA	4	262.5	0.83	− 5.78	11.34	− 117.48	101.81
7,12-dichlorobenz[a]anthracene	7,12-Cl₂BaA	4	297.0	0.10	− 6.57	12.05	− 125.40	108.90
6-chlorochrysene	6-ClChr	4	262.5	2.10	− 5.72	11.29	− 116.95	101.34
6,12-dichlorochrysene	6,12-Cl₂Chr	4	297.0	0.03	− 6.60	12.08	− 125.94	109.38
6-chlorobenzo[a]pyrene	6-ClBaP	5	286.5	0.09	− 7.36	12.76	− 132.91	115.62
Dichlorobenzo[a]pyrene	Cl₂BaP	5	321.0	–	− 8.10	13.42	− 139.64	121.65
Trichlorobenzo[a]pyrene	Cl₃BaP	5	355.5	–	− 8.73	13.98	− 145.40	126.81
BrPAHs								
2-bromofluorene	2-BrFlu	3	245.0	0.02	− 2.12, − 2.46[d]	8.06	− 77.83	33.31
9-bromophenanthrene	9-BrPhe	3	257.0	0.02	− 3.01, − 2.83[d]	8.87	− 87.78	75.21
9-bromoanthracene	9-BrAnt	3	257.0	0.01	− 3.09	8.94	− 88.55	75.90
9,10-dibromoanthracene	9,10-Br₂Ant	3	336.0	–	− 4.33	10.05	− 101.08	87.12
1-bromopyrene	1-BrPyr	4	281.0	0.04	− 4.38	10.09	− 101.48	87.48
7-bromobenz[a]anthracene	7-BrBaA	4	307.0	0.84	− 6.21, − 6.25[d]	11.73	− 121.47	105.38
4,7-dibromobenz[a]anthracene	4,7-Br₂BaA	4	386.0	0.77	− 7.38	12.78	− 132.48	115.24
5,7-dibromobenz[a]anthracene	5,7-Br₂BaA	4	386.0	0.02	− 7.43	12.83	− 133.04	115.74

Table 1 continued

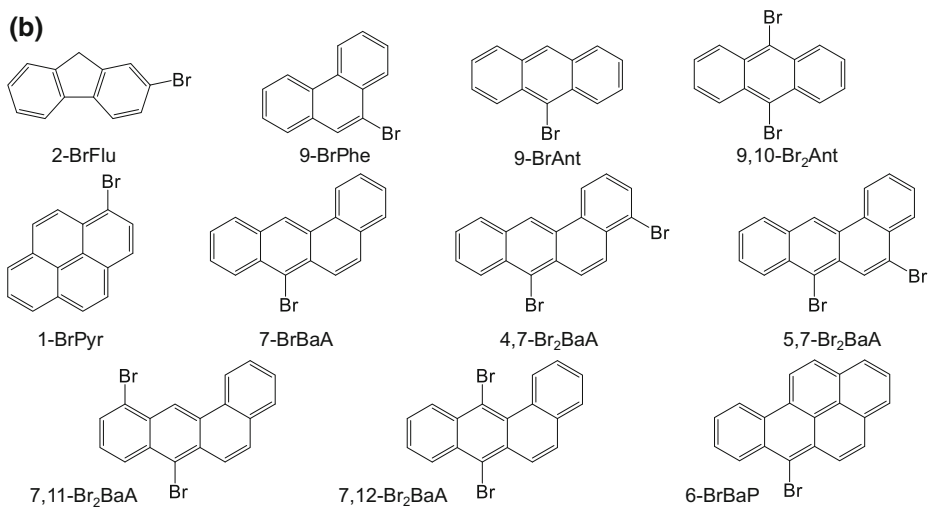| Compound	Abbreviation	N_R^a	Mass (g/mol)	REP_{BaP}^b	$\log P_L$ $(Pa)^c$	$\log K_{OA}^c$	ΔH_L $(kJ/mol)^c$	ΔU_{OA} $(kJ/mol)^c$
7,11-dibromobenz[a]anthracene	7,11-Br$_2$BaA	4	386.0	0.06	− 7.20	12.62	− 130.82	113.75
7,12-dibromobenz[a]anthracene	7,12-Br$_2$BaA	4	386.0	0.09	− 7.25	12.66	− 131.23	114.11
6-bromobenzo[a]pyrene	6-BrBaP	5	331.0	0.002	− 7.57	12.95	− 133.85	116.47

[a]Number of aromatic rings, [b]values obtained from previous studies (Ohura et al. 2007, 2009), [c]values obtained using the gas chromatographic retention time technique (Vuong et al. 2020b), [d]values obtained using the Knudsen effusion technique (Fu and Suuberg 2012), [e]a value calculated using EPI Suite 4.11 (US EPA); [f]a value calculated using Eq. (1); [g]not available

PAHs have been extensively studied for decades (Harner and Bidleman 1998; Ichikawa et al. 2018; Sonnefeld et al. 1983; Zhang et al. 2019). They can be produced by the incomplete burning of organic matter from natural processes and/or anthropogenic activity (Choi et al. 2007, 2012b). Due to industrialization and urbanization, many new groups of organic pollutants have been generated, and they interact within the atmosphere. In particular, a group of PAH derivatives that includes chlorinated PAHs (ClPAHs) and brominated PAHs (BrPAHs) is considered to be of significant concern (Ohura et al. 2018).

The synthesis for the two groups of halogenated PAHs (Halo-PAHs) and their toxicological effects, including genotoxicity, tumorigenicity, and metabolism impacts, have been documented in detail (Fu et al. 1999), with several reviews summarizing the distribution and behavior of ClPAHs and BrPAHs within all environmental compartments (Jin et al. 2020a; Ohura 2007; Sun et al. 2013). However, many recent studies have focused on atmospheric ClPAHs and BrPAHs, and a specific review of these two groups has become necessary. Although an overview of ClPAHs and BrPAHs in the air has been published previously (Ohura et al. 2012), there have been limited reviews about seasonal variation in and profiles of atmospheric ClPAHs and BrPAHs. Halo-PAHs may also include fluorinated and iodinated PAHs; however, we are unable to cover all results about Halo-PAHs; therefore, this review aims to summarize information on the physicochemical properties, toxicology, formation mechanisms, and atmospheric patterns, with a particular focus on the seasonal patterns, phase distributions, and particle-size distributions of atmospheric ClPAHs and BrPAHs with 3–5 rings.

ClPAHs and BrPAHs have a similar chemical structure to their corresponding parent PAHs, with chlorine or bromine atoms attached to the aromatic rings (Fig. 1). Polychlorinated naphthalenes (PCNs), which can be considered 2-ring ClPAHs, have been widely investigated (Helm et al. 2004; Ishaq et al. 2003; Liu et al. 2014). ClPAHs can be categorized into substituted and added forms depending on how the chlorine atoms are attached (Haglund et al. 1987; Nilsson and Colmsjö 1991, 1992). The former group is produced when chlorine atoms compete with and replace hydrogen atoms in the PAH rings, while the latter involves the addition of chlorine atoms, which destroys the aromatic structure of PAHs. Added ClPAHs have been reported to be less stable, more reactive (Nilsson and Colmsjö 1990), and more polar (Colmsjö et al. 1984) than substituted ClPAHs. Because the majority of published studies have investigated substituted ClPAHs, this review mainly focuses on substituted ClPAHs and BrPAHs with 3–5 rings. The abbreviations ClPAHs and BrPAHs used in this paper refer to their substituted forms. The term Halo-PAHs specifically refers to substituted ClPAHs and BrPAHs.

A list of ClPAHs and BrPAHs, their toxicity, and physicochemical properties are presented in Table 1. There are many potential species for these two types of Halo-PAHs that differ in the number and the position of the chlorine and bromine atoms in their PAH structures. However, 1,3,6,8-Cl$_4$Pyr (340 g/mol), Cl$_3$-BaP (355.5 g/mol), and Br$_2$BaA (386 g/mol) are the heaviest species that have been studied to date, with the highest number of halogen atoms.
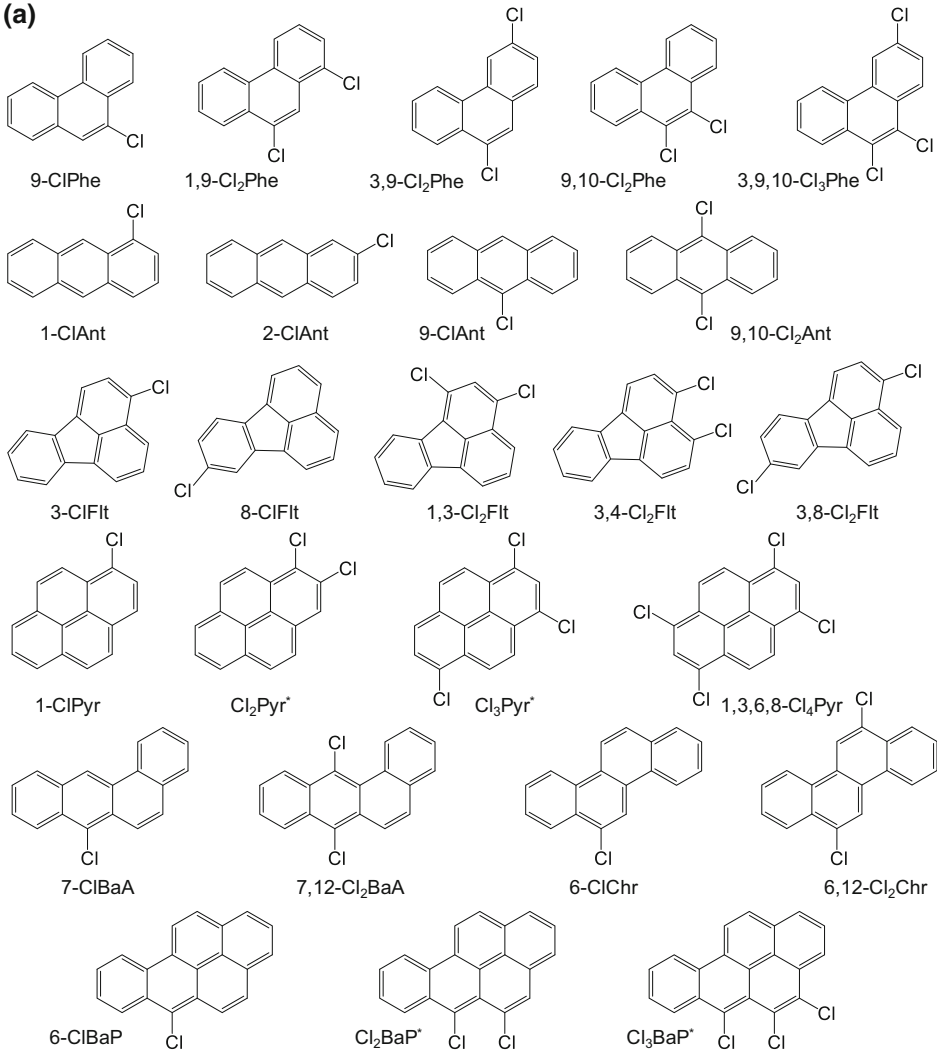
(a)

9-ClPhe   1,9-Cl$_2$Phe   3,9-Cl$_2$Phe   9,10-Cl$_2$Phe   3,9,10-Cl$_3$Phe

1-ClAnt   2-ClAnt   9-ClAnt   9,10-Cl$_2$Ant

3-ClFlt   8-ClFlt   1,3-Cl$_2$Flt   3,4-Cl$_2$Flt   3,8-Cl$_2$Flt

1-ClPyr   Cl$_2$Pyr*   Cl$_3$Pyr*   1,3,6,8-Cl$_4$Pyr

7-ClBaA   7,12-Cl$_2$BaA   6-ClChr   6,12-Cl$_2$Chr

6-ClBaP   Cl$_2$BaP*   Cl$_3$BaP*

(b)

2-BrFlu   9-BrPhe   9-BrAnt   9,10-Br$_2$Ant

1-BrPyr   7-BrBaA   4,7-Br$_2$BaA   5,7-Br$_2$BaA

7,11-Br$_2$BaA   7,12-Br$_2$BaA   6-BrBaP

2 Physicochemical properties of Halo-PAHs

Since the 1980–1990s, sub-cooled liquid vapor pressures (P_L) and octanol–air partition coefficients (K_{OA}) for organic compounds have been determined using the gas saturation (Sonnefeld et al. 1983; Spencer and Cliath 1983) and generator column (Harner and Mackay 1995; Harner and Bidleman 1996, 1998) methods. However, these conventional techniques are time-consuming, operate at low temperatures, and involve complex procedures. An alternative approach based on the retention times of the compounds of interest as determined using gas chromatography has been developed and refined for the estimation of P_L (Hamilton 1980; Hinckley et al. 1990; Lei et al. 2002) and K_{OA} (Odabasi et al. 2006; Wania et al. 2002). A recent work using the gas chromatographic retention time (GC-RT) technique to estimate the P_L and K_{OA} of ClPAHs and BrPAHs for any temperature of interest is of vital importance (Vuong et al. 2020b). Following this reference, P_L and K_{OA} are calculated and reported on a logarithmic scale (Table 1). The logP_L values of five Halo-PAH species obtained using the Knudsen effusion method (Fu and Suuberg 2012) were also provided in Table 1. The Estimation Program Interface (EPI Suite 4.11, US EPA) was applied to estimate a logP_L value at 25 °C for 1-ClAnt. According to a previous study (Harner and Bidleman 1998), the logK_{OA} and logP_L values for parent PAHs are linearly correlated with each other. Because ClPAHs are derivatives of PAHs, the logK_{OA} value of 1-ClAnt was estimated using the following equation:

$$\log K_{OA} = -1.040 \log P_L + 6.441, \ r^2 = 0.992.$$

(1)

As a result, the Halo-PAHs have logP_L values ranging from -8.73 (Cl_3BaP) to -1.68 (1-ClAnt) and logK_{OA} values ranging from 8.06 (1-BrFlu) to 13.98 (Cl_3BaP). A limitation of EPI Suite is that the position of the chlorine atom is not considered when estimating P_L, leading to a higher value of logP_L for 1-ClAnt compared with 2-ClAnt and 9-ClAnt (-2.57).

Enthalpy of vaporization, ΔH_L (kJ/mol), and internal energy of phase transfer, ΔU_{OA} (kJ/mol), were also calculated based on the previous study (Vuong et al. 2020b) and reported in Table 1 for ClPAHs and BrPAHs. The absolute values of ΔH_L and ΔU_{OA} are significantly correlated with the molecular mass of ClPAHs ($r = 0.91$, $p < 0.01$, Pearson correlation) and BrPAHs ($r = 0.79$, $p < 0.01$, Spearman correlation). In addition, the effects of position and number of chlorine or bromine atoms (n_{Cl} or n_{Br}) in the PAH structures to ΔH_L and ΔU_{OA} of ClPAHs or BrPAHs are apparent. For example, the values of ΔH_L and ΔU_{OA} for $1,3\text{-}Cl_2Flt$, $3,4\text{-}Cl_2Flt$, and $3,8\text{-}Cl_2Flt$ are -102.00, -105.97, and -104.53 kJ/mol and 87.95, 91.50, and 90.21 kJ/mol, respectively. The absolute values of ΔH_L and ΔU_{OA} for Cl_n-Phe and Cl_n-Pyr increase significantly when n_{Cl} increases from 1 to 3 or 4. Regarding BrPAHs, the values of ΔH_L and ΔU_{OA} vary among $4,7\text{-}Br_2BaA$, $5,7\text{-}Br_2BaA$, $7,11\text{-}Br_2BaA$, and $7,12\text{-}Br_2BaA$. While n_{Br} increasing from 1 to 2 changes the values of ΔH_L and ΔU_{OA} for Br_n-Ant and Br_n-BaA by 14 and 10%. Further studies are necessary to explain clearly the influence of position and number of chlorine and bromine atoms on the physicochemical properties of ClPAHs and BrPAHs.

3 Toxicology of Halo-PAHs

Although added ClPAHs have been shown to have strong and/or direct impacts on genetic mutation (Colmsjö et al. 1984), the toxicology of substituted Halo-PAHs is discussed here because they are the main focus of this review. Halo-PAHs have been reported to be carcinogenic and mutagenic by toxicological tests in living organisms (Fu et al. 1999; Yoshino and Urano 1997). In particular, several previous studies for *Salmonella* and aryl hydrocarbon hydroxylase (AHH) induction in chick embryos have indicated that 9-ClAnt exhibits strong direct-acting mutagenicity (Löfroth et al. 1985), whereas 6-ClChr and $6,12\text{-}Cl_2Chr$ are more toxic than their parent compound (Gustafsson et al. 1994). Unlike 9-ClAnt, 6-BrBaP requires metabolic activation to exert its mutagenicity by producing 6-BrBaP *trans*-4,5-dihydrodiol and *trans*-7,8-dihydrodiol in rat liver microsomes (Fu and Yang 1982). Among ClPAHs and BrPAHs, 7-ClBaA and 7-BrBaA have been widely investigated for their toxicological effects. The

carcinogenicity of 7-ClBaA and 7-BrBaA has been confirmed in the male B6C3F$_1$ neonatal mouse with hepatocellular adenomas and carcinoma, respectively (Fu et al. 1996). In rat and mouse liver microsomes, these two compounds can be metabolized at carbon positions 3, 4, 5, 6, 8, 9, 10, and 11 as the main metabolism region to form 7-ClBaA *trans*-3,4-dihydrodiol and 7-BrBaA *trans*-3,4-dihydrodiol (Fu et al. 1991). These metabolites are much more potent than the corresponding parent Halo-PAHs and have been proven to cause DNA adducts and initiate tumors. Furthermore, mutations from 7-ClBaA and 7-BrBaA in B6C3F$_1$ mouse liver tumors may induce at the first base of K-*ras* codon 13 and cause a pattern of GGC to CGC (Xia et al. 1998).

Research on aryl hydrocarbon receptor (AhR)-mediated activity in the YCM3 cell assay system has found that some ClPAHs are much more toxic than their parent PAHs (Ohura et al. 2007, 2009). The relative equivalency potency of Halo-PAHs compared to benzo[a]pyrene (REP$_{BaP}$) is listed in Table 1. Of the ClPAHs, the most toxic substances are 3,8-Cl$_2$Flt and 6-ClChr (REP$_{BaP}$ = 5.70 and 2.10, respectively), indicating that these two compounds are much more toxic than BaP. The toxicity of Cl$_n$-Phe, Cl$_n$-Ant, and Cl$_n$-Flt homologues is significantly higher when the number of chlorine atoms increases. In particular, REP$_{BaP}$ values for Cl$_n$-Phe increase approximately tenfold from Cl$_1$-Phe (9-ClPhe: 0.03) to Cl$_2$-Phe (3,9-Cl$_2$Phe: 0.32) and 25-fold to Cl$_3$-Phe (3,9,10-Cl$_3$Phe: 0.77). The position of the chlorine atoms also affects REP$_{BaP}$. For example, the REP$_{BaP}$ of Cl$_1$-Ant homologues has been reported to be 0.03 (9-ClAnt), 0.04 (1-ClAnt), and 0.10 (2-ClAnt), while that of Cl$_2$-Phe ranges from 0.12 (1,9-Cl$_2$Phe) to 0.20 (9,10-Cl$_2$Phe) and 0.32 (3,9-Cl$_2$Phe). For BrPAHs, the position of the bromine atoms has a stronger influence on toxicity than does their number. However, toxicological research on Halo-PAHs has been limited due to the lack of native standard stocks; thus, more specific studies are essential to provide a more detailed understanding of Halo-PAH toxicology.
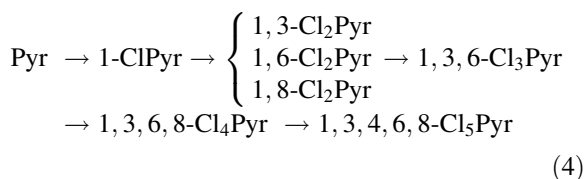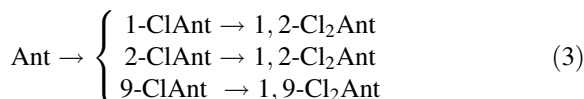
4 Formation mechanisms

Several studies have focused on the mechanisms responsible for the presence of Halo-PAHs in ambient air. In general, Halo-PAHs are believed to be generated by the incomplete burning of organic materials in the presence of halogen sources, e.g., organic halides naturally found in lead-free fuels or occurring due to contamination during refining and shipment (Haglund et al. 1987). The direct chlorination of parent PAHs from emission sources has been reported as a major formation mechanism (Fujima et al. 2006; Horii et al. 2008; Miyake et al. 2017). During the combustion of polyvinylchloride (PVC), hydrogen chloride (HCl) is produced, which then reacts with the PAHs that form in the cooler zones of the furnace. When the temperature of a furnace rises above 600 °C up to 900 °C, PAHs have a higher chance of being exposed to HCl, which can lead to the direct chlorination of parent PAHs and subsequently higher levels of ClPAHs (Wang et al. 2001). Experiments have also been conducted on the chlorination of PAHs using HCl and chlorine (Cl$_2$) gases to investigate ClPAH formation mechanisms from the incineration of municipal waste (Yoshino and Urano 1997). The results found that the ClPAH yield using HCl was much lower than that using Cl$_2$. The chlorination of parent PAHs by HCl and Cl$_2$ is described by the following reaction.

$$PVC \xrightarrow{combustion} HCl + Cl_2 \xrightarrow{PAHs} ClPAHs \qquad (2)$$
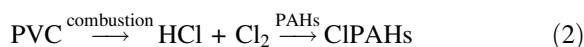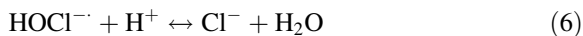
The reaction series of anthracene (Ant) (Dang and He 2016) and pyrene (Pyr) (Miyake et al. 2017) with supply of HCl or Cl$_2$ to produce Cl$_n$-Ant and Cl$_n$-Pyr, respectively, have also been proposed.

$$Ant \rightarrow \begin{cases} 1\text{-ClAnt} \rightarrow 1,2\text{-Cl}_2\text{Ant} \\ 2\text{-ClAnt} \rightarrow 1,2\text{-Cl}_2\text{Ant} \\ 9\text{-ClAnt} \rightarrow 1,9\text{-Cl}_2\text{Ant} \end{cases} \qquad (3)$$

$$\begin{aligned} Pyr \rightarrow 1\text{-ClPyr} &\rightarrow \begin{cases} 1,3\text{-Cl}_2\text{Pyr} \\ 1,6\text{-Cl}_2\text{Pyr} \rightarrow 1,3,6\text{-Cl}_3\text{Pyr} \\ 1,8\text{-Cl}_2\text{Pyr} \end{cases} \\ &\rightarrow 1,3,6,8\text{-Cl}_4\text{Pyr} \rightarrow 1,3,4,6,8\text{-Cl}_5\text{Pyr} \end{aligned}$$
$$(4)$$

Similarly, BrPAHs are often assumed to be generated from the direct bromination of parent PAHs. However, several studies of waste incinerators and secondary copper smelters have revealed very poor correlations between BrPAHs and their corresponding parent PAHs (Horii et al. 2008; Jin et al. 2017a). Therefore, BrPAHs may form via other mechanisms rather than the direct bromination of PAHs.

Another important mechanism is photochemical reactions between parent PAHs and various radicals (Cl·, Br·, and OH·) in ambient air. Some of the chemical reactions involved in this process have been proposed by a previous study (Ohura and Miwa 2016).

$$OH^{\cdot} + Cl^{-} \rightarrow HOCl^{-\cdot} \tag{5}$$

$$HOCl^{-\cdot} + H^{+} \leftrightarrow Cl^{-} + H_2O \tag{6}$$

$$PAHs + Cl^{-} \rightarrow ClPAHs \tag{7}$$

Cl· and OH· are added to the first and second positions in the PAH ring structure, followed by the separation of HCl or H_2O to create monochloro-homologues. The photochemical reaction between parent PAHs and Br· appears to be very weak due to the instability of Br· in the atmosphere. Nevertheless, photochemical reactions have been reported to be the major generation mechanism for atmospheric Halo-PAHs (Jin et al. 2017a; Nilsson and Oestman 1993; Ohura et al. 2005; Vuong et al. 2020a). Recently, the monitoring of atmospheric Halo-PAHs (Ohura et al. 2018, 2019; Vuong et al. 2020a) and their behavior have been increasingly investigated (Jin et al. 2017d; Ohura et al. 2008b). Although the processes underlying the generation of Halo-PAHs have started to become understood, BrPAHs have received less attention than ClPAHs. Therefore, how BrPAHs are generated in the atmosphere is not yet clear.

Table 2 Summary of studies monitoring atmospheric Halo-PAHs in selected cities

Nation	City	Type of sampling site	Sampling period	Phase	ClPAHs (pg/m³)	BrPAHs (pg/m³)	Reference
South Korea	Ulsan	Semi-rural	1–12/2015	Gas	9 (24)*	12 (11)	Vuong et al. (2020c)
				Particle	10 (24)	2 (11)	
China	Tibetan Plateau	Mountainous	7/2016–6/2017	Mostly gas	4 (19)	0.3 (19)	Jin et al. (2020b)
South Korea	Ulsan	Urban, industrial, rural	3–5/2013	Mostly gas	207 (24)	84 (11)	Vuong et al. (2020a)
Japan	Tokyo	Industrial	4/2004	Gas	40 (18)		Ohura et al. (2018)
				Particle	14 (18)		
China	Beijing	Urban	8/2015–3/2016	Gas	89 (19)	5 (19)	Jin et al. (2017c)
				Particle	312 (19)	35 (19)	
Japan	Nagoya	Urban and industrial	5/2011 –2/2012	Particle	68 (24)		Ohura et al. (2016)
China	Shanghai	Suburban	10/2011 –3/2013	Particle	21 (20)		Ma et al. (2013)
Japan	Sapporo	Urban and industrial	8/2009	Particle	1 (19)		Kakimoto et al. (2014)
			2/2010	Particle	8 (19)		
	Sagamihara	Suburban	8/2009	Particle	1 (19)		
			2/2010	Particle	8 (19)		
	Kanazawa	Suburban	8/2009	Particle	1 (19)		
			2/2010	Particle	3 (19)		
	Kitakyushu	Suburban	8/2009	Particle	1 (19)		
			2/2010	Particle	14 (19)		
South Korea	Busan	Urban and industrial	8/2009	Particle	1 (19)		
			2/2010	Particle	14 (19)		
Japan	Shizuoka	Rural	9/2005 –6/2006	Particle	15 (16)	9 (11)	Ohura et al. (2009)

*Total mean concentration (number of target compounds)

5 Air sampling and analytical methods

The levels of Halo-PAHs in the atmosphere are generally very low (1–100 pg/m^3), around three orders of magnitude lower than those of parent PAHs (1–100 ng/m^3) (Jin et al. 2017c; Vuong et al. 2020c). More detailed information about the atmospheric concentrations of ClPAHs and BrPAHs can be found in Sect. 6. Therefore, high-volume (HiVol) air samplers are more suitable than medium- or low-volume air samplers for the collection of atmospheric samples. HiVol samplers generally operate for 24 h, with the particulate and gaseous phases of Halo-PAHs collected using glass/quartz fiber filters (GFFs/QFFs) and polyurethane foam plugs (PUFs), respectively (Jin et al. 2017d; Nilsson and Oestman 1993; Ohura et al. 2013). Recently, passive air samplers have been used effectively to collect mostly gaseous Halo-PAHs on PUF disks over 84 days (Vuong et al. 2020a) and on XAD resin (Jin et al. 2020b).

Pre-treatment processes for the analysis of Halo-PAHs are very similar to those for parent PAHs. However, the details of these processes vary widely between studies because no standard method for the analysis of Halo-PAHs has yet been established. In general, a retrieved sample is extracted then cleaned up prior to instrumental analysis. For extraction from both GFFs and PUFs, a Soxhlet system containing different solvent mixtures, e.g., *n*-hexane/dichloromethane (1:1, v/v) (Ohura et al. 2013), *n*-hexane/acetone (9:1, v/v) (Vuong et al. 2020a), or only *n*-hexane (Ohura et al. 2008b), and benzene (Nilsson and Oestman 1993), can be used for 16–24 h. Particulate ClPAHs have been more frequently studied than gaseous ClPAHs and BrPAHs. In these studies, the ClPAHs are frequently extracted from GFFs using ultra-sonication (39 kHz) for 20–30 min with *n*-hexane (Ohura et al. 2008b) or dichloromethane (Kakimoto et al. 2014; Kitazawa et al. 2006; Ohura et al. 2009).

For clean-up, various packing materials have been used in glass columns with different eluting solvents (Kakimoto et al. 2014; Nilsson and Oestman 1993; Ohura et al. 2008b, 2009). An evaluation of different packing materials (silica gel, sulphoxide, activated alumina, and activated carbon) and eluents (*n*-hexane, *n*-hexane/dichloromethane [9:1, v/v], toluene, and *n*-hexane/acetone [9:1, v/v]) has been conducted to optimize the clean-up method for Halo-PAH analysis (Kamiya et al. 2015), with the results indicating that clean-up using silica gel with *n*-hexane/dichloromethane (9:1, v/v) has the highest efficiency.

In the early stages of Halo-PAH research, monochloro-2,2′-binaphthyl was used as an internal standard to estimate recovery from pre-treatment (Nilsson and Oestman 1993). Recently, deuterated PAHs such
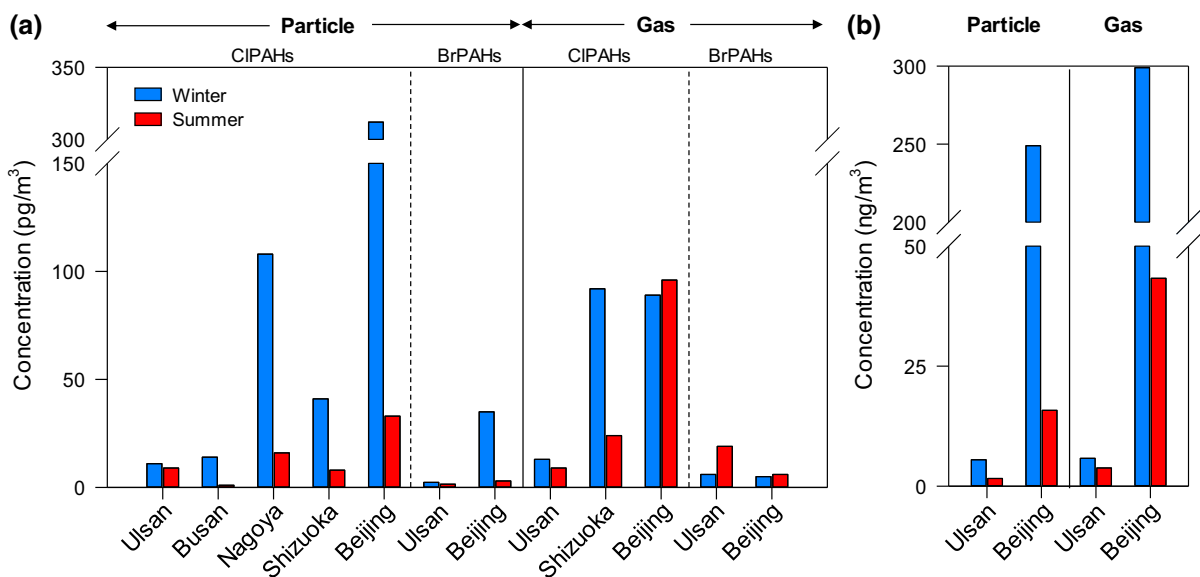

Fig. 2 Seasonal variation in particulate and gaseous **a** Halo-PAHs (Jin et al. 2017c; Kakimoto et al. 2014; Ohura et al. 2013, 2016; Vuong et al. 2020c) and **b** PAHs (Jin et al. 2017c; Nguyen et al. 2018) in selected Asian cities

as phenanthrene-d$_{10}$, fluoranthene-d$_{10}$, pyrene-d$_{10}$, chrysene-d$_{12}$, perylene-d$_{12}$, and p-terphenyl-d$_{14}$ have been spiked into samples alternately as surrogate and internal standards (Kakimoto et al. 2014; Kitazawa et al. 2006; Ohura et al. 2008b; Vuong et al. 2020a). In addition, $^{13}C_6$ and d-labeled Halo-PAHs have been added to samples, e.g., $^{13}C_6$-9-ClPhe, $^{13}C_6$-2-ClAnt, $^{13}C_6$-1-ClPyr, $^{13}C_6$-7-ClBaA, $^{13}C_6$-7-BrBaA, and 9-BrPhe-d$_9$ as surrogate standards and $^{13}C_6$-7,12-Cl$_2$BaA as an internal standard (Jin et al. 2017a, c, d).

The instruments used to analyze Halo-PAHs are very similar to those used for PAHs. To measure trace concentrations of Halo-PAHs in ambient air, the final sample volume in the test vial should be 50–100 μL and a high-resolution gas chromatograph coupled to a high-resolution mass spectrometer (HRGC-HRMS) is generally preferred (Jin et al. 2017b, c; Kakimoto et al. 2014; Ohura et al. 2008b, 2009). A GC–MS can also be employed to analyze Halo-PAHs (Ma et al. 2013; Nilsson and Oestman 1993; Vuong et al. 2020a). Its performance is inferior to that of high-resolution instruments; however, the sensitivity and selectivity can be significantly improved by using a two-dimensional GC and/or MS (GC × GC–MS, GC–MS/MS, or GC × GC–MS/MS) (Tang et al. 2020). A capillary column (DB-5MS, 0.25 mm i.d., 0.25 μm film thickness) with two length options (30 or 60 m) has been used for GC separation, while MS was operated under selected ion monitoring and positive electron impact (EI) mode (38 eV for HRMS and 70 eV for normal MS). Negative chemical ionization (NCI) mode has also been tested, leading to significantly higher sensitivity, but some Cl$_n$-Phe and Cl$_n$-Chr species could not be detected (Kamiya et al. 2015).

6 Levels of Halo-PAHs

6.1 Overall Halo-PAH concentrations

Most research on Halo-PAHs in ambient air over the past decade has been conducted in Northeast Asia (South Korea, Japan, and China; Table 2). It can be seen that ClPAHs have received more attention than BrPAHs, particularly those in the particulate phase. Because the target compounds, sampling periods, and types of sampling site differ between individual studies, they are compared in the present study in order to roughly evaluate Halo-PAH pollution levels.

Of the selected Asian cities in Table 2, Beijing, China, has the highest particulate concentration of ClPAHs (Σ_{19} ClPAHs = 312 pg/m^3; (Jin et al. 2017c), significantly higher than the concentration in Busan, South Korea (Σ_{19} ClPAHs = 14 pg/m^3; (Kakimoto et al. 2014), Japanese cities (average Σ ClPAHs ∼ 10 pg/m^3) and Shanghai, China (Σ_{20} ClPAHs = 21 pg/m^3; (Ma et al. 2013). This can be explained by the widespread burning of coal for heating during the cold season in remote areas of Beijing (Jin et al. 2017c). On the other hand, sampling sites in Ulsan, one of the largest industrial cities in South Korea, are greatly affected by industrial activity, leading to the highest level of the gaseous ClPAHs (Σ_{24} ClPAHs = 207 pg/m^3; (Vuong et al. 2020a). This level is 2.4 times higher than that in Beijing (Σ_{19} ClPAHs = 87 pg/m^3; (Jin et al. 2017c).

The levels of BrPAHs in the atmosphere have been less investigated (Jin et al. 2017c; Ohura et al. 2009; Vuong et al. 2020a), possibly due to their lower toxicity (Table 1) and concentration compared with ClPAHs (Table 2). The particulate levels of BrPAHs in Beijing (Σ_{19} BrPAHs = 35 pg/m^3) are four times higher than those in Shizuoka, Japan (Σ_{11} BrPAHs = 9 pg/m^3), while the gaseous concentration in Beijing (Σ_{19} BrPAHs = 5 pg/m^3) is much lower than that in Ulsan (Σ_{11} BrPAHs = 84 pg/m^3).

Air samples have also been collected from mountainous areas in the Tibetan Plateau, China, mostly within a natural reserve. The levels of Halo-PAHs (Σ_{19} ClPAHs = 4 pg/m^3 and Σ_{19} BrPAHs = 0.3 pg/m^3) in these areas are lower than those at other sampling sites (Jin et al. 2020b). A potentially major source of Halo-PAHs may be long-range atmospheric transport (LRAT) from the southern and western regions of Asia, with local sources and photochemical reactions as minor sources (Jin et al. 2020b).

6.2 Seasonal variation in Halo-PAHs

Though seasonal variation in Halo-PAHs in the atmosphere has also been investigated, the majority of this research has focused on particulate ClPAHs (Fig. 2a). The concentration of this group has been reported to be highest during winter and lowest during summer (Jin et al. 2017c; Kakimoto et al. 2014; Ohura et al. 2013, 2016; Vuong et al. 2020c), with levels that are fivefold (Shizuoka) to over tenfold (Busan) higher during winter than during summer. The seasonal
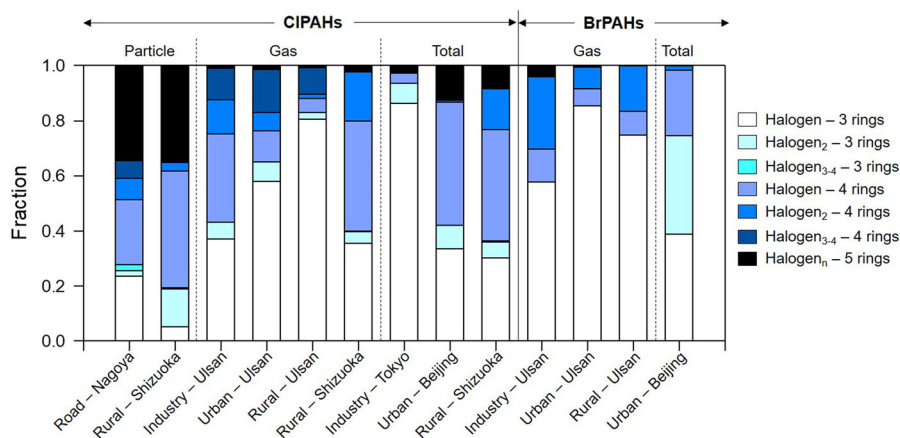
Fig. 3 Fractions of Halo-PAHs classified by the number of halogen atoms and rings at selected sampling sites. These data were obtained from previous studies (Jin et al. 2017c; Ohura et al. 2008b, 2018; Oishi et al. 2019; Vuong et al. 2020a)

variation in gaseous ClPAHs in Ulsan and Shizuoka differs significantly from that in Beijing, with levels that are slightly lower and four times lower during summer than during winter in Ulsan (Vuong et al. 2020c) and Shizuoka (Ohura et al. 2013), respectively, compared to levels that are slightly higher during summer in Beijing (Jin et al. 2017c). The pattern in Ulsan and Shizuoka can be explained by strong seasonal sources at rural sites. In particular, coal combustion for heating is highlighted during winter. In contrast, the sampling site in Beijing is an urban site with a dense population. Thus, gaseous ClPAHs may be produced by constant sources, e.g., traffic emissions, over the entire year.

In general, particulate BrPAHs have been found to be higher during winter than during summer, while gaseous BrPAHs exhibit a reverse trend (Fig. 2a) (Jin et al. 2017c; Vuong et al. 2020c). Long-term monitoring and/or specific research on the physicochemical properties of BrPAHs should be conducted to more clearly understand their behavior.

In previous studies reporting seasonal variation in parent PAHs (Jin et al. 2017c; Nguyen et al. 2018), the concentrations of PAHs are higher in the gaseous phase than in the particulate phase (Fig. 2b), with winter tending to have higher PAH levels than summer. The phase distribution of parent PAHs has been used to distinguish between the effects of local sources and LRAT (Choi et al. 2012a; Nguyen et al. 2018) because gaseous PAHs can degrade during LRAT and are thus detected at low levels (Ravindra et al. 2008). Based on this, it has been concluded that

parent PAHs in Ulsan (Nguyen et al. 2018) and Beijing (Jin et al. 2017c) may be influenced by local sources rather than LRAT. Because Halo-PAHs are derivatives of PAHs, they are expected to share common sources in ambient air (Kitazawa et al. 2006; Ohura et al. 2009). However, Halo-PAHs have recently been reported to have specific sources that differ from those of their parent PAHs (Kamiya et al. 2016; Ohura et al. 2019). The sampling sites in Ulsan (Nguyen et al. 2018) and Shizuoka (Ohura et al. 2013) are in rural areas and may be affected by similar sources; as a result, the ClPAHs and parent PAHs at these two sites exhibit similar seasonal patterns. In contrast, the concentrations of particulate ClPAHs and BrPAHs are much higher than those of their gaseous counterparts during winter in Beijing, which is the opposite of the trend for their parent PAHs (Jin et al. 2017c). Hence, ClPAHs and BrPAHs during winter in Beijing might be more strongly influenced by LRAT than by the same local sources as their parent PAHs. A study in Nagoya, Japan, found that 31% of total ClPAHs are influenced by specific industrial sources, whereas 37% of total PAHs are generated by oil combustion, the petrochemical industry, and vessel operations (Kamiya et al. 2016). Another study in Japan that collected air samples at different types of sampling site (e.g., forest, agricultural, residential, urban, commercial, and industrial) also found that ClPAHs have an origin that differs from the potential sources of parent PAHs at 30% of the sampling sites (Ohura et al. 2019).
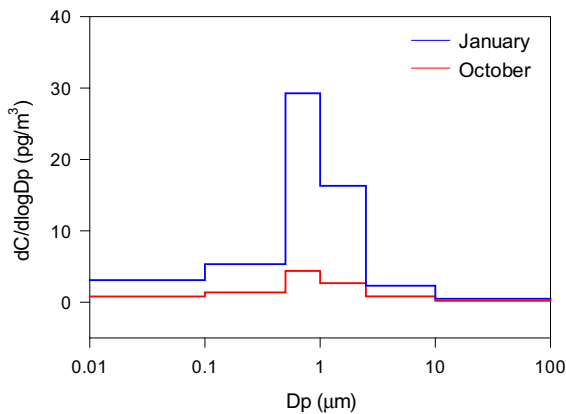
Fig. 4 Particle-size distribution of ClPAHs in Osaka, Japan (Kakimoto et al. 2017). dC denotes the ClPAH concentration for each particle-size range. dlogD$_p$ represents the logarithmic size interval for each size range in terms of diameter D$_p$

7 Profiles of Halo-PAHs

Figure 3 presents the particulate, gaseous, and total (i.e., particle + gas) profiles of Halo-PAHs classified by the number of halogen atoms and aromatic rings for different types of sampling site (i.e., road, industrial, urban, and rural sites). In general, the Halo-PAH profile at each sampling site is unique. In terms of particulate ClPAHs, Cl$_n$-5 rings, which represent high-molecular-weight (HMW) compounds, are frequently observed, with an average fraction of 35% at a road site in Nagoya (Oishi et al. 2019) and a rural site in Shizuoka (Ohura et al. 2008b). However, the profile of particulate ClPAHs at the road site contains all ClPAH groups, with a significant contribution from poly-Cl-4 rings (14%), whereas the rural site is dominated by
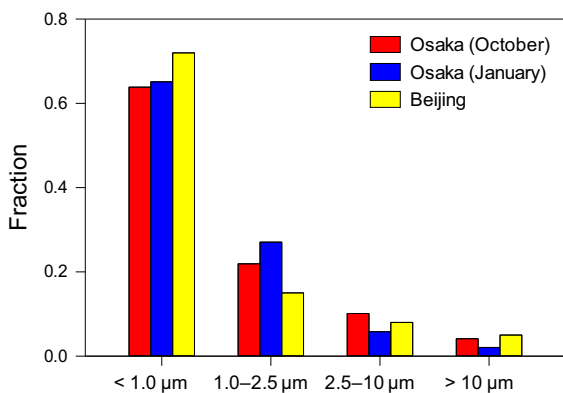

Fig. 5 Particle-size fractions of ClPAHs in Osaka (Kakimoto et al. 2017) and Beijing (Jin et al. 2017d)

mono-Cl-4 rings (42%). The profile of gaseous ClPAHs in Ulsan is characterized by the proportion of HMW compounds decreasing and that of low-molecular-weight (LMW) compounds increasing from industrial to urban and rural sites (Vuong et al. 2020a). The two rural sites in Ulsan and Shizuoka have different gaseous ClPAH profiles, which could be due to different local sources or sampling periods. Interestingly, the industrial site in Tokyo, Japan, is dominated by mono-Cl-3 rings, accounting for 86% of total ClPAHs (Ohura et al. 2018) and about threefold higher than that observed at the urban site in Beijing (34%) (Jin et al. 2017c) and the rural site in Shizuoka (30%) (Ohura et al. 2008b).

Because BrPAHs have been generally underrepresented in research, their atmospheric profiles have not been investigated in depth. According to a previous study in Ulsan, the contributions of LMW and HMW compounds to the total BrPAH concentration differ from those for ClPAHs (Vuong et al. 2020a). The industrial sites in Ulsan have high fractions of HMW compounds and low fractions of LMW compounds, whereas urban sites exhibited the opposite relationship. This contrast between BrPAHs and ClPAHs could be partly explained by differences in their formation mechanisms. It has been reported that BrPAHs do not share the same potential sources as ClPAHs in other environmental media (Ni and Zeng 2012); however, little is known about the occurrence and fate of BrPAHs in ambient air.

8 Potential sources of Halo-PAHs

Potential sources of Halo-PAHs have mainly been identified using the recorded fractions of specific species. Previous research has highlighted several compounds that can be used to indicate particular sources. In a previous study, the effects of vehicular emissions on two sampling sites via short-range air transport were evaluated using the two diagnostic ratios [8-ClFlt]/[3-ClFlt] and [7-ClBaA]/[3-ClFlt] based on particulate concentrations (Oishi et al. 2019). These three compounds had been investigated earlier and reported to be resistant to photochemical degradation (Ohura et al. 2008a). Therefore, they can be transported short distances from a source to a receptor site. The [8-ClFlt]/[3-ClFlt] and [7-ClBaA]/[3-ClFlt] ratios ranged from 2.2 and 4.2 to 3.2 and 7.0,

respectively, in the presence of traffic emissions. As a result, 8-ClFlt and 7-ClBaA are considered indicators of vehicular exhaust emissions.

The highly-resolved spatial distribution of gaseous ClPAHs was reported by a previous study conducted in Ulsan, and the results indicated that various forms of industrial activity can produce several unique ClPAH species (Vuong et al. 2020a). The combined fraction of two compounds (9-ClPhe and 9-ClAnt) account for approximately 70% of total ClPAHs at sampling sites located on-site at automobile and shipbuilding industries. The two ClPAHs are also transported via northwesterly winds to nearby areas, leading to two other sampling sites (urban and rural sites) having very similar ClPAH profiles. Therefore, 9-ClPhe and 9-ClAnt are indicative of these two industrial activities. In addition, 6-ClChr can be considered a potential indicator for petrochemical operations because it accounts for the highest contribution (30%) at industrial sites. On the other hand, 9-ClPhe (27%), 9-ClAnt (12%), 3-ClFlt (4%), and 1-ClPyr (26%) have been reported at secondary copper smelters in China (Jin et al. 2017a), and a similar ClPAH profile has also been found in a non-ferrous industrial zone in Ulsan (Vuong et al. 2020a). Thus, these four ClPAH species are likely to be generated by non-ferrous industrial activity.

During the cold season in Beijing, coal combustion for heating increases dramatically, which leads to elevated 3-ClFlt and 1-ClPyr levels in the atmosphere (Jin et al. 2017c). Their corresponding parents, fluoranthene (Flt) and pyrene (Pyr), are also reported to be higher in winter than in summer. Because Flt and Pyr have been proven to be produced by the burning of coal (Harrison et al. 1996), their daughter species, 3-ClFlt and 1-ClPyr, can also be considered possible indicators of the same source.

Regarding BrPAHs, several indicators of industrial operations have been reported. For example, 2-BrFlu is mostly produced by the automobile industry and can be transported to surrounding areas on the wind, while Br_2-4 rings, e.g., 4,7-Br_2BaA and 7,12-Br_2BaA, are often associated with petrochemical industrial activity (Vuong et al. 2020a).

9 Particle-size distribution of Halo-PAHs

In a previous study in Osaka, Japan (Fig. 4), six particle-size fractions of ClPAHs were analyzed, and a unimodal size distribution with only one distinct peak located at 0.5–1 μm (ultrafine mode) was observed over the entire sampling period (Kakimoto et al. 2017). This phenomenon is more apparent in January (29.3 pg/m^3) than in October (4.4 pg/m^3) in Osaka. Note that most of the target species are ClPAHs with 3–4 rings (Table 1). Their particle-size distribution differs from parent PAHs with 3 and 4 rings, which have been reported to exhibit a bimodal size distribution in Shanghai (Lv et al. 2016). In particular, PAHs with 3 rings (phenanthrene and anthracene) exhibit their highest peak within the fine particle range (2.5–10 μm) and their second-highest peak within the ultrafine range, a direct contrast to PAHs with 4 rings (fluoranthene, pyrene, benz[a]anthracene, and chrysene), which have a distinct peak for ultrafine particles and a lower peak for fine particles. Similarly, parent PAHs tend to accumulate in smaller particles with an increasing ring number. In particular, PAHs with 5–6 rings (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene) exhibit a unimodal distribution with a peak in the ultrafine range.

Figure 5 compares the particle-size distributions of ClPAHs in Osaka (Kakimoto et al. 2017) and Beijing (Jin et al. 2017d). A similar distribution pattern is observed for these two locations, with most particles found in the ultrafine mode (64% in Osaka in October and 65% in January and 72% in Beijing). This unique particle-size distribution of ClPAHs may originate from their formation mechanisms and potential sources within the environment; however, knowledge on how ClPAHs are generated and their photochemical interaction with atmospheric radicals and/or other substances is extremely limited.

According to a previous study in Beijing, BrPAHs have a similar distribution pattern to ClPAHs (Jin et al. 2017d). The largest fraction of BrPAHs (54%) consists of ultrafine particles, but the reasons for this remain unclear. Further research on the formation of Halo-PAHs, particularly the influence of halogen atoms on the accumulation of Halo-PAHs into ultrafine particles, is thus necessary.

10 Conclusion

Halo-PAHs share similar characteristics to their parent PAHs. Gaseous Halo-PAHs are found at their highest levels during summer, while particulate Halo-PAHs are more common during winter. In addition, Halo-PAH profiles tend to differ by sampling location. Halo-PAHs mainly originate from anthropogenic activity, and some have specific sources that differ from those of their parent PAHs. In particular, 3-ClFlt and 1-ClPyr are produced from coal combustion, 8-ClFlt and 7-ClBaA are reported to be generated from traffic emissions, and 9-ClPhe, 9-ClAnt, 6-ClChr, 3-ClFlt, 1-ClPyr, 4,7-Br$_2$BaA, and 7,12-Br$_2$BaA can be considered indicators of industrial operations. Halo-PAHs also tend to accumulate as ultrafine particles with an aerodynamic diameter of less than 1.0 μm (about 70% of ClPAHs and 54% of BrPAHs). Even though several Halo-PAHs exhibit significantly higher toxicity than their parent PAHs, details of their formation mechanisms, physicochemical properties, and atmospheric behavior remain unclear. Further research and long-term monitoring of Halo-PAHs are thus essential to gain a better understanding of these carcinogenic compounds. In particular, the size distribution and formation mechanism of ClPAHs and BrPAHs in particulate matter should be concerned more. In addition, risk assessment of atmospheric Halo-PAHs is of vital importance for policymakers and residents.

Author contributions Quang Tran Vuong: Writing—original draft. Phan Quang Thang: Data curation. Takeshi Ohura: Supervision, Resources. Sung-Deuk Choi: Supervision, Project administration.

Compliance with ethical standards

References

Abdel-Shafy HI, Mansour MSM (2016) A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt J Pet 25:107–123

Armstrong BG, Gibbs G (2009) Exposure–response relationship between lung cancer and polycyclic aromatic hydrocarbons (PAHs). Occup Environ Med 66:740–746

Choi S-D, Baek S-Y, Chang Y-S (2007) Influence of a large steel complex on the spatial distribution of volatile polycyclic aromatic hydrocarbons (PAHs) determined by passive air sampling using membrane-enclosed copolymer (MECOP). Atmos Environ 41:6255–6264

Choi S-D, Ghim YS, Lee JY, Kim JY, Kim YP (2012a) Factors affecting the level and pattern of polycyclic aromatic hydrocarbons (PAHs) at Gosan, Korea during a dust period. J Hazard Mater 227–228:79–87

Choi S-D, Kwon H-O, Lee Y-S, Park E-J, Oh J-Y (2012b) Improving the spatial resolution of atmospheric polycyclic aromatic hydrocarbons using passive air samplers in a multi-industrial city. J Hazard Mater 241–242:252–258

Colmsjö A, Rannug A, Rannug U (1984) Some chloro derivatives of polynuclear aromatic hydrocarbons are potent mutagens in *Salmonella typhimurium*. Mutat Res Genet Toxicol 135:21–29

Dang J, He M (2016) Mechanisms and kinetic parameters for the gas-phase reactions of anthracene and pyrene with Cl atoms in the presence of NOx. RSC Adv 6:17345–17353

Fu J, Suuberg EM (2012) Thermochemical properties and phase behavior of halogenated polycyclic aromatic hydrocarbons. Environ Toxicol Chem 31:486–493

Fu PP, Yang SK (1982) Stereoselective metabolism of 6-bromobenzo[a]pyrene by rat liver microsomes: absolute configuration of trans-dihydrodiol metabolites. Biochem Biophys Res Commun 109:927–934

Fu PP, Tungeln LSV, Unruh LE, Ni Y-C, Chou MW (1991) Comparative regioselective and stereoselective metabolism of 7-chlorobenz[a]anthracene and 7-bromobenz[a]anthracene and 7-bromobenz[a]anthracene by mouse and rat liver microsomes. Carcinogenesis 12:371–378

Fu PP, Von Tungeln LS, Zhan D-J, Bucci T (1996) Potent tumorigenicity of 7-chlorobenz[α]anthracene and 7-bromobenz[α]anthracene in the neonatal B6C3F1 male mouse. Cancer Lett 101:37–42

Fu PP, Von Tungeln LS, Chiu LH, Own ZY (1999) Halogenated-polycyclic aromatic hydrocarbons: a class of genotoxic environmental pollutants. Environ Carcino Ecotox Rev C 17:71–109

Fujima S, Ohura T, Amagai T (2006) Simultaneous determination of gaseous and particulate chlorinated polycyclic aromatic hydrocarbons in emissions from the scorching of polyvinylidene chloride film. Chemosphere 65:1983–1989

Gustafsson E, Brunström B, Nilsson U (1994) Lethality and EROD-inducing potency of chlorinated chrysene in chick embryos. Chemosphere 29:2301–2308

Haglund P, Alsberg T, Bergman A, Jansson B (1987) Analysis of halogenated polycyclic aromatic hydrocarbons in urban

air, snow and automobile exhaust. Chemosphere 16:2441–2450

Hamilton DJ (1980) Gas chromatographic measurement of volatility of herbicide esters. J Chromatogr A 195:75–83

Harner T, Bidleman TF (1996) Measurements of octanol-air partition coefficients for polychlorinated biphenyls. J Chem Eng Data 41:895–899

Harner T, Bidleman TF (1998) Measurement of octanol-air partition coefficients for polycyclic aromatic hydrocarbons and polychlorinated naphthalenes. J Chem Eng Data 43:40–46

Harner T, Mackay D (1995) Measurement of octanol-air partition coefficients for chlorobenzenes, PCBs, and DDT. Environ Sci Technol 29:1599–1606

Harrison RM, Smith DJT, Luhana L (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. Environ Sci Technol 30:825–832

Helm PA, Bidleman TF, Li HH, Fellin P (2004) Seasonal and spatial variation of polychlorinated naphthalenes and non-/mono-ortho-substituted polychlorinated biphenyls in arctic air. Environ Sci Technol 38:5514–5521

Hinckley DA, Bidleman TF, Foreman WT, Tuschall JR (1990) Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatograhic retention data. J Chem Eng Data 35:232–237

Horii Y, Ok G, Ohura T, Kannan K (2008) Occurrence and profiles of chlorinated and brominated polycyclic aromatic hydrocarbons in waste incinerators. Environ Sci Technol 42:1904–1909

Ichikawa Y, Watanabe T, Horimoto Y, Ishii K, Naito S (2018) Measurements of 50 non-polar organic compounds including polycyclic aromatic hydrocarbons, n-alkanes and phthalate esters in fine particulate matter (PM2.5) in an industrial area of Chiba prefecture, Japan. Asian J Atmos Environ 12:274–288

Ishaq R, Näf C, Zebühr Y, Broman D, Järnberg U (2003) PCBs, PCNs, PCDD/Fs, PAHs and Cl-PAHs in air and water particulate samples-patterns and variations. Chemosphere 50:1131–1150

Jin R et al (2017a) Secondary copper smelters as sources of chlorinated and brominated polycyclic aromatic hydrocarbons. Environ Sci Technol 51:7945–7953

Jin R et al (2017b) Congener-specific determination of ultratrace levels of chlorinated and brominated polycyclic aromatic hydrocarbons in atmosphere and industrial stack gas by isotopic dilution gas chromatography/high resolution mass spectrometry method. J Chromatogr A 1509:114–122

Jin R et al (2017c) Profiles, sources and potential exposures of parent, chlorinated and brominated polycyclic aromatic hydrocarbons in haze associated atmosphere. Sci Total Environ 593:390–398

Jin R, Zheng M, Yang H, Yang L, Wu X, Xu Y, Liu G (2017d) Gas–particle phase partitioning and particle size distribution of chlorinated and brominated polycyclic aromatic hydrocarbons in haze. Environ Pollut 231:1601–1608

Jin R, Zheng M, Lammel G, Bandowe BAM, Liu G (2020a) Chlorinated and brominated polycyclic aromatic hydrocarbons: sources, formation mechanisms, and occurrence in the environment. Prog Energy Combust Sci 76:100803

Jin R et al (2020b) New classes of organic pollutants in the remote continental environment—chlorinated and brominated polycyclic aromatic hydrocarbons on the Tibetan Plateau. Environ Int 137:105574

Kakimoto K, Nagayoshi H, Konishi Y, Kajimura K, Ohura T, Hayakawa K, Toriba A (2014) Atmospheric chlorinated polycyclic aromatic hydrocarbons in East Asia. Chemosphere 111:40–46

Kakimoto K et al (2017) Size distribution of chlorinated polycyclic aromatic hydrocarbons in atmospheric particles. Arch Environ Contam Toxicol 72:58–64

Kamiya Y, Ikemori F, Ohura T (2015) Optimisation of pretreatment and ionisation for GC/MS analysis for the determination of chlorinated PAHs in atmospheric particulate samples AU. Int J Environ Anal Chem 95:1157–1168

Kamiya Y, Iijima A, Ikemori F, Okuda T, Ohura T (2016) Source apportionment of chlorinated polycyclic aromatic hydrocarbons associated with ambient particles in a Japanese megacity. Sci Rep 6:38358

Kitazawa A, Amagai T, Ohura T (2006) Temporal trends and relationships of particulate chlorinated polycyclic aromatic hydrocarbons and their parent compounds in urban air. Environ Sci Technol 40:4592–4598

Lei YD, Chankalal R, Chan A, Wania F (2002) Supercooled liquid vapor pressures of the polycyclic aromatic hydrocarbons. J Chem Eng Data 47:801–806

Liu G, Cai Z, Zheng M (2014) Sources of unintentionally produced polychlorinated naphthalenes. Chemosphere 94:1–12

Löfroth G, Nilsson L, Agurell E, Sugiyama T (1985) Salmonella/microsome mutagenicity of monochloro derivatives of some di-, tri- and tetracyclic aromatic hydrocarbons. Mutat Res Genet Toxicol 155:91–94

Lv Y et al (2016) Size distributions of polycyclic aromatic hydrocarbons in urban atmosphere: sorption mechanism and source contributions to respiratory deposition. Atmos Chem Phys 16:2971–2983

Ma J, Chen Z, Wu M, Feng J, Horii Y, Ohura T, Kannan K (2013) Airborne PM2.5/PM10-associated chlorinated polycyclic aromatic hydrocarbons and their parent compounds in a suburban area in Shanghai. China. Environ Sci Technol 47:7615–7623

Menzie CA, Potocki BB, Santodonato J (1992) Exposure to carcinogenic PAHs in the environment. Environ Sci Technol 26:1278–1284

Miyake Y, Tokumura M, Wang Q, Amagai T, Horii Y, Kannan K (2017) Mechanism of formation of chlorinated pyrene during combustion of polyvinyl chloride. Environ Sci Technol 51:14100–14106

Nguyen TNT, Jung K-S, Son JM, Kwon H-O, Choi S-D (2018) Seasonal variation, phase distribution, and source identification of atmospheric polycyclic aromatic hydrocarbons at a semi-rural site in Ulsan, South Korea. Environ Pollut 236:529–539

Ni H-G, Zeng EY (2012) Environmental and human exposure to soil chlorinated and brominated polycyclic aromatic hydrocarbons in an urbanized region. Environ Toxicol Chem 31:1494–1500

Nilsson UL, Colmsjö AL (1990) Formation of chlorinated polycyclic aromatic hydrocarbons in different chlorination reactions. Chemosphere 21:939–951

Nilsson UL, Colmsjö AL (1991) Retention characteristics of chlorinated polycyclic aromatic hydrocarbons in normal phase HPLC. I. Chloro-added PAHs. Chromatographia 32:334–340

Nilsson UL, Colmsjö AL (1992) Retention characteristics of chlorinated polycyclic aromatic hydrocarbons in normal phase HPLC. II. Chloro-substituted PAHs. Chromatographia 34:115–120

Nilsson UL, Oestman CE (1993) Chlorinated polycyclic aromatic hydrocarbons: method of analysis and their occurrence in urban air. Environ Sci Technol 27:1826–1831

Odabasi M, Cetin E, Sofuoglu A (2006) Determination of octanol-air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: application to gas–particle partitioning in an urban atmosphere. Atmos Environ 40:6615–6625

Ohura T (2007) Environmental behavior, sources, and effects of chlorinated polycyclic aromatic hydrocarbons. Sci World J 7:372–380

Ohura T, Miwa M (2016) Photochlorination of polycyclic aromatic hydrocarbons in acidic brine solution. Bull Environ Contam Toxicol 96:524–529

Ohura T, Kitazawa A, Amagai T, Makino M (2005) Occurrence, profiles, and photostabilities of chlorinated polycyclic aromatic hydrocarbons associated with particulates in urban air. Environ Sci Technol 39:85–91

Ohura T, Morita M, Makino M, Amagai T, Shimoi K (2007) Aryl hydrocarbon receptor-mediated effects of chlorinated polycyclic aromatic hydrocarbons. Chem Res Toxicol 20:1237–1241

Ohura T, Amagai T, Makino M (2008a) Behavior and prediction of photochemical degradation of chlorinated polycyclic aromatic hydrocarbons in cyclohexane. Chemosphere 70:2110–2117

Ohura T, Fujima S, Amagai T, Shinomiya M (2008b) Chlorinated polycyclic aromatic hydrocarbons in the atmosphere: seasonal levels, gas-particle partitioning, and origin. Environ Sci Technol 42:3296–3302

Ohura T, Sawada K, Amagai T, Shinomiya M (2009) Discovery of novel halogenated polycyclic aromatic hydrocarbons in urban particulate matters: occurrence, photostability, and AhR activity. Environ Sci Technol 43:2269–2275

Ohura T, Kamiya Y, Ikemori F, Imanaka T, Ando M (2012) Analysis of halogenated polycyclic aromatic hydrocarbons in the air. In: Badilla GL, Valdez B, Schorr M (eds) Air quality—new perspective. IntechOpen, Rijeka

Ohura T, Horii Y, Kojima M, Kamiya Y (2013) Diurnal variability of chlorinated polycyclic aromatic hydrocarbons in urban air, Japan. Atmos Environ 81:84–91

Ohura T, Kamiya Y, Ikemori F (2016) Local and seasonal variations in concentrations of chlorinated polycyclic aromatic hydrocarbons associated with particles in a Japanese megacity. J Hazard Mater 312:254–261

Ohura T, Horii Y, Yamashita N (2018) Spatial distribution and exposure risks of ambient chlorinated polycyclic aromatic hydrocarbons in Tokyo Bay area and network approach to source impacts. Environ Pollut 232:367–374

Ohura T, Suhara T, Kamiya Y, Ikemori F, Kageyama S, Nakajima D (2019) Distributions and multiple sources of chlorinated polycyclic aromatic hydrocarbons in the air over Japan. Sci Total Environ 649:364–371

Oishi R, Imai Y, Ikemori F, Ohura T (2019) Traffic source impacts on chlorinated polycyclic aromatic hydrocarbons in PM2.5 by short-range transport. Atmos Environ 216:116944

Ravindra K, Sokhi R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos Environ 42:2895–2921

Sonnefeld WJ, Zoller WH, May WE (1983) Dynamic coupled-column liquid-chromatographic determination of ambient-temperature vapor pressures of polynuclear aromatic hydrocarbons. Anal Chem 55:275–280

Spencer WF, Cliath MM (1983) Measurement of pesticide vapor pressures, vol 85. Springer, New York

Sun J-L, Zeng H, Ni H-G (2013) Halogenated polycyclic aromatic hydrocarbons in the environment. Chemosphere 90:1751–1759

Tang J et al (2020) The pollution profiles and human exposure risks of chlorinated and brominated PAHs in indoor dusts from e-waste dismantling workshops: comparison of GC–MS, GC–MS/MS and GC × GC–MS/MS determination methods. J Hazard Mater 394:122573

Vuong QT, Kim S-J, Nguyen TNT, Thang PQ, Lee S-J, Ohura T, Choi S-D (2020a) Passive air sampling of halogenated polycyclic aromatic hydrocarbons in the largest industrial city in Korea: spatial distributions and source identification. J Hazard Mater 382:121238

Vuong QT, Thang PQ, Ohura T, Choi S-D (2020b) Determining sub-cooled liquid vapor pressures and octanol-air partition coefficients for chlorinated and brominated polycyclic aromatic hydrocarbons based on gas chromatographic retention times: application for gas/particle partitioning in air. Atmos Environ 229:117461

Vuong QT, Thang PQ, Nguyen TNT, Ohura T, Choi S-D (2020c) Seasonal variation and gas/particle partitioning of atmospheric halogenated polycyclic aromatic hydrocarbons and the effects of meteorological conditions in Ulsan, South Korea. Environ Pollut 263:114592

Wang D, Piao M, Chu S, Xu X (2001) Chlorinated polycyclic aromatic hydrocarbons from polyvinylchloride combustion. Bull Environ Contam Toxicol 66:326–333

Wania F, Lei YD, Harner T (2002) Estimating octanol-air partition coefficients of nonpolar semivolatile organic compounds from gas chromatographic retention times. Anal Chem 74:3476–3483

Xia Q, Yi P, Zhan D-J, Von Tungeln LS, Hart RW, Heflich RH, Fu PP (1998) Liver tumors induced in B6C3F1 mice by 7-chlorobenz[a]anthracene and 7-bromobenz[a]anthracene contain K-ras protooncogene mutations. Cancer Lett 123:21–25

Yoshino H, Urano K (1997) Formation of chlorinated PAHs in exhaust gas from municipal waste incinerators, and their mutagenic activities. Toxicol Environ Chem 63:233–246

Zhang L et al (2019) Characteristics and health risks of particulate polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons at urban and suburban elementary schools in Shanghai, China. Asian J Atmos Environ 13:266–275