



# Identification of specific halogenated polycyclic aromatic hydrocarbons in surface soils of petrochemical, flame retardant, and electronic waste dismantling industrial parks

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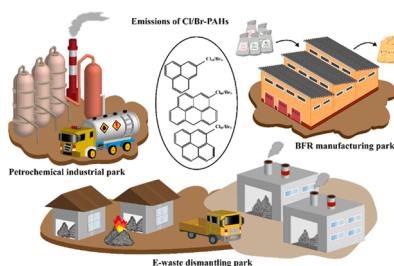
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## HIGHLIGHTS

- There were varied Cl/Br-PAH pollution found in the three typical industrial parks.
- Cl/Br-PAH emission fingerprints in the industries were established.
- Br-PAHs in the BFR manufacturing park were much higher than in the other two parks.
- The homologue distribution in inside and outside the three parks were corresponding.
- Specific Cl/Br-PAHs of the three typical industrial parks were identified.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Halogenated polycyclic aromatic hydrocarbons (Cl/Br-PAHs) have received tremendous attention due to their high toxicity. To identify the emission pattern of Cl/Br-PAHs from various industrial productions, understand the formation mechanisms and the influence on the surroundings, this study investigated the surface soils of three typical industrial parks. Generally, traces of Cl-PAHs were much lower than Br-PAHs. The mean Cl-PAH concentrations followed the trend of petrochemical industrial park (3.12 ng/g), brominated flame retardant (BFR) manufacturing park (1.48 ng/g), and electronic waste dismantling park (0.26 ng/g). However, the BFR manufacturing park had the highest mean Br-PAH concentration (21.6 ng/g), significantly higher than the other two parks. Generally, higher levels of the chemicals were found in the parks than in their surroundings, except for the electronic waste dismantling park. The massive addition of chlorine additives in crude oil and its by-products, plus the enormous quantity of brominated brines used in BFR productions, favor Cl/Br-PAH formation. Analyzing the homolog compositions of Cl/Br-PAHs suggested that 3- or 4-ring Cl/Br-PAHs were typically come from the petrochemical industrial park and electronic waste dismantling park. Contrarily, 4- or 5-ring Cl/

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Br-PAHs were predominantly come from the BFR manufacturing activity. This study provides fingerprints to trace the Cl/Br-PAH emissions during industrial production and analyzes the formation mechanism.

## 1. Introduction

Halogenated polycyclic aromatic hydrocarbons (Cl/Br-PAHs) are PAH derivatives whose one or more hydrogen atoms have been substituted by halogens (Jin et al., 2020a). According to the number of benzene rings and Cl or Br ions, the type and position of the halogen substitutes, various Cl/Br-PAH homologues can be formed (Jin et al., 2020a; Vuong et al., 2020a). Chlorinated and brominated PAHs (Cl-PAHs and Br-PAHs) were more discussed because of their high toxicity (Jin et al., 2020a; Vuong et al., 2020a). For example, Cl/Br-PAHs can increase the risk of cancer mediated by AhR activation compared to their corresponding parent PAHs (Horii et al., 2009; Ohura et al., 2007). The Cl/Br-PAHs reportedly found in secondary copper smelters and cement kilns presented a high toxic equivalent quantity, higher than polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) (Jin et al., 2017a, 2018). The Cl/Br-PAHs can be transported long distances through the atmosphere to places with few or no industrial activities, such as the Tibetan Plateau (Czub et al., 2008; Fernandez et al., 2021; Jin et al., 2020b). Besides, the chemicals can accumulate in organisms, causing chronic defects (Jin et al., 2020b; Myers et al., 2014; Wickrama-Arachchige et al., 2020).

These halogenated chemicals mainly come from the combustion process of industrial activities, such as metallurgical processes, cement production, waste combustion, electronic waste (E-waste) dismantling and automobile emissions (Cai et al., 2018; Hatanaka et al., 2005; Vuong et al., 2020a; Wang et al., 2012). Among them, metal smelting and cement production were considered as the main emission sources of Cl/Br-PAHs because of their high emission concentration and large output (Conesa et al., 2011; Jiang et al., 2015; Wu et al., 2019). As the world's largest producer of E-waste, the emission of Cl/Br-PAHs in e-waste dismantling has aroused great concern (Ling et al., 2022; Patil and Ramakrishna, 2020; Yu et al., 2006). Due to imperfect management systems and crude disassembly techniques, Cl/Br-PAH pollution from E-waste dismantling has become severe (Liu et al., 2020a; Tang et al., 2020; Yu et al., 2006). Although many industries contain industrial heat sources and may emit Cl/Br-PAHs, the relevant data are still limited, and the formation mechanism of Cl/Br-PAHs remains unclear.

Thermal and photochemical reactions have been reported as two main mechanisms for Cl/Br-PAHs generation (Jin et al., 2020a; Vuong et al., 2020a). In addition to being formed during industrial combustion, Cl/Br-PAHs could be formed in the atmosphere through photochemical reaction of discharged PAH and halogen elements (Jin et al., 2017b; Ohura and Miwa, 2016). Therefore, various chlorine or bromine sources and the parent PAHs or aromatic precursors could contribute to Cl/Br-PAH formation (Horii et al., 2008; Jin et al., 2018; Liu et al., 2020b; Ohura, 2007; Wang et al., 2003). Particles are the essential carriers of industrial Cl/Br-PAHs and could belong to the direct emission source of industry (Jin et al., 2020a; Vuong et al., 2020a). Owing to the different sizes, the particles may undergo different atmospheric transport or deposition processes and be transported to the surface soil by wet or dry deposition (Ge et al., 2020; Jin et al., 2017b). Therefore, the surface soil can represent the pollution degree of an area. However, research on industrial Cl/Br-PAH contamination of surrounding soils has not been adequately studied.

Therefore, to explore the emission features of Cl/Br-PAHs in the production activities of various industrial chains, understand the potential formation mechanisms, and establish the influence of the chemicals on the surrounding areas, this study investigated three typical industrial parks, viz. a petrochemical industrial park, a brominated flame retardant (BFR) manufacturing park, and an E-waste dismantling park. These three parks represent three industrial chains from upstream

to downstream. This study analyzed 14 Cl-PAHs and 17 Br-PAHs in the surface soil samples from the sampling locations. The fingerprints of Cl/Br-PAHs from various industrial productions can provide helpful information to trace Cl/Br-PAH emissions, and understand the formation mechanisms and the influence on the surrounding environments.

## 2. Materials and methods

### 2.1. Reagents and materials

The chemicals used were supplied by AccuStandard, Inc. (CT, USA). They included deuterated PAHs as the surrogate standard, fluorinated PAHs as the internal standard, 14 Cl-PAHs, and 17 Br-PAHs (detailed information is available in Table S1). The organic solvents: ethyl acetate, dichloromethane, n-hexane, and isooctane were all high-performance liquid chromatography (HPLC) grade, and they were purchased from CNW Technologies GmbH (Germany), along with the solid phase extraction (SPE) cartridges. The copper sheets used for desulfurization were highly pure and activated with dilute hydrochloric acid.

### 2.2. Sample collection and pretreatment

Soil samples were collected from Gansu province, Shandong province, and Guangdong province. In May 2021, the soils of a petrochemical industrial park in Gansu province were sampled with a 500 m × 500 m grid (n = 15). The surface soil (n = 26) within 5 km outside the park was collected with a 3 km × 3 km grid. In December 2020, the soil samples of the production area (n = 15) and office buildings (n = 1) were sampled at a BFR manufacturing park in Shandong province. Also, the surface soils were collected (n = 24) within 3 km outside the park, with a grid of 1 km × 1 km. In November 2018, the soils of an E-waste dismantling park were obtained (n = 24) in Guangdong province. Surface soil samples (n = 83) were collected in a 9 km × 9 km area surrounding the park. Details of the sampling sites are listed in Table S2-S4. Each sample was an aggregate of five sub-samples, collected in aluminum foil and placed in airtight bags before being transported to the laboratory. The soil samples were lyophilized, ground, and sieved to facilitate subsequent processing. The final powders were preserved at −20 °C until use.

Generally, 0.5 g of each soil sample was extracted with a 10 mL solvent mixture of ethyl acetate, dichloromethane, and n-hexane in 1:2:2 (v/v) after spiking with surrogate standards of naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, and perylene-d<sub>12</sub>. Ultrasonic extraction was performed for 10 min before centrifuging at 2500 rpm for 10 min after vortex-mixed for 1 min. The extraction was repeated thrice.

Hydrochloric acid-activated copper sheets were added to the extracted organic phase to remove sulfur. The extract was concentrated by rotary evaporation and loaded on an SPE cartridge containing 1 g Florisil. Before use, it was activated sequentially with ethyl acetate, dichloromethane, and n-hexane.

The target Cl-PAHs and Br-PAHs were eluted with a 10 mL solvent mixture of 1:1 ethyl acetate and dichloromethane (v/v). Finally, the eluate was concentrated and reconstructed with 50 μL isooctane after internal standard fluorinated PAHs were spiked and stored at −20 °C until further concentration determination.

### 2.3. Instrumental analysis

The target Cl-PAHs and Br-PAHs were detected by gas chromatography coupled with triple quadrupole mass spectrometry (GC-MS-TQ8040, Shimadzu, Japan) on electron impact ion source and separated

by a DB-5 MS capillary column (30 m × 0.25 mm × 0.25 μm). The mass spectrometry acquisition mode was multiple reaction monitoring. The oven operation procedure was as follows: onset temperature was 80 °C (held for 0.5 min), raised to 280 °C at 5 °C/min, then to 300 °C at 15 °C/min, and finally increased to 315 °C at 20 °C/min, before holding for 0.5 min. The injection volume and temperature were 1 μL and 280 °C, respectively. The high-purity He gas flow rate was consistently 1 mL/min.

## 2.4. Quality assurance and quality control

We added one procedural blank and one matrix spiked sample to every dozen samples to ensure data accuracy. The linear regression coefficients ( $R^2$ ) of Cl-PAHs and Br-PAHs were > 0.99, and their recoveries were 87.1–119% and 80.4–107%, respectively. Details of the limit of quantitation (LOQ), the limit of detection (LOD), and the Cl/Br-PAH abbreviations are described in Table S1.

## 2.5. Statistical analysis

The data were analyzed with SPSS 13 software (IBM, USA) and the data below LOD were considered as not detected. Non-parametric statistical analyses were performed because of the non-normal distribution of the data. Also, the Mann-Whitney U test calculated the concentrations of  $\sum_{14}$ Cl-PAHs and  $\sum_{17}$ Br-PAHs. In addition, Spearman's correlation explored the correlations among variables at  $p < 0.05$  significant level. Finally, contour plots and thematic maps were obtained using Surfer (Golden Software, USA), while other figures were drawn with Origin (Origin Lab, USA).

## 3. Results and discussion

### 3.1. Occurrence of Cl/Br-PAHs

The detection frequencies of target Cl/Br-PAHs in the study area are shown in Table S5–S7. Most of the detection frequencies of Cl/Br-PAHs were lower in the petrochemical industrial park than its surrounding area, especially for Cl-PAHs. As shown in Fig. S1, the detection frequencies of high ring Cl/Br-PAHs in the petrochemical park were higher, while there was a similar trend of Cl-PAHs inside and outside the park.

The predominant species and the highest overall detection frequencies of Br-PAHs were detected in the BFR manufacturing park, which is a large BFR production in China. The detection of Cl-PAHs in the park was concentrated in the high ring compounds, with the

detection frequencies of low ring Cl-PAHs were < 50.0%. Therefore, Br-PAHs were significantly concentrated both inside and outside the park.

By comparison, the detection frequencies of Cl/Br-PAHs inside and outside the E-waste dismantling park were comparatively lower to other sites. The detection frequencies of 1,5-Cl<sub>2</sub>-Ant and 9,10-Cl<sub>2</sub>-Ant reached 71.1% and 72.3% outside the park, respectively, but almost all the Cl-PAHs were < 20.0% in the park. The Br-PAHs showed higher detection frequencies than Cl-PAHs in the park, but the detection frequencies surrounding the park were generally lower.

### 3.2. Concentrations of Cl/Br-PAHs

The  $\sum_{14}$ Cl-PAHs,  $\sum_{17}$ Br-PAHs, and total concentrations are listed in Table 1. The median concentrations of Cl/Br-PAHs inside and outside the petrochemical industrial park reached 7.39 and 6.43 ng/g, respectively. These values are obviously lower than that found in the BFR manufacturing park (19.7 ng/g) but not in its surrounding area (3.16 ng/g). Unexpectedly, the concentrations were higher than those inside and outside the E-waste dismantling park. Comparatively, the present results were lower than those from previous studies, wherein samples were collected from workshops or directly from various emission sources (Table 2). Except for the E-waste dismantling park, Cl/Br-PAHs pollution levels were higher in the sampling areas than in the surroundings. The lower median concentrations of the chemicals in the E-waste dismantling park than outside the park might be because it is a relatively new park, built in 2015, where the topsoil may have been replaced (Wang and Xu, 2015; Zhang et al., 2017). However, the surrounding areas have been polluted for an extended period because of the unchecked early E-waste dismantling activities (Ling et al., 2022; Xu et al., 2016; Yu et al., 2006; Zheng et al., 2008). Meanwhile, sporadic private dismantling activities still exist in the park's residential areas. Therefore, Cl/Br-PAH concentrations in the E-waste dismantling park were lower than those outside the park.

Regarding Cl-PAHs, the  $\sum_{14}$ Cl-PAH concentrations in the BFR manufacturing park were noticeably higher than those outside the park ( $p < 0.05$ ). On the contrary, the petrochemical industrial park and the E-waste dismantling park had higher concentrations in the surroundings than within the park (Fig. 1A and Table 1). These conditions were attributed to the high concentrations and detection frequencies of Cl-PAHs in their surrounding area (Table 1 and Fig. S1A). The more abundant detection than in the park indicated that there were other emission sources outside the park. Similar situation appeared in the study by Tang et al. (2020), who detected equal  $\sum_{16}$ Cl-PAH concentrations in both E-waste dismantling workshop and residential area

**Table 1**  
Concentrations (ng/g•dw) of Cl-PAHs and Br-PAHs in soil samples.

Compounds	Industrial parks			Surrounding areas		
	PIP	BFRP	EWDP	PIS	BFRS	EWDS
$\sum_{14}$ Cl-PAHs						
Mean	3.12 ± 5.33	1.48 ± 1.12	0.26 ± 0.75	3.23 ± 5.02	0.48 ± 0.76	2.57 ± 4.98
Median	0.69	1.05	0.05	1.48	0.09	0.88
Range	n.d.–20.5	n.d.–3.87	n.d.–3.52	0.19–25.8	n.d.–3.18	n.d.–26.7
DF	86.7%	100%	70.8%	100%	70.8%	89.2%
$\sum_{17}$ Br-PAHs						
Mean	7.45 ± 9.03	21.6 ± 17.8	6.68 ± 19.9	6.27 ± 9.31	5.60 ± 6.18	2.99 ± 7.00
Median	5.64	17.61	1.09	4.31	3.14	0.61
Range	n.d.–35.9	0.52–72.4	0.25–99.1	0.31–49.1	0.11–23.8	0.01–53.0
DF	93.3%	100%	100%	100%	100%	100%
Total						
Mean	10.6 ± 11.6	23.0 ± 18.5	6.94 ± 20.1	9.49 ± 11.3	6.08 ± 6.77	5.56 ± 9.31
Median	7.39	19.7	1.13	6.43	3.16	1.97
Range	n.d.–39.4	0.52–75.3	0.30–99.3	1.26–57.1	0.11–27.0	0.08–56.7
DF	93.3%	100%	100%	100%	100%	100%

DF: detection frequency; PIP: petrochemical industrial park; BFRP: brominated flame retardant manufacturing park; EWDP: electronic waste dismantling park; PIS: the surrounding area of the petrochemical industrial park; BFRS: the surrounding area of brominated flame retardant manufacturing park; EWDS: the surrounding area of electronic waste dismantling park.

**Table 2**

Mean concentrations (ng/g•dw) of Cl-PAHs and Br-PAHs in previous studies.

Sampling sites	Matrices	Compounds	Concentrations	References
Electronic waste dismantling workshop	Indoor dust	$\sum_{16}\text{Cl-PAHs}$	137	(Tang et al., 2020)
		$\sum_{18}\text{Br-PAHs}$	60.0	
Raw materials crushing workshop		$\sum_{16}\text{Cl-PAHs}$	35.1	
		$\sum_{18}\text{Br-PAHs}$	399	
Secondary copper furnace workshop		$\sum_{16}\text{Cl-PAHs}$	53.8	
		$\sum_{18}\text{Br-PAHs}$	152	
Residential area		$\sum_{16}\text{Cl-PAHs}$	137	
		$\sum_{18}\text{Br-PAHs}$	25.7	
Industrial area	Soil	$\sum_3\text{Cl-PAHs}$	0.22	(Ni and Zeng, 2012)
		$\sum_6\text{Br-PAHs}$	3.90	
Traffic area		$\sum_3\text{Cl-PAHs}$	2.16	
		$\sum_6\text{Br-PAHs}$	14.5	
Agricultural area		$\sum_3\text{Cl-PAHs}$	n.d.	
		$\sum_6\text{Br-PAHs}$	0.94	
E-waste dismantling park		$\sum_{20}\text{Cl-PAHs}$	26.8	(Ma et al., 2009)
		$\sum_{20}\text{Cl-PAHs}$	88.0	
Chemical industrial complex park				
Garbage power plant	Fly ash	$\sum_3\text{Cl-PAHs}$	5.83	
		$\sum_6\text{Br-PAHs}$	17.7	(Ni and Zeng, 2012)

(Table 2). Comparatively, the present Cl-PAH concentrations were lower than those found in the surface soils of the chemical industrial complex park in Shanghai and the E-waste dismantling park in Taizhou, wherein more concentrated 20 Cl-PAHs were detected (Table 2). However, the Cl-PAHs in this study were more concentrated than those in the soils of industrial and traffic areas found in Shenzhen (Table 2). Overall, petrochemical, BFR manufacturing, and E-waste dismantling industries can produce or release Cl-PAHs into the environment.

For Br-PAHs, the  $\sum_{17}\text{Br-PAH}$  concentrations were generally higher than those of  $\sum_{14}\text{Cl-PAHs}$ . For example, the  $\sum_{17}\text{Br-PAH}$  concentrations in the petrochemical industrial park were almost twice that of  $\sum_{14}\text{Cl-PAHs}$ . Similar results have been widely reported elsewhere (Table 2). Moreover,  $\sum_{17}\text{Br-PAHs}$  were more concentrated in the BFR manufacturing park among the sampling sites (Fig. 1B). Besides, they varied substantially from 0.52 to 72.4 ng/g within the BFR manufacturing park and were remarkably higher than outside the park ( $p < 0.05$ ). It is expected because excess brominated brines are used during the production process of BFR manufacturing, which provides a suitable condition for generating Br-PAHs. Unlike Cl-PAHs, a higher Br-PAH concentration was detected in the E-waste dismantling park than outside the park. This occurrence may be attributed to the wide BFR applications in electronic materials (Liu et al., 2020a; Tang et al., 2020), with plenty of bromine sources. Therefore, the concentrations and composition patterns of Cl/Br-PAHs during industrial activity are hugely influenced by industrial processes, raw materials, and fuels.

### 3.3. Spatial distribution of Cl/Br-PAHs

To trace the Cl/Br-PAHs sources and clarify their environmental impact, this study analyzed their spatial distribution trends (Fig. 2). High concentrations of Cl-PAHs and Br-PAHs were measured in the petrochemical industrial park (Fig. 2A and B). The petrochemical industrial park was divided into four functional zones and the high concentration points were found in the ethylene production zones, especially at site N11, where the concentration of Cl-PAHs was higher than that of Br-PAHs (Fig. S2A). The petrochemical industrial park, representing the heavy industry park, has high-temperature furnaces for

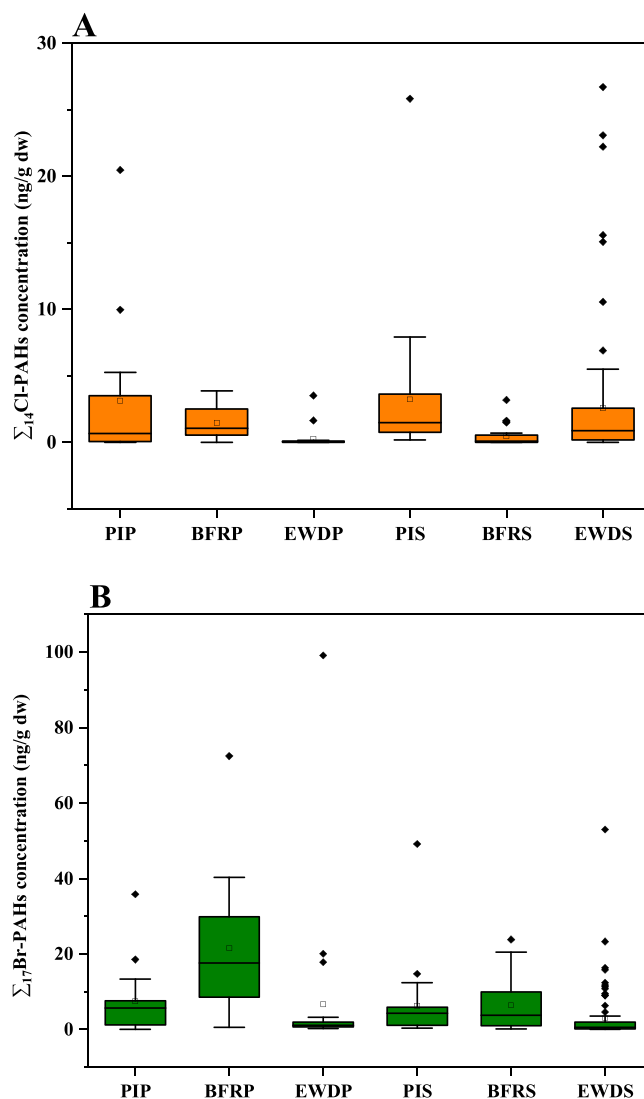
**Fig. 1.**

Fig. 1. The concentrations of  $\sum_{14}\text{Cl-PAHs}$  (A) and  $\sum_{17}\text{Br-PAHs}$  (B) in soil samples from three industrial parks and their surrounding areas. Each box's upper and lower limits denote the 25.0% and 75.0% quartiles. The open square symbols represent the mean, while the horizontal lines within the boxes show the median value. The whiskers extend to 1.5 times of the interquartile range.

catalytic cracking in the functional zones. The optimum production temperature of ethylene was considered at 500–950 °C (Ranjan et al., 2012; Wen et al., 2020), and the concentrations of some Cl/Br-PAHs and their parent PAHs could increase with combustion temperature increasing in this range (Miyake et al., 2017; Wang et al., 2003). The gaseous hydrocarbon intermediates released by incomplete combustion could form stable aromatic hydrocarbons at high temperature through cyclization reaction, which may be the formation of Cl/Br-PAHs in combustion (Altarawneh et al., 2022; Wang et al., 2003). Therefore, the furnaces in the zones also provide the appropriate temperature and conditions for the formation of Cl/Br-PAHs while reaching the high temperature required for production (Altarawneh et al., 2019; Miyake et al., 2017). Unexpectedly, high concentrations of Cl-PAHs and Br-PAHs were also detected in the residential areas respectively, indicating that there were other emission sources of Cl/Br-PAHs in the area.

The spatial distribution of Cl/Br-PAHs in the BFR manufacturing park was similar to that of the petrochemical industrial park with a high



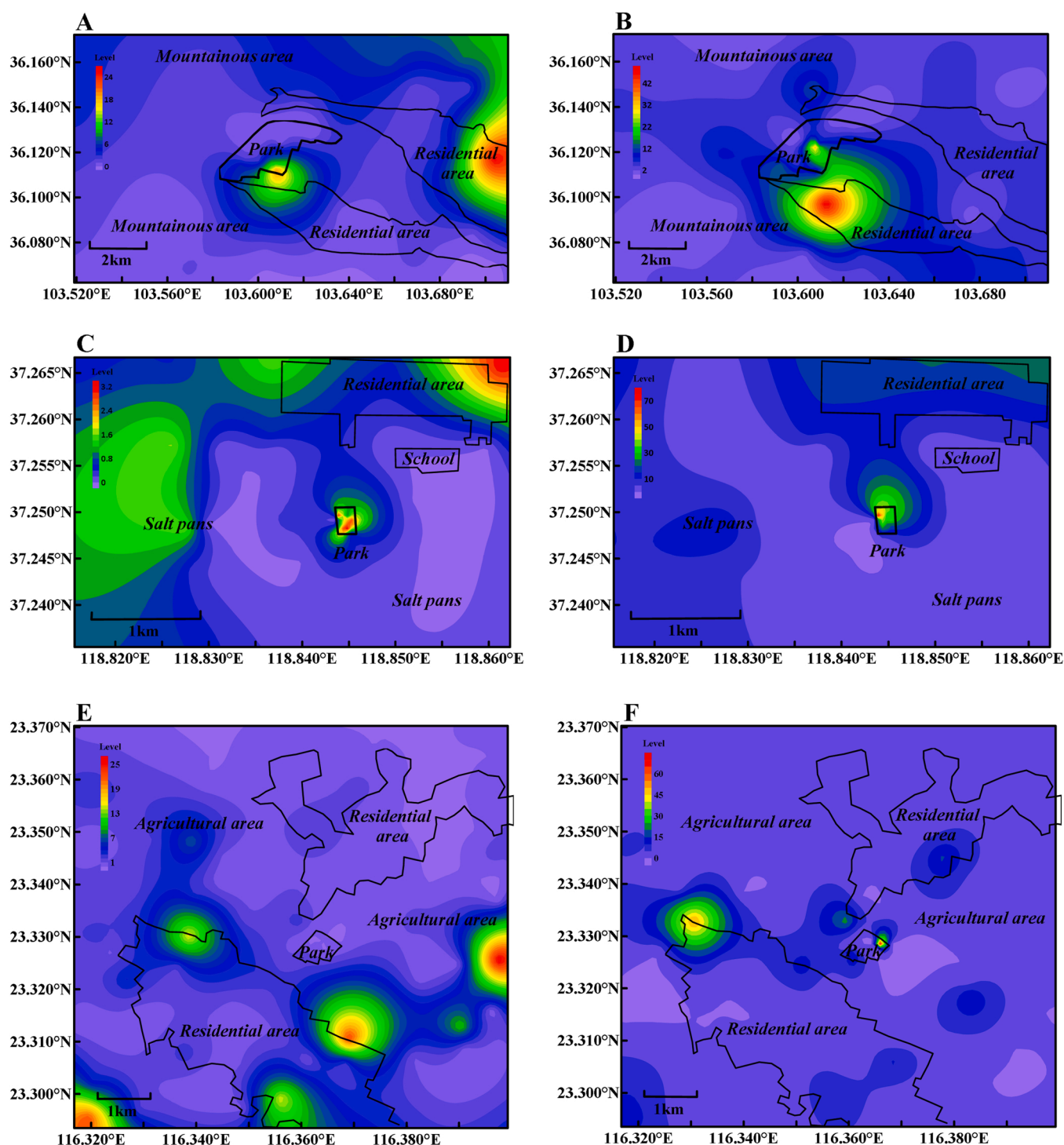


Fig. 2. The spatial distributions of Cl-PAHs and Br-PAHs in the parks and their surrounding areas (A and B: petrochemical industrial park; C and D: brominated flame retardant manufacturing park; E and F: electronic waste dismantling park).

concentration point detected inside the park and gradually northward spread (Fig. 2C and D). However, the Br-PAH concentrations were higher than those at the petrochemical industrial park. Moreover, a school located 1 km away from the park would be affected by such high Br-PAH concentrations. Unlike the petrochemical industrial park, there were no abundant high-temperature boilers in the BFR manufacturing park, mostly obtained from corresponding chemicals through oxidation-reduction reaction. The high concentration points were distributed in the production areas, which could contribute to the volatilization of bromine and chlorine during production, thereby providing the

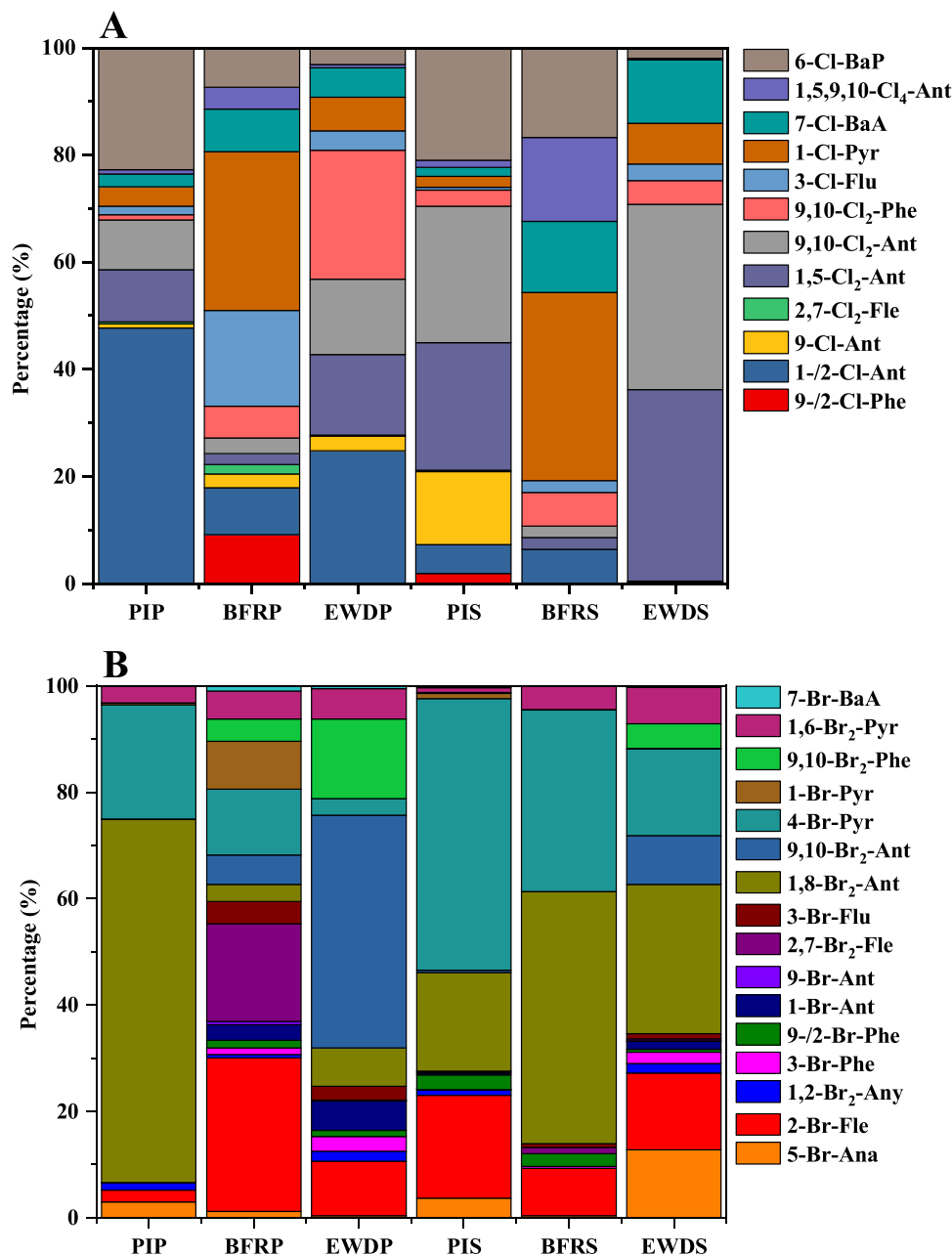
necessary conditions for Cl/Br-PAH formation (Fig. S2B).

The spatial distribution of the E-waste dismantling park was different from the other parks. Therein, the high concentration points were almost detected in its surrounding area (Fig. 2E and F). The main processes in the park were dismantling and crushing aided by some small electrical appliances. However, the pyrometallurgical area in the eastern of the park recovered precious metals from printed circuit boards through high temperatures and detected an extremely high concentration of Br-PAHs (Fig. 2F and S2C). This result may be attributed to the chemical transformation and degradation of BFR in the printed circuit board,

which were the chief synthesis route of Br-PAHs in E-waste dismantling (Altarawneh et al., 2019, 2022; Liu et al., 2020a; Tang et al., 2020). As reported in the literature, Br atoms formed Br-PAHs through electrophilic bromination or hydrogen abstraction acetylene addition mechanism under high temperatures (Altarawneh et al., 2019, 2022; Jin et al., 2020a). The copper in the waste printed circuit boards could not only play a catalytic role but also transfer the inorganic halides to the aromatic ring to form Br-PAHs (Altarawneh et al., 2009, 2022; Wang et al., 2019). Therefore, the pyrometallurgical treatment of E-waste provided the raw materials and conditions for the formation of Br-PAHs.

Before the park was established, the main E-waste dismantling was done in some family workshops, adopting crude manual dismantling methods and open-air waste burning with no recycling value (Wang and Xu, 2015; Yu et al., 2006). Therefore, the detected concentrations in the

current study may be attributed to previous residual emissions (not fully degraded) in the soil, and the few household disassembly workshops still operational. According to the surveys, gasoline and briquettes were used more in the southern part of the park (Ling et al., 2022; Xu et al., 2016). The present study has the corresponding results that higher Cl/Br-PAHs concentration points were mainly distributed in the southern part. Published studies have also shown the same trend. For example, Tang et al. (2020) quantitated  $\sum_{16}\text{Cl-PAHs}$  in a residential area where was as high as in the E-waste dismantling workshops. The same year, Ge et al. (2020) detected high concentrations of polybrominated diphenyl ethers and dechlorane plus in the E-waste dismantling park and its surroundings, originating from the dismantling, crushing, and incineration of printed circuit boards and wires (Miyake et al., 2017; Paine et al., 2014; Zheng et al., 2008).



**Fig. 3.**

Fig. 3. The composition profile of Cl-PAHs (A) and Br-PAHs (B) in soil samples from three industrial parks and their surrounding areas.

### 3.4. Characteristics of Cl/Br-PAHs

The composition characteristics of Cl/Br-PAHs are indispensable for the establishment of fingerprints. The fingerprints can be used to track the emission sources, transportation and transformation routes of chemicals, which is very important for the control of environmental pollution (Jin et al., 2017a, 2020a). The characteristic compositions of the target Cl/Br-PAHs in the study sites are shown in Fig. 3 and Table S8. A previous study showed that Br-PAHs have weaker photostability than Cl-PAHs (Ohura et al., 2008, 2009). However, Altarawneh et al. (2019) pointed out that the pyrolysis or incineration of BFR-containing materials could provide more molecular bromine and promote the formation of bromine compounds, while the yield of chlorine compounds becomes relatively low. Therefore, the proportions of  $\Sigma_{17}$ Br-PAHs in the three parks and their environs were significantly higher than those of  $\Sigma_{14}$ Cl-PAHs, especially in the BFR manufacturing park and E-waste dismantling park, which contained brominated brines or printed circuit boards (Fig. S3). Besides, the proportions of  $\Sigma_{17}$ Br-PAHs in the three parks were all higher than found in their surroundings (Fig. S3). These occurrences were also reported in metal smelting, E-waste dismantling, chemical rubber production, and other industries (Ma et al., 2009; Ni and Zeng, 2012; Tang et al., 2020; Wang et al., 2022).

The three parks had their own compositional characteristics for the individual homologs, predominantly halides of Phe, Ant, Pyr, and Flu (Table S8). As proposed in previous studies, these aromatic compounds are stable and favor cyclization at high temperatures (Daso et al., 2016; Neff et al., 2005; Ohura et al., 2008; Wang et al., 2003). Specifically, 1,8-Br<sub>2</sub>-Ant (68.2%) and 4-Br-Pyr (21.5%) accounted for approximately 90% of Br-PAHs in the petrochemical industrial park, while accounted for 18.5% and 51.0% in its surroundings, respectively (Fig. 3B). Significantly, the predominant Br-PAHs in the vicinities of all parks were similar, although their proportions were different (Fig. 3B). Additionally, the 2-Br-Fle accounted for 19.3% of Br-PAHs outside the petrochemical industrial park, while Vuong et al. (2020b) suggested that 2-Br-Fle could be a typical marker for the automobile industry. Therefore, 1,8-Br<sub>2</sub>-Ant could be a significant Br-PAHs in petrochemical industry activities, while 2-Br-Fle outside the park might arise from vehicular exhaust emissions.

In the BFR manufacturing park, the distributions of 2-Br-Fle and 2,7-Br<sub>2</sub>-Fle accounted for 28.8% and 18.3%, respectively (Fig. 3B). The Br-PAHs outside the park were dominated by 1,8-Br<sub>2</sub>-Ant (47.4%) and 4-Br-Pyr (34.0%). The sites with high Br-PAH concentration inside the park were distributed near the production lines, indicating plausible generation of Br-PAHs during BFR production (Fig. S2B). Inside the E-waste dismantling park, 9,10-Br<sub>2</sub>-Ant and 9,10-Br<sub>2</sub>-Phe accounted for 43.7% and 15.0%, respectively, while 1,8-Br<sub>2</sub>-Ant and 4-Br-Pyr respectively accounted for 28.1% and 16.3% in the surroundings (Fig. 3B). However, these contaminant patterns of Br-PAHs in the present study were different from the dust (Tang et al., 2020) and atmospheric samples (Liu et al., 2020a) from E-waste dismantling parks. Therefore, the Br-PAHs produced by BFR manufacturing were mainly low-ring, whereas the Br<sub>2</sub>-3 ring group suggested that the emissions arose from E-waste dismantling activity.

As for the Cl-PAHs, 1-/2-Cl-Ant dominated (47.6%) in the petrochemical industrial park (Fig. 3A), followed by 6-Cl-BaP, 1,5-Cl<sub>2</sub>-Ant, and 9,10-Cl<sub>2</sub>-Ant, accounting for 22.8%, 9.7%, and 9.3%, respectively. In the surrounding area, 9,10-Cl<sub>2</sub>-Ant, 1,5-Cl<sub>2</sub>-Ant, and 6-Cl-BaP showed 25.5%, 23.8%, and 21.0% abundance, respectively. According to the previous studies, the PAHs in petroleum crude oil and its by-products were mainly low molecular weight with 2–3 benzene rings (Neff et al., 2005; Stout et al., 2002). However, 1-Cl-Pyr (29.6%) and 3-Cl-Flu (17.9%) concentrated within the BFR manufacturing park. The 1-Cl-Pyr accounted for the highest proportion (35.1%) surrounding the park, followed by 6-Cl-BaP (16.8%) and 1,5,9,10-Cl<sub>4</sub>-Ant (15.7%). The high-ring Cl-PAHs were predominated in the BFR manufacturing park, and the 4–5 rings Cl-PAHs inside and outside the park were both > 60%.

As mentioned in the literature, chlorination occurs where the highest frontier electron density and the chlorides are more stable than their parent PAHs (Ohura et al., 2005, 2008), such as found with 7-Cl-BaA, 1-Cl-Pyr, 3-Cl-Flu, and 6-Cl-BaP. In addition, these compounds would more easily deposit onto soil from fly ash and stack gas, being the high molecular weight compounds with 4- or 5-ring (Jin et al., 2017b). Therefore, the dominated Cl-PAHs in the petrochemical and BFR manufacturing parks may be chlorinated from respective parent PAHs.

In contrast, the abundant Cl-PAHs in the E-waste dismantling park were the Cl<sub>2</sub>-3 ring group, especially the chlorinated Ant (Fig. 3A). The 1-/2-Cl-Ant predominated in Cl-PAHs at 24.9%, followed by 9,10-Cl<sub>2</sub>-Phe (24.1%), 1,5-Cl<sub>2</sub>-Ant (15.0%), and 9,10-Cl<sub>2</sub>-Ant (14.0%) (Fig. 3A). In its surrounding area, 1,5-Cl<sub>2</sub>-Ant, 9,10-Cl<sub>2</sub>-Ant, and 7-Cl-BaA accounted for 35.7%, 34.5%, and 11.8%, respectively. Liu et al. (2020a) reported similar profiles in the air samples from different E-waste dismantling workspaces (Table S8). Earlier, Ohura et al. (2008) estimated the photolysis rates of compounds with various chlorinated positions and quantities, indicating that more chlorine atoms in the substituted Cl-PAHs were more stable. Therefore, in the E-waste dismantling park, the predominant Cl/Br-PAHs may be accumulated from incomplete degradation.

Generally, the composition characteristics of Cl/Br-PAHs in the vicinities of the three parks were similar to that in the park, which could be considered as the migration from the parks to their vicinities (Fig. 3). The petrochemical industrial park in the present study mainly produced low-ring Cl/Br-PAHs, of which 1-/2-Cl-Ant and 1,8-Br<sub>2</sub>-Ant were its characteristic Cl-PAHs and Br-PAHs, respectively. The distribution Cl/Br-PAHs in the BFR manufacturing park were characterized by high-ring Cl-PAHs and low-ring Br-PAHs, which may reveal its Cl-PAHs and Br-PAHs were formed in different pathways (Jin et al., 2017a; Ohura et al., 2005; Wang et al., 2022). Owing to the enrichment of 2-Br-Fle in the BFR manufacturing park, the chemical in its surroundings may be transported from the park, while other parks come from vehicular exhaust emissions. The Cl/Br-PAHs distributions of E-waste dismantling park were different from that of other studies (Liu et al., 2020a; Tang et al., 2020). In the present study, the distribution Cl/Br-PAHs in the E-waste dismantling park were characterized by Br<sub>2</sub>-3 ring compound and Cl<sub>2</sub>-3 ring compound, especially halogenated Ant. The distribution characteristics of these Cl/Br-PAHs constitute the fingerprints of the three parks, which can be used to track their emissions and identify their sources.

## 4. Conclusions

The Cl/Br-PAH concentrations inside and outside the three industrial parks (petrochemical industrial park, BFR manufacturing park, and E-waste dismantling park) were quantitated. Br-PAH concentrations in the parks were higher than those of Cl-PAHs to varying degrees. The concentration of Br-PAHs from the BFR manufacturing park was 1–3 folds higher than that in the other two parks. The parks evidenced different compositional profiles of Cl/Br-PAHs; low-ring and 4–5-ring Cl/Br-PAHs predominated in the petrochemical industrial park and BFR manufacturing park, respectively. However, the characteristic compositions of the E-waste dismantling park were Cl<sub>2</sub>/Br<sub>2</sub>-3 ring compound. Through spatial distribution analysis, the petrochemical industrial park and BFR manufacturing park showed a point source pollution pattern in the parks, while other emission sources of Cl/Br-PAHs were found in their surrounding areas. Owing to history, there were relatively high concentrations of Cl/Br-PAHs in the vicinity of the E-waste dismantling park. The present study confirmed individual characteristic emissions of Cl/Br-PAH in the three parks and established their fingerprints. However, the research on the formation mechanism was still insufficient and it should be further studied for effective control of the chemicals.

## CRediT authorship contribution statement

**Yujie Wang:** Methodology, data analysis, writing. **Peixin Su:** Methodology, Data analysis, Writing. **Xiang Ge:** Methodology. **Helong Ren:** Methodology. **Shengtao Ma:** Methodology. **Guofeng Shen:** Design, Methodology. **Qiang Chen:** Design, Methodology. **Yingxin Yu:** Design, Formal analysis, Writing – review & editing. **Taicheng An:** Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Declaration of competing financial interests

There were no potential competing financial interests.

## Statement of environmental implication

Cl-PAHs can increase the risk of cancer mediated by AhR activation (like PAHs), and studies also indicated that Cl/Br-PAHs presented a high toxic equivalent quantity, even higher than polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans.

The fingerprints of Cl/Br-PAHs from various industrial productions can provide helpful information to trace Cl/Br-PAH emissions. This study investigated three typical industrial parks, viz. a petrochemical industrial park, a brominated flame retardant manufacturing park, and an electronic waste dismantling park, from upstream to downstream of industrial chain, to identify emission pattern of Cl/Br-PAHs from industrial productions, understand the formation mechanisms and the influence on the surrounding environments.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2022.129160](https://doi.org/10.1016/j.jhazmat.2022.129160).

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