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# Atmospheric halogenated hydrocarbons emitted from a flame retardant production base and the influence on ozone formation potential and health risks

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#### ABSTRACT

The flame retardant industrial park is a significant source of atmospheric volatile organic compound (VOC) emissions. A flame retardant factory is generally associated with abundant salt pans, which facilitate brine raw materials for flame retardant production. However, the concentrations and compositions of these VOCs from the factories and the surrounding salt pans are still unclear. Therefore, this study characterized the VOCs from various production areas in a flame retardants factory and its surrounding salt pans. We investigated five VOC types: alkanes, aromatic hydrocarbons (AHs), halogenated hydrocarbons (HHs), halogenated aromatic hydrocarbons, and halogenated olefin. AHs (41.0  $\pm$  26.3  $\mu$ g/m<sup>3</sup>) were the dominant VOC type in the factory, followed by HHs (7.64  $\pm$  6.52  $\mu$ g/m<sup>3</sup>). As for the surrounding salt pans, HHs (89.6  $\pm$  55.9  $\mu$ g/m<sup>3</sup>), followed by AHs (20.9  $\pm$  13.8  $\mu$ g/m<sup>3</sup>). Generally, HHs and AHs were found to be potential cancer risks, especially 1,2-dichlorothane, 1,2-trichlorothane, and benzene. Furthermore, the diffusion of AHs or HHs from the study areas may affect the local residential area and school. AHs were the study region's most significant contributor to ozone formation potential. Consequently, this study provides detailed characteristics of VOCs in flame retardant industrial parks and contributes to developing targeted control strategies.

# Introduction

Atmospheric volatile organic compound (VOC) emissions significantly influence the environment (Wang et al., 2020), climate (Li et al., 2021), and human health (Nuvolone et al., 2018). VOCs are known to participate in atmospheric photochemical reactions, the key precursors of secondary organic aerosol and ozone formations (Yang et al., 2020). The contribution of VOCs to secondary organic aerosol formation was up to 67% in Shanghai (Wang et al., 2020). Some VOCs, such as toluene, ethane, and butane, are crucial to ozone formation (Zheng et al., 2021). Furthermore, poisonous VOCs, including benzene, toluene, ethylbenzene, and xylene, adversely affect human health, causing acute and chronic respiratory diseases, nervous system dysfunction, and so on (Chang et al., 2010; Liu et al., 2021). Understanding the sources and evolution of VOCs in the atmosphere is necessary to reduce their emissions and effects on the environment, climate, and human health.

Airborne VOCs originate from various natural and anthropogenic sources (Hui et al., 2018). The natural sources consist of forests, rice fields, grasslands, and other vegetation emissions (Wu et al., 2020; Yu et al., 2008), while the anthropogenic emission sources include fossil fuel combustion, industrial process emissions, and transportation emissions (Rantala et al., 2016). Anthropogenic sources contribute six–eighteen times those of natural sources in some polluted areas and cities (Wang et al., 2021). With the rapid economic development in China, anthropogenic VOCs increased by 11% from 2010 to 2017 (Simayi et al., 2022). Industrial VOC emissions have already become the most critical anthropogenic VOCs, accounting for more than 50% of the total (Li et al., 2019; Simayi et al., 2019).

Industrial production is essential to anthropogenic VOC emission (Zhang et al., 2020). Several studies have focused on VOC emissions

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from petrochemical and other chemical industries (Chen et al., 2020; Zhang et al., 2022; Zheng et al., 2020). For example, Zheng et al. (2020) measured VOC emissions from a petrochemical park in the Yangtze River region. The authors found aromatic hydrocarbons (AHs) as the most abundant VOCs (Zheng et al., 2020). Elsewhere, Li et al. (2017) studied the VOC emissions of a chemical park. They reported that the main emission source was stack emissions, with 1-butene and ethane being the predominant components (Li et al., 2017). In addition, VOC concentrations during winter in northern China were 1.5–2.4 times higher than in other seasons (Wang et al., 2022). The contribution of combustion source to VOC emission increased during winter, reaching more than twice that of summer (Mozaffar et al., 2021; Zhao et al., 2020).

Flame retardant production is a crucial source of industrial VOCs (Shen et al., 2019). The production of flame retardants in China reached  $5.98 \times 10^5$  tons in 2020, representing more than half of the global output (Lao et al., 2022). In China, the production areas of flame retardants are mainly located in the coastal regions of Shandong, Hebei, and Jiangsu provinces (Wu et al., 2012). However, the VOC emissions from flame retardant production in China are yet to be investigated. In addition, VOCs have various composition patterns in varied industrial processes (Borén et al., 2018). However, there is no data on the VOC emission during flame retardant production. Considering the health risks of VOC exposure, understanding their compositional characteristics can help screen out the species that should be prioritized for control.

Therefore, the present study sampled the air from various production lines in a flame retardant industry. Moreover, VOCs in the atmosphere were analyzed around the factory to assess the impact of VOCs from the flame retardant production industry. The priority-controlled VOCs were screened based on the evaluation of the health risk assessment and ozone formation potential (OFP). This study would significantly help understand the emission characteristics of VOCs in flame retardant industries.

#### Materials and methods

#### Sample collection

The studied flame retardant production factory is 20 square kilometers in area. Its production capacity (e.g., for decabromodiphenyl ether) reaches 25,000 tons per year, representing 20% of the production capacity in China. The concentration of total VOCs (TVOCs) from exhaust gas emission is generally below 10 mg/m<sup>3</sup>.

Using a 2.7 L stainless steel vacuum Summa tank, we sampled 96 VOCs from a flame retardant production factory and surroundings during the winter of 2020 and 2021 (**Table S1**). Before sampling, the sampling tanks were pre-cleaned five times with high-purity nitrogen (99.999%) and pre-vacuum-pumped with a tank cleaner (pressure below 10 Pa). A grid sampling was used on the rectangular-shaped factory, whose width and length are 120 m (east to west) and 320 m (north to south) (Fig. 1). Twenty-four sampling locations were identified in the factory. VOC samples within 5 km distance from the factory were also collected. Each sampling location was 1 km in the east-west and north-south directions.

According to the distribution characteristics of the production process, the park is divided into various areas, including research and



Fig. 1. Grid sampling layout map of flame retardant park and surrounding area.

development (RD) (used for chemical experiments), office zone (OZ), decabromodiphenyl ethane production line (DL), bromopropane production line (BL), finished product area of decabromodiphenyl ethane (FD), abandoned park (AP), abandoned, raw material bisphenol A carbonate oligomer (RBC), bisphenol A carbonate oligomer production line (BCL), finished product hydrobromic acid (FH), and finished product bisphenol A carbonate oligomer (FBC). Heating, melting, and agitation during production may release VOCs, such as benzene and benzene series, into the atmosphere via fugitive emission. Residential areas and schools were located north of the factory, and some salt pans were situated south of the factory. The halogen-rich brine in the salt pans can be used to obtain the raw materials.

# Instrumental analysis

The VOCs were determined on an ENTECH 7200 pre-concentrator (ENTECH Instruments Inc., Silonite TM, CA, USA) combined with gas chromatography/mass spectrometry. The qualitative analysis was based on the TO-15 method of the U.S. Environmental Protection Agency (USEPA). Briefly, the ENTECH 7200 pre-concentrator concentrated 200 mL gas sample, separating VOCs from water vapor, CO<sub>2</sub>, and other impurities. Then, the VOCs were injected into the GC and separated by a DB-5MS capillary column ( $60 \ m \times 0.32 \ mm \times 0.25 \ \mum$ , Agilent Technology, USA). The stream was directed to the MS for chemical determination. The oven operation procedure was as follows: onset temperature was 40 °C (held for 5 min); raised to 150 °C at 5 °C/min; finally increased to 250 °C at 15 °C/min and held for 2 min. The temperature of the transmission line was set at 290 °C. Mass spectrometry's scanning range mass-to-charge ratio (m/z) was 45 – 260. The carrier gas was high pure nitrogen (99.99%), set at a 1.2 mL/min flow rate.

## Quality assurance and quality control

One Summa tank was used as a blank sample during sampling. The blank sample underwent the same procedure. The blank was refilled after sampling and analyzed with high-purity nitrogen to ensure the Summa tank was not contaminated during sampling. To ensure an accurate standard curve, standard samples (TO-15 air VOC mixed standard sample gas; 36 types were used) were diluted, and then the standard curve was used for quantitative analysis. The deviation between the result and the theoretical concentration value was less than 30%. The limit of quantitation (LOQ) and limit of detection (LOD) of the target analytes are presented in **Table S2**.

## Health risk assessment

The non-carcinogenic and carcinogenic risks of the VOCs were considered to estimate their human health risk. According to the USEPA method, the non-carcinogenic and carcinogenic risks were evaluated using hazard quotient (HQ) and cancer risk (CR), respectively (USEPA, 2009). Also, the hazard index (HI) was evaluated using the sum of the HQ of the target non-carcinogenic VOCs. The non-carcinogenic risk was calculated as follows based on the exposure concentration (EC) and reference concentration (RfC) by inhalation of the VOCs:

$$EC = (CA \times ET \times EF \times ED)/AT$$
<sup>(1)</sup>

$$HQ = EC/(RfC \times 1000) \tag{2}$$

$$HI = \sum HQ \tag{3}$$

where EC is the exposure concentration of a target VOC for chronic or sub-chronic exposures ( $\mu g/m^3$ ); CA is the environmental concentration of a target VOC species in air ( $\mu g/m^3$ ); ET is the exposure time (8 h/day was used in the present study); EF is the exposure frequency (260 day/ year was used); ED is the exposure duration (adult: 50 years; children:

10 years); AT is the mean time (70 × 365 × 24 h was used); and RfC is the reference concentration (mg/m<sup>3</sup>). The RfC values used in this study were from USEPA integrated risk information system (IRIS) (Table 1). The HI value of the target non-carcinogenic VOC > 1 was considered a non-carcinogenic health risk.

The carcinogenic risk assessment, evaluated using the CR value (calculated by the estimated daily intake (EDI<sub>daily</sub>)) and the slope factor for the carcinogenic pollutant (CSF), were derived as follows:

$$EDI_{daily} = (CA \times CF \times IR \times EF \times ED) / (BW \times AT)$$
(4)

$$CR = EDI_{daily} \times CSF$$
 (5)

where CF is the conversion factor fixed at 0.001; IR is the daily inhalation rate of air (adult: 15.8 m<sup>3</sup>/day; children: 12.7 m<sup>3</sup>/day); BW is the body weight of a person (62 kg (adult) and 32 kg (children) for this study); mean exposure period for cancer estimation (AT, 25,550 days) values rely on working hours in the flame retardant industry units; CSF is the slope factor for carcinogenic pollutant (mg/kg·day), and the data was from USEPA IRIS (Table 1). The CR of the target carcinogenic VOC >10<sup>-6</sup> was considered a carcinogenic health risk.

#### Estimation of ozone formation potential

To evaluate the contributions of VOCs to ozone formation, the OFP was calculated by multiplying the VOC concentrations by the corresponding maximum incremental activity (MIR):

$$OFP_i = C_i \times MIR_i \tag{6}$$

where OFP<sub>i</sub> is the OFP of VOC i ( $\mu g/m^3$ ); C<sub>i</sub> is the VOC i concentration ( $\mu g/m^3$ ) and MIR<sub>i</sub> is the maximum incremental reactivity of the VOC i (gm O<sub>3i</sub>/gm VOC<sub>i</sub>). The MIR for the target VOCs are listed in **Table S2**.

### Statistical analysis

An SPSS13 (IBM, USA) software carried out the statistical analysis. To display the pollution distribution of the plant and surrounding areas, we employed the Kriging method to grid the data, while Surfer 12 (Golden Software, USA) drew the contour map. The concentration was the LOD when the signal-to-noise ratio was 3 and the LOQ when the signal-to-noise ratio was 10. When the concentration was less than the LOQ and the DF (detection frequency) was greater than 50%, 50% LOQ

Table	1
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Non-carcinogenic risk assessment and carcinogenic risk assessment.

Compounds	RfC (mg∕ m <sup>3</sup> )	CSF (mg/kg/ dav <sup>-1</sup> )	2020	
	ŕ	5	HQ	Risk
n-Hexane	0.7	-	$6.63 \times 10^{-5}$	-
Benzene	0.03	$2.90  imes 10^{-2}$	$7.47 \times 10^{-4}$	$4.97 \times 10^{-6}$
Toluene	5	-	$7.42 \times 10^{-5}$	_
Ethylbenzene	1	-	$1.84{ imes}10^{-5}$	_
Xylene	0.1	-	$3.63 \times 10^{-4}$	-
1,3,5-	0.06	-	$2.06 \times 10^{-4}$	-
Trimethylbenzene				
Chloromethane	0.09	-	$1.51 \times 10^{-4}$	-
Dichloromethane	0.6	-	$1.41 \times 10^{-4}$	-
Chloroform	-	-	-	-
1,2-Dichloroethane	-	$9.10 \times 10^{-2}$	-	$1.47{ imes}10^{-5}$
1,1,1-Trichlorothane	5	-	$5.04 \times 10^{-6}$	-
1,1,2-Trichlorothane	-	$5.70 \times 10^{-2}$	-	$8.75 \times 10^{-6}$
1,2-Dichloropropane	0.004	-	$5.29 \times 10^{-3}$	_
1,4-Dichlorobenzene	0.8	-	$1.45 \times 10^{-5}$	-
Trichloroethylene	0.002	$6.00 \times 10^{-3}$	$1.13{ imes}10^{-2}$	$1.04{ imes}10^{-6}$
Perchloroethylene	0.04	$2.00 \times 10^{-3}$	$5.66 \times 10^{-4}$	$3.46 \times 10^{-7}$
HI			$1.90 \times 10^{-2}$	

RfC: reference concentration; CSF: the slope factor for carcinogenic pollutant; HQ: hazard quotient; "-" indicates no relevant data.

was treated as the final concentration. When the concentration was less than the LOQ and the DF was less than 50%, 25% LOQ was treated as the final concentration (Ge et al., 2020). The VOC concentrations are reported in  $\mu$ g/m<sup>3</sup> unless otherwise specified.

## **Results and discussion**

#### VOC concentrations in the study area

The VOC concentrations in the study area in 2020 and 2021 are summarized in Table 2 and shown in Fig. S1. In 2020, the mean concentration of TVOCs inside and outside the factory was 52.0 and 97.2  $\mu$ g/m<sup>3</sup>, respectively. Whereas the values in 2021 were, respectively 37.7 and 35.6  $\mu$ g/m<sup>3</sup>, lower than those in 2020. This difference was due to the snowfall before sampling in 2021. Starokozhev et al. (2009) reported that the removal ratio of VOCs by snow can reach up to 35%. Therefore, the wet deposition effect of the snow may lead to decreased TVOC concentrations in 2021.

A total of 36 VOCs were detected and quantified in this study. The chemicals can be divided into five groups: alkanes, AHs, halogenated hydrocarbons (HHs), halogenated aromatic hydrocarbons (HAHs), and halogenated olefins (HOs) (**Table S2**). The concentrations of the five VOC types are illustrated in **Fig. S2** and **Table S3**. The mean concentration of HHs was the highest ( $32.5 \ \mu g/m^3$ ) in 2020, accounting for 43.5% of the TVOCs, while those of AHs and HAHs were 27.9 (37.3% of total) and  $3.71 \ \mu g/m^3$  (the lowest), respectively. The mean concentration of AHs in the factory was  $41.0 \ \mu g/m^3$ , much higher than  $14.8 \ \mu g/m^3$  in the surrounding area in 2020 (**Table S3**). This result is mainly

attributed to the fugitive emission of AHs during production, as detailed in the next section. In 2020, the HH concentration  $(23.5 \ \mu g/m^3)$  in the surrounding area was higher than the  $5.23 \ \mu g/m^3$  inside the factory. This result suggests that HHs in the surrounding areas would be released from other sources rather than factory emissions. Therefore, higher VOC concentrations outside the factory relative to those inside the factory in 2020 were due to the abundant HHs outside the factory, originating from other sources. The mean concentrations of AHs and HHs in 2021 were 14.5 and 10.2  $\ \mu g/m^3$ , respectively. AHs and HHs accounted for 38.6% and 27.1% of TVOCs in 2021, respectively. The AHs and HHs inside and outside the factory in 2021 remained low (5–12  $\ \mu g/m^3$ ) because of wet deposition effect of the snow.

#### VOCs in flame retardant factory

There were significant differences in TVOCs among various production areas in the factory (Figs. 2 and S3). In 2020, the mean TVOC concentrations in the DL1, BL, BCL, and AP areas were 78.1, 72.1, 65.9, and 64.6  $\mu$ g/m<sup>3</sup>, respectively. High TVOC concentrations in these areas were mainly concentrated near the production regions. Heating and stirring in the production regions quickly resulted in VOC volatilization and leakage. The mean concentrations of AHs in the DL1, BL, BCL, and AP areas were 72.7, 60.8, 44.5, and 40.2  $\mu$ g/m<sup>3</sup>, respectively, representing 62%–92% of the TVOCs therein. Moreover, >90% of the AH was toluene in the DL1, BL, BCL, and AP areas. Interestingly, toluene is an essential intermediate in flame retardants production (Gelmont et al., 2020).

Yang et al. found that AHs accounted for 65%-99% of VOCs emission

#### Table 2

Concentrations (µg/m<sup>3</sup>) of VOCs in air samples from the flame retardants factory and its surrounding area.

Compounds	2020				2021			
	Mean	Median	Range	$\mathrm{DF}^{\mathrm{a}}$	Mean	Median	Range	DF
n-Hexane	2.74±3.53	1.29	0.51-18.3	100%	$2.19{\pm}2.73$	1.31	0.65-14.9	100%
n-Heptane	$1.09 \pm 1.80$	0.25	n.d6.38	75.0%	$1.42{\pm}0.56$	1.21	1.21 - 3.22	100%
Benzene	$1.32{\pm}1.85$	0.28	0.12-6.57	100%	$0.84{\pm}0.53$	0.69	0.18 - 3.08	100%
Toluene	$21.9 \pm 26.1$	8.84	0.26-130	100%	$3.47{\pm}5.66$	1.99	0.79-29.1	100%
Ethylbenzene	$1.09 \pm 1.51$	0.24	n.d5.85	91.7%	$2.06 {\pm} 0.46$	1.88	1.78-3.98	100%
o-Xylene	$0.97 {\pm} 1.56$	0.21	n.d5.55	66.7%	$2.18{\pm}0.48$	2.01	1.94-4.65	100%
m/p-Xylene	$1.17{\pm}1.62$	0.20	n.d7.09	85.4%	$2.31 {\pm} 0.80$	2.10	1.99-6.87	100%
1,3,5-Trimethylbenzene	$0.73 {\pm} 1.30$	0.11	n.d5.77	50.0%	$1.68 {\pm} 0.58$	1.88	n.d1.88	89.4%
4-Ethyltoluene	$0.73 \pm 1.33$	0.32	n.d6.46	52.1%	$1.92{\pm}0.55$	1.97	n.d3.08	93.6%
Chloromethane	$0.80{\pm}1.28$	0.11	n.d4.42	70.8%	$1.30 {\pm} 0.74$	1.18	n.d2.60	85.1%
Dibromochloromethane	$1.92 {\pm} 3.65$	n.d.	n.d12.0	47.9%	$0.05 {\pm} 0.28$	n.d.	n.d.–1.74	4.30%
Dichloromethane	$4.98 {\pm} 5.50$	2.84	n.d27.1	95.8%	$1.91{\pm}1.82$	1.22	n.d9.92	87.2%
Dichlorodifluoromethane	$2.98 {\pm} 3.28$	1.38	0.40-13.6	100%	$1.95 {\pm} 0.73$	2.04	n.d4.71	95.7%
Bromodichloromethane	$1.66 \pm 3.19$	n.d.	n.d10.1	41.7%	n.d.	n.d.	n.d.	n.d.
Chloroform	$1.66 {\pm} 2.76$	0.24	n.d10.2	85.4%	$0.08 {\pm} 0.44$	n.d.	n.d2.85	4.30%
Bromoform	$2.06 \pm 3.77$	0.41	n.d12.6	54.2%	n.d.	n.d.	n.d	n.d.
Trichlorofluoromethane	$1.86 {\pm} 3.66$	n.d.	n.d.–13.7	29.2%	$0.85 {\pm} 0.35$	0.83	n.d2.60	97.9%
Carbon tetrachloride	$1.98 {\pm} 3.35$	0.14	n.d.–10.3	95.8%	n.d.	n.d.	n.d.	n.d.
1,2-Dichloroethane	$1.24{\pm}2.15$	0.11	n.d7.20	89.6%	$0.15 {\pm} 0.24$	n.d.	n.d0.78	29.8%
1,1-Dichloroethane	$1.10{\pm}2.11$	n.d.	n.d7.79	41.7%	n.d.	n.d.	n.d.	n.d.
1,2-Dichlorotetrafluoroethane	$2.14{\pm}3.84$	0.18	n.d13.8	56.3%	n.d.	n.d.	n.d.	n.d.
1,1,1-Trichlorothane	$1.49{\pm}2.77$	0.07	n.d8.60	56.3%	$0.26 {\pm} 0.38$	n.d.	n.d0.82	31.9%
1,1,2-Trichlorothane	$1.18{\pm}2.28$	n.d.	n.d7.24	33.3%	$0.77 {\pm} 0.17$	0.79	n.d1.09	95.7%
1,2,2-Trifluoro-1,1,2-Trichloroethane	$2.70 {\pm} 4.38$	0.64	0.20-16.5	100%	n.d.	n.d.	n.d.	n.d.
1,2-Dibromoethane	$1.69{\pm}2.72$	0.20	n.d.–9.51	66.7%	$2.58{\pm}1.24$	2.39	n.d.–8.77	95.7%
1,2-Dichloropropane	$1.25{\pm}2.24$	n.d.	n.d6.52	43.8%	$0.29{\pm}0.34$	0.36	n.d.–1.42	53.2%
Chlorobenzene	$1.58{\pm}2.21$	0.37	n.d11.0	85.4%	$1.50 {\pm} 0.53$	1.44	n.d4.79	97.9%
1,3-Dichlorobenzene	$0.68 {\pm} 1.44$	0.09	n.d.–7.35	50.0%	$0.60{\pm}2.85$	n.d.	n.d.–9.90	10.6%
1,2-Dichlorobenzene	$0.75 {\pm} 1.46$	0.12	n.d8.15	89.6%	$2.85{\pm}2.64$	2.01	n.d.–17.7	93.6%
1,4-Dichlorobenzene	$0.68{\pm}1.41$	0.12	n.d7.60	64.6%	$0.45 {\pm} 0.90$	n.d.	n.d3.99	38.3%
1,1-Dichloroethylene	$0.93{\pm}1.87$	n.d.	n.d7.15	20.8%	n.d.	n.d.	n.d.	n.d.
(Z)-1,2-Dichloroethene	$1.07{\pm}2.04$	n.d.	n.d7.14	45.8%	$0.02{\pm}0.11$	n.d.	n.d.–0.76	2.10%
trans-1,2-Dichloroethylene	$1.04{\pm}1.99$	n.d.	n.d.–7.11	37.5%	$0.03{\pm}0.18$	n.d.	n.d.–1.28	2.10%
Trichloroethylene	$1.34{\pm}2.48$	0.10	n.d.–7.98	50.0%	$1.27{\pm}0.39$	1.37	n.d.–1.72	91.5%
Perchloroethylene	$1.33{\pm}2.75$	n.d.	n.d9.06	25.0%	$0.03{\pm}0.23$	n.d.	n.d.–1.57	2.10%
cis-1,3-Dichloropropene	$0.99{\pm}1.93$	n.d.	n.d6.58	33.3%	$2.62{\pm}0.80$	2.86	n.d.–2.95	91.5%
TVOCs	$\textbf{74.8} \pm \textbf{73.8}$	47.6	7.23–287	100%	$\textbf{37.6} \pm \textbf{11.8}$	35.3	23.8-86.4	100%

DF: detection frequency.



**Fig. 2.** The concentrations and composition profile of VOCs in air samples from industrial parks in 2020 (A: the concentration of VOCs; B: the composition of VOCs). (AHs: aromatic hydrocarbons; HHs: halogenated hydrocarbons; HAHs: halogenated aromatic hydrocarbons; HOs: halogenated olefin). (RD: research and development area; OZ: office zone; DL: decabromodiphenyl ethane production line; BL: bromopropane production line; FD: finished product area of decabromodiphenyl ethane; AP: abandoned park; RBC: the raw material area of bisphenol A carbonate oligomer; BCL: bisphenol A carbonate oligomer production line; FH: finished product area of hydrobromic acid; FBC: finished product area of bisphenol A carbonate oligomer).

from acrylic resins, plastic tapes, plastic coatings, and stencil printing industries (Yang et al., 2020). AHs were the predominant contributor to VOC emissions from the five major industrial sources: plastics, rubber, chemical fiber, chemical industry, and oil refining (Niu et al., 2016). AHs represented up to 92% of TVOCs in the retardant production industry in this study. Therefore, AH emissions from the flame retardant production industry cannot be ignored except for other industrial sources. Abundant fugitive toluene emissions occurred during distillation and vacuum pumping, causing high values of toluene in the DL1, BL, BCL, and AP areas. The concentration of HHs in the factory was 7.94  $\mu$ g/m<sup>3</sup>. Relatively high HH concentrations were found in the AP (19.9

 $\mu$ g/m<sup>3</sup>) and BCL (17.1  $\mu$ g/m<sup>3</sup>) areas. AHs accounted for > 40% of TVOCs in the FD, DL1, and DL2 areas, despite the wet deposition in 2021. These results further demonstrated that AHs contributed significantly to VOC emissions from the flame retardant factory. Therefore, complete airtightness of the equipment or lines in the flame retardant factory was expected, reducing AH emissions from the flame retardant factory.

Low TVOC concentrations inside the factory were mainly distributed in the OZ, FBC, FH, and RD areas, with mean concentrations of 35.0, 33.9, 29.6, and 24.4  $\mu$ g/m<sup>3</sup>, respectively. The low TVOC values in these office and product storage areas were due to these areas far from the production sources. However, their components mainly comprise AHs (i. e., toluene), accounting for 69%, 61.8%, 81.2%, and 54.8% in OZ, FBC, FH, and RD areas, respectively. These values indicate that these factory areas were still influenced by the diffusion of AHs (i.e., toluene) from the production areas inside the factory. In 2021, AHs still dominated in RD and FD areas, with mean concentrations of 29.2 and 32.8  $\mu$ g/m<sup>3</sup>, respectively. The results reflect that diffusion of AHs (i.e., toluene) from the production line to the RD and FD areas existed, although the occurrence of wet deposition occurred in 2021.

#### Spatial distribution of VOCs

A spatial analysis of airborne VOC distributions can deepen our understanding of industrial emissions' impact on the surroundings. The spatial distributions of TVOCs in the factory and the surrounding area are depicted in Figs. 3 and S4. High TVOC concentrations were distributed in the surrounding area where some salt pans existed. HHs accounted for 59% of TVOCs in these salt pans. The main HH pollutants in the salt pans were 1, 2-dibromoethane, dichloromethane, and chloromethane. This observation significantly differed from the abundant toluene in the factory.

Halide ions on the salt pan are converted to reactive halogen species (RHS) by reactions with secondary reactive oxygen species (ROS) through sunlight-initiated (Yang et al., 2017; Ofner et al., 2012). The volatilization RHS may react with alkanes and alkenes in the natural environment to form halogenated hydrocarbons (Zhao et al., 2018; Zhao et al., 2011). Therefore, the concentrated HHs in the surrounding area were mostly attributed to these salt pans. Likewise, a relatively high value of TVOCs was found in the factory. As previously discussed, AHs (such as toluene) were a dominant content of factory emission. AHs accounted for 85% of TVOCs in the factory (**Fig. S5**). These findings suggest that the main sources of VOCs in the factory and the surrounding area were released from flame retardant production and salt pans, respectively.

The low TVOC concentrations were mainly located around the school and local residential area. HHs accounted for 55% of TVOCs in the school. The main HH pollutants in the school were 1, 2-dibromoethane, dichloromethane, and chloromethane, agreeing with those from the salt pans. This result implies that HHs in the school were mainly influenced by HH diffusion from the salt pans. The mean TVOC concentration in the local residential area was only 8.49  $\mu$ g/m<sup>3</sup>. AHs and HHs, respectively accounted for 33.2% and 38.9% of TVOCs in the residential area. Moreover, the main components of AHs and HHs in the local residential area were toluene and dichloromethane, respectively. Therefore, it cannot be excluded that the local residential area was still affected by diffused VOCs from the factory and salt pans, even though it was distant from the factory and salt pans.

## Health risk assessment of VOC exposure

Because of the significant discrepancy in the VOCs in the factory, the surrounding area, the school, and the local residential area, we evaluated the health risks of VOC exposure therein. Table 1 lists the non-carcinogenic and carcinogenic health risks of VOCs. The HI values of the target VOCs in 2020 varied from  $2.77 \times 10^{-4}$  to  $2.11 \times 10^{-2}$  in the flame retardant factory. The highest VOC HI value  $(3.31 \times 10^{-3})$  was



**Fig. 3.** The spatial distributions of  $\sum_{36}$ VOCs in the park and its surrounding area (A: the surrounding area in 2020; B: the industrial park in 2020). (AHs: aromatic hydrocarbons; HHs: halogenated hydrocarbons; HAHs: halogenated aromatic hydrocarbons; HOs: halogenated olefin). (RD: research and development area; OZ: office zone; DL: decabromodiphenyl ethane production line; BL: bromopropane production line; FD: finished product area of decabromodiphenyl ethane; AP: abandoned park; RBC: the raw material area of bisphenol A carbonate oligomer; BCL: bisphenol A carbonate oligomer production line; FH: finished product area of hydrobromic acid; FBC: finished product area of bisphenol A carbonate oligomer).

found in the DL2 area, followed by the BCL  $(3.11 \times 10^{-3})$  area, with the FBC area exhibiting the lowest value  $(8.77 \times 10^{-4})$ . Trichloroethylene had the highest HQ value in the DL2 and BCL areas, accounting for > 50% of the HI values. Trichloroethylene also dominated the contribution to the HI value in 2021 (**Table S4**).

The HI values of the target VOCs ranged from 0.000201 to 0.11 in the surrounding area. In 2020, the highest HI ( $5.99 \times 10^{-2}$ ) value was observed in the salt pans, followed by the school ( $1.27 \times 10^{-2}$ ) and then the local residential area ( $1.03 \times 10^{-3}$ ). Trichloroethylene had the highest HQ value in the salt pans, accounting for >60% of the HI values. In the school, 1, 2-dichloropropane contributed the most (>71%) to the HI value. In contrast, trichloroethylene contributed the highest HI value in 2021. These results suggest that trichloroethylene should be of concern in these areas, despite having an HI <1.

Moreover, the CR values of the target VOCs varied from  $4.08 \times 10^{-7}$  to  $1.16 \times 10^{-5}$ . The CR in the various functional areas of the factory were also dissimilar. VOCs' highest CR value  $(2.21 \times 10-6)$  occurred in the DL1 area in 2020, followed by the BL area  $(1.6 \times 10^{-6})$ . Substances with potential carcinogenic risk (CR >  $1.00 \times 10^{-6}$ ) were 1,2-dichlorothane, 1,1,2-trichlorothane, and benzene. In 2020, the region with the largest CR value around the plant was salt pans  $(9.26 \times 10^{-5})$ , followed by the local residential area  $(3.83 \times 10^{-6})$  and then the school  $(8.76 \times 10^{-7})$ . This trend suggests that the salt pans and the residential area might be exposed to cancer risks. The constitutors, including 1, 2-dichloroethane, 1,2-trichlorothane, and benzene, showed higher CR in the salt pans, accounting for 48.8%, 30.8%, and 15.6% of the CR values, respectively. Benzene predominantly contributed to the CR in the residential area, accounting for >55%.

#### Estimating ozone formation potential

VOCs are essential precursors for atmospheric ozone formation, and variations in VOCs have different contributions to ozone formation (Wang et al., 2021). The potential contribution of various VOCs to ozone formation in ambient air was evaluated using OFPs (Figs. 4 and **S6**). We observed that AHs were the largest contributor to OFPs in the factory, ranging from 54.8 to 291  $\mu$ g/m<sup>3</sup> in 2020. AHs represented 94% of the total OFP values of all VOCs in 2020. The OFP values of AHs in the DL1, FD, and BL areas were significantly higher than in other areas. Toluene and xylene were the crucial contributors responsible for 67.6% and

16.0% of the AH OFP, respectively.

Similar results were also observed in the surrounding areas. The OFPs in the surrounding area ranged from 14.9 to 212.0  $\mu$ g/m<sup>3</sup> in 2020, accounting for 74% of the total (**Fig. S7**). These findings indicate that AHs (including toluene and xylene) significantly affected the OFP in the study region. Wang et al. (2021) reported a similar observation; they found that AHs in metal packaging enterprises were the largest OFP contributor, accounting for 65% of the total OFP. In the same year, Li et al. (2021) found that AHs (e.g., toluene, xylene, m-ethyl toluene, and trimethylbenzene) accounted for 50.6%–99% of the total OFP caused by VOC emissions from the organic solvent industry. However, olefin contributed the most to the OFP, accounting for 37.2%–69.1% of the total observed in the investigated rubber industry (Li et al., 2019). Comparing the results from various industries, AHs are the largest contributor to ozone generation potential in the flame retardant industry.

# Conclusion

To investigate VOCs from the flame retardant industrial park, we collected atmospheric VOCs from the various production areas of the flame retardant factory, surrounding salt pans, the local residential area, and the school. AHs were crucial in VOC emission from the different production areas of the factory. On the contrary, HHs were the key species in the surrounding salt pans. This difference suggested that the contribution of flame retardant production and material areas to the emission of VOCs changed in the flame retardant industrial park. Moreover, AHs and HHs exhibit potential carcinogenic risks in the factory or its surroundings salt pans. The local residential area and the school might be influenced by the diffusion of AHs and HHs from the factory or its surroundings salt pans. AHs were the largest contributor to ozone formation potential in the study region. This study highlights that abundant HHs emitted from the salt pans differed from the flame retardant factory emissions. Hence, formulating effective VOC emission reduction strategies in the flame retardant industrial park might be helpful.

#### Supporting information

Information related to this article can be found in supporting figures



**Fig. 4.** The contribution and percentage of five VOC types to the ozone formation potential (OFP) in the plant area (A and B: the industrial park in 2020;). (AHs: aromatic hydrocarbons; HHs: halogenated hydrocarbons; HAHs: halogenated aromatic hydrocarbons; HOs: halogenated olefin). (RD: research and development area; OZ: office zone; DL: decabromodiphenyl ethane production line; BL: bromopropane production line; FD: finished product area of decabromodiphenyl ethane; AP: abandoned park; RBC: the raw material area of bisphenol A carbonate oligomer; BCL: bisphenol A carbonate oligomer production line; FH: finished product area of hydrobromic acid; FBC: finished product area of bisphenol A carbonate oligomer).

and tables (Figs. S1-S7 and Tables S1-S4).

# **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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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.heha.2023.100070.

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