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Pollution profiles and human health risk assessment of atmospheric organophosphorus esters in an e-waste dismantling park and its surrounding area



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- High-level of tri-OPEs were found in the atmosphere of an e-waste dismantling park.
- TPhP was the dominant tri-OPEs found in the e-waste dismantling park.
- The concentrations of tri-OPEs were 5–6 orders of magnitude higher than di-OPEs.
- Tri-OPEs and di-OPEs generated from ewaste dismantling spread to surrounding area.
- The non-carcinogenic risk via inhalation decreased with age (0–70 years old).

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ABSTRACT

Recycling e-waste has been recognized as an important emission source of organophosphate triesters (tri-OPEs) and organophosphate diesters (di-OPEs), but the presence of di-OPEs in atmosphere has not been studied. Herein, tri-OPEs and di-OPEs in atmosphere of an e-waste dismantling park and surrounding area in South China were monitored for three consecutive years. Thirteen tri-OPEs and seven di-OPEs were identified. In 2017, 2018, and 2019, tri-OPE concentrations in e-waste dismantling park were 1.30 \times 10⁸, 4.60 \times 10⁶, and 4.01 \times 10⁷ pg/m³, while di-OPE concentrations were 1.14 \times 10³, 1.10 \times 10³, and 0.35 \times 10³ pg/m³, respectively, which were much higher than the surrounding area. Tri-OPEs and di-OPEs generated during e-waste dismantling affected surrounding area through diffusion. Triphenyl phosphate (TPhP) and diphenyl phosphate (DPhP) were the predominant congeners of tri-OPEs, so TPhP could be used as an indicator of e-waste dismantling. Spearman correlation analysis showed significant correlations between DPhP and TPhP (R² = 0.53, *p* < 0.01), bis-(1-chloro-2-propyl) phosphate (BCIPP) and tris(2-chloropropyl) phosphate (TCIPP) (R² = 0.49, *p* < 0.01), as well as dibutyl phosphate

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(DBP) and tributyl phosphate (TBP) ($R^2 = 0.53$, p < 0.01), indicating that they had the same source. Further, non-carcinogenic risk of them to people via inhalation was acceptable and non-carcinogenic risk of tri-OPEs decreased year by year in surrounding area.

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1. Introduction

Organophosphate triesters (tri-OPEs) are widely used as plasticizers and flame retardants in different products including textiles, furniture, plastics, and electronic devices (Hou et al., 2016; Stapleton et al., 2012). Generally, tri-OPEs can be divided into three groups according to their different substituents, including alkyl phosphate triesters (Alkyl-tri-OPEs), chlorinated alkyl phosphate triesters (Cl-tri-OPEs), and aryl phosphate triesters (Aryl-tri-OPEs) (Kim et al., 2017). As polybrominated diphenyl ethers (PBDEs) are being phased out, tri-OPEs are becoming one of the most common alternative flame retardants (Hou et al., 2016). In addition, most of them are additives, which are easily released into the environment during their production (Ma et al., 2017; Wang et al., 2020a; Wannomai et al., 2021). Thus, the elevated concentrations of tri-OPEs have been reported recently in atmosphere (Ma et al., 2020; Wang et al., 2018), dust (Tan et al., 2019), sludge (Wang et al., 2019), soil (Ge et al., 2020), sediment (Li et al., 2019a), biota (Liu et al., 2019) and even in human beings (Zhao et al., 2016). The concentration of tri-OPEs even exceeds that of traditional flame retardants (Li et al., 2019a; Wei et al., 2015), raising concerns about their potential ecological effects and human health risks. Several reports have suggested that exposure to tri-OPEs is linked with adverse health issues, such as mutagenic, carcinogenic, and neurotoxic effects on humans and organisms (Meeker et al., 2013; Veen and Boer, 2012).

Apart from tri-OPEs, organophosphate diesters (di-OPEs) are commonly used as industrial products or exist as impurities of tri-OPEs products (Matsukami et al., 2015), which are released during production and usage, similar to tri-OPEs. However, studies of di-OPEs in the environment are very limited. At present, the works on environmental di-OPEs are mainly concentrated on di-OPEs present in dust (Du et al., 2020; Tan et al., 2019) and sludge (Fu et al., 2017; Wang et al., 2019). The major sources of di-OPEs include degradation of tri-OPEs, impurities in tri-OPEs formulations, and direct commercial applications (Du et al., 2020). Recent study also reported that di-OPEs are potentially toxic and disrupt the endocrine system. For example, dibutyl phosphate (DBP) can negatively impact the reproductive system of male rats through oxidative stress mechanisms (Chen et al., 2011). Both triphenyl phosphate (TPhP) and diphenyl phosphate (DPhP) can impact the cardiac development of zebrafish (Mitchell et al., 2019).

Primitive e-waste recycling activities have been recognized as an important source of tri-OPEs and di-OPEs in the environment (Ali et al., 2017; Du et al., 2020). As the largest e-waste dismantling base, a typical e-waste dismantling park in southern China has attracted much attention. In the past decade, informal dismantling has been gradually prohibited this area. The local government began to establish an ewaste dismantling park in 2013, which was formally put into use at the end of 2015 (Wang et al., 2020b). After the establishment of ewaste dismantling park, different workshops were established and more environmentally-friendly technologies were introduced (Ge et al., 2020). In addition, according to our actual survey, disassembly is more concentrated and detailed, mainly divided into disassembly area, baking plate area, crushing area and cutting area. Pollutants, released into the atmosphere by e-waste dismantling activities, may adversely affect the human health (Chen et al., 2019; Ma et al., 2020). The atmospheric environment also plays an important role in transporting volatile organic compounds (VOCs) (Chen et al., 2021) and semi-volatile organic compounds (SVOCs) (Chen et al., 2019) to the surrounding area. For example, pollutants can enter water and soil through dry and wet deposition, or combine with atmospheric particles to form dust,

and also can enter plants through absorption and bioaccumulation (Li et al., 2019b). Furthermore, inhalation of polluted air is one of the major routes of tri-OPEs exposure (Ma et al., 2020). The gas-particle partitioning of tri-OPEs plays an important role in their environmental behavior, which is mainly related to vapor pressure and octanol/air partition coefficient (K_{OA}) (Salthammer and Schripp, 2015). To the best of our knowledge, there are very limited reports on the tri-OPEs present in the atmosphere of e-waste dismantling areas for several years, especially gas/particle distribution profiles. And there also exists a gap in the knowledge on the environmental behaviors and fates of di-OPEs in the atmosphere. Therefore, it is significant to explore the impact of tri-OPEs and di-OPEs in the atmosphere released from the e-waste dismantling area.

To obtain a better understanding of the environmental occurrences, sources, and fates of tri-OPEs and di-OPEs in the atmosphere, as well as the influence of e-waste recycling on the nearby area, both atmospheric particulate and gaseous phase samples were collected and the pollution characteristics of di-OPEs and tri-OPEs were measured within a typical e-waste dismantling site and its surrounding area in South China. The aims of this study were to (1) investigate the environmental occurrences, geographical distribution, and composition profiles of di-OPEs and tri-OPEs in the atmosphere within this area; (2) explore gas/particle distribution profiles and potential sources of tri-OPEs and di-OPEs; and (3) assess possible human inhalation exposure risk to di-OPEs and tri-OPEs from e-waste dismantling activities over three consecutive years.

2. Materials and methods

2.1. Sample collection

Atmospheric samples were collected from a typical e-waste dismantling park (EP) and its surrounding area (there are 18 sampling points around the e-waste dismantling park, which are named as "S1-S18") in a $9 \text{ km} \times 9 \text{ km}$ square in South China. The geographic information of sampling sites include EP (22.3275°N, 116.3621°E), S1 (23.3602°N, 116.3582°E), S2 (23.3354°N, 116.3968°E), S3 (23.3600°N, 116.3580°E), S4 (23.3301°N, 116.4099°E), S5 (23.3293°N, 116.3676°E), S6 (23.2971°N, 116.3491°E), S7 (23.3103°N, 116.3388°E), S8 (23.3458°N, 116.3239°E), S9 (23.3083°N, 116.3659°E), S10 (23.3570°N, 116.3857°E), S11 (23.3443°N, 116.3677°E), S12 (23.3569°N, 116.3717°E), S13 (23.3457°N, 116.3957°E), S14 (23.3544°N, 116.3882°E), S15 (23.3641°N, 116.3994°E), S16 (23.3249°N, 116.3525°E), S17 (23.3401°N, 116.3528°E) and S18 (23.3091°N, 116.3987°E). During the sampling period, the weather was sunny or cloudy (no sampling on rainy days), the wind direction was mainly northeast, and the sampling volume was recorded at 25 °C. The information of meteorological data was obtained from https://www.gd121.cn/index.shtml. Total suspended particulate (TSP) samples and corresponding gaseous samples were collected using medium-volume (0.3 m³/min) air samplers (Guangzhou Mingye Company) for approximately 8 h (from 9:00 am to 17:00 pm) at approximately 1.5-2 m above the ground. Quartz fiber filter membrane $(10 \times 12.5 \text{ cm}^2, \text{Munktell}, \text{Sweden})$ and polyurethane foam (Restek, China) were used to collect the particulate and gaseous phase respectively. The detailed information is provided in Supporting Information (SI), and the details of sampling points are shown in Table S1 and Fig. S1. Total of 114 samples with 19 pairs (EP and S1-S18) of samples (TSP samples and gaseous phase samples) were collected each year in October from 2017 to 2019. After sampling, samples were wrapped in aluminum foil and placed in a sealed bag, then stored in a refrigerator (-20 °C) until final analysis.

2.2. Sample analysis

After spiking with surrogate standards (TCEP-d₁₂, TPhP-d₁₅, and tributyl phosphate (TBP)-d₂₇), PUF plugs and filters were soxhlet extracted with solvent mixture (hexane: dichloromethane: acetone = 2:2:1, v/v/v) for 24 h. The extracts were concentrated and purified using Florisil SPE cartridge (2 g/12 mL), and then a solvent mixture (10 mL, ethyl acetate: dichloromethane = 1:1, v/v) was used to elute target compounds. The eluted extract was concentrated under nitrogen gas and stored in a refrigerator (-20 °C) before analysis.

Tri-OPEs were analyzed by gas chromatography coupled with triple quadrupole mass spectrometry (GC–MS-TQ8040, Shimadzu, Japan) using an electron impact ionization. An HP-5MS capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$) was used for chromatographic separation. A 1 µL sample was injected in the splitless mode, and ion source and interface temperatures were set at 230 °C and 300 °C, respectively. The oven temperature was programmed as follows: the initial temperature was set at 60 °C (held for 1 min), then raised to 200 °C at 10 °C/min, to 280 °C at 5 °C/min, to 300 °C at 10 °C/min and finally held for 10 min at 300 °C. The detailed information about column and analysis procedure is provided in SI, and the MS/MS parameters are summarized in Table S2.

Di-OPEs were analyzed by high performance liquid chromatography (HPLC, Agilent 1260 Infinity II) coupled with a 6470 triple quadrupole mass spectrometer (equipped with Agilent 1260 series binary pump (G7112B) and an autosampler (G7129A)). An HPLCONE-5C8A column $(250 \text{ mm} \times 4.6 \text{ mm i.d.})$ was used to separate different di-OPEs. The injection volume for LC/MS-MS analysis was 10 µL. H₂O (containing 0.1% formic acid, v/v) and MeOH were used as mobile phases A and B, respectively. The gradient started at 35% B and was ramped up to 75% phase B within 2 min, to 95% phase B within 20 min, and then held for 5 min before reverting to 35% phase B at a flow rate of 0.400 mL/min. Source temperature was optimized as 300 °C and nebulizer pressure was set as 45 psi. Detailed information of HPLC and MS/MS parameters is given in Table S3. Thirteen tri-OPEs congeners and seven di-OPEs were analyzed, chemical properties of them were listed in Table S4. It must be noted that DoCP (di-o-cresyl phosphate) and DpCP (di-p-cresyl phosphate) cannot be separated successfully on HPLC column, so both compounds were quantified as a compound of mDCP (DoCP + DpCP) in this work. Thus, pollution profiles of only seven instead of eight kinds of di-OPEs were reported in this study.

2.3. Quality assurance and quality control

One matrix blank and one matrix spiked sample were run with every batch of ten samples. Relative standard deviation was confirmed to be <10%. Quantitative standard curves of tri-OPEs and di-OPEs were obtained with seven concentration points each and the regression coefficient (R^2) for the calibration curve was \geq 0.99. The recoveries of di-OPEs and tri-OPEs were 71–113% and 78–106% in the spiked matrix, respectively. The method detection limits (MDLs) and the limit of quantitation (LOQ) for each compound were calculated as 3 times and 10 times S/N (ratio of signal to noise) of standard, respectively (Table S5). The concentrations of target analytes in sample were corrected by subtracting concentration of blank sample of the same batch, but not according to the recovery rate of the substitute. Detailed results can be found in Table S5.

2.4. Human exposure risk assessments

SVOCs in the atmosphere are not fully absorbed via inhalation exposure. Therefore, assessment of the non-carcinogenic risk via inhalation exposure to tri-OPEs and di-OPEs should consider inhalation bioaccessibility (Wannomai et al., 2021). The average daily dose (ADD) of di-OPEs and tri-OPEs via inhalation exposure was calculated using Eq. (1). The hazard index (HI) of di-OPEs and tri-OPEs can be calculated by Eq. (2).

$$ADD = C \times IF \times IR \times ET/BW \tag{1}$$

$$HI = ADD/RfD$$
(2)

In the above equations, C is the concentration of tri-OPEs and di-OPEs measured in atmosphere (pg/m^3) ; IF is inhalable fraction (%) (Hu et al., 2019); ET represents outdoor exposure time, the average time spent in an outdoor environment per person is 6 h per day (Syed et al., 2020); IR represents inhalation rate (m^3/d) ; and BW represents average body weight (kg). The values of IR and BW vary with age (Table S6) (Guida et al., 2021) and the recommended values of oral reference dose (RfD) are from the USEPA (Table S7) (Ali et al., 2012). HI value < 1 means no non-carcinogenic risks of these chemicals to human health.

3. Results and discussion

3.1. Concentrations and composition profiles of tri-OPEs and di-OPEs

The detection frequencies (DFs) and concentrations (gaseous + particulate phase) of thirteen tri-OPEs and seven di-OPEs from e-waste dismantling park and surrounding area are summarized in Table 1. All these target chemicals were detected in atmospheric samples from ewaste dismantling park, while DFs of the samples in surrounding area were relatively lower. Specifically, DFs of three tri-cresyl phosphates (p-TCP, m-TCP, and o-TCP) ranged from 44.5 to 94.5%, and DFs of other di-OPEs except bis-(1-chloro-2-propyl) phosphate (BCIPP), DPhP, and DBP ranged from 72.2 to 100%.

Total concentrations of tri-OPEs (\sum tri-OPEs) in atmospheric samples from e-waste dismantling park in 2017, 2018, and 2019 were 1.30×10^8 , 4.60×10^6 , and 4.01×10^7 pg/m³, respectively, which were 1757, 194, and 10,897 times higher than the corresponding median concentrations of the surrounding area. Similar to tri-OPEs, \sum di-OPEs in e-waste dismantling park were 1.14×10^3 , 1.10×10^3 , and 0.35×10^3 pg/m³, respectively, which were also higher than the corresponding values of surrounding areas (ranging from 1.36 to 141 pg/ m³). From the perspective of time variation, the concentrations of tri-OPEs in atmosphere in e-waste dismantling park were the highest in 2017, decreased dramatically in 2018, and then increased again in 2019 (the concentration in 2019 was lower than that in 2017, but higher than that in 2018). In contrast, the concentrations of di-OPEs in 2017 and 2018 were similar, but decreased in 2019. Therefore, it can be concluded that the concentration of tri-OPEs in the e-waste dismantling park was undulant, while the concentration of di-OPEs decreased year by year. This is because the concentrations of di-OPEs and tri-OPEs in the e-waste dismantling park mainly depend on the dismantling activity intensity on sampling day. The concentrations of both di-OPEs and tri-OPEs in surrounding area decreased year by year, demonstrating that the pollution of them in surrounding area was improved after strengthening the management. The above results indicated that primitive e-waste recycling activity might be an important source for the emissions of tri-OPEs and di-OPEs into the surrounding atmospheric environment. However, there are some limitations of these findings due to the limitation of sample size and time.

Since distinct congeners of tri-OPEs were targeted in previous reports, the direct comparison of the concentrations of \sum tri-OPEs among these reports might be misleading. Nevertheless, \sum tri-OPEs found in e-waste dismantling park of this research was the highest $(4.60 \times 10^6 - 1.30 \times 10^8 \text{ pg/m}^3)$ ever reported in atmospheric particles, which was substantially higher than that found around an airport in New York state, United States (ranging from 1.32×10^3 to $2.07 \times 10^4 \text{ pg/m}^3$) (Li et al., 2019b) and four sites in the Houston metropolitan area in TSP samples (ranging from 3.20×10^2 to $3.50 \times 10^3 \text{ pg/m}^3$)

	Target	E-waste dism	antling park		Surrounding a	area							
		2017	2018	2019	2017 (n = 18	3)		2018 (n = 18	(2019 (n = 18)		
					Median ^b	Range	$DF(\%)^{a}$	Median	Range	DF (%)	Median	Range	DF (%)
	tri-OPEs												
	TPrP	$3.77 imes 10^1$	$1.10 imes 10^1$	$5.30 imes10^1$	6.63	$1.44\text{-}4.59 \times 10^1$	100	0.73	0.30-2.38	100	0.87	0.42-4.08	100
	TEP	4.55×10^3	$3.61 imes 10^4$	$7.11 imes 10^4$	4.32×10^{3}	$5.25 imes 10^2$ - $2.52 imes 10^4$	100	$5.29 imes10^2$	$1.41 imes 10^2 - 1.78 imes 10^3$	100	$5.39 imes 10^2$	3.19×10^2 -1.40 $\times 10^3$	100
	TBP	8.37×10^3	12.0×10^{3}	$5.28 imes10^3$	7.33×10^{1}	3.37×10^{1} -1.47 $\times 10^{2}$	100	$1.77 imes10^1$	$7.61 - 8.72 \times 10^{1}$	100	5.13	$1.19-4.98 imes 10^{1}$	100
	TCEP	2.47×10^5	$3.78 imes 10^4$	1.41×10^{5}	$9.71 imes 10^2$	$3.59 imes 10^2 - 5.49 imes 10^3$	100	$1.40 imes 10^2$	$4.51\times10^{1}\text{-}4.06\times10^{2}$	100	$1.79 imes 10^2$	4.03×10^{1} -7.78 $\times 10^{2}$	100
	TCPP	$2.26 imes 10^7$	$1.30 imes10^6$	$1.01 imes 10^7$	$1.86 imes 10^4$	$2.80 imes 10^3 - 2.09 imes 10^5$	100	$1.12 imes10^4$	2.83×10^{2} - 1.37×10^{5}	100	6.98×10^2	$2.59 imes 10^2 - 4.09 imes 10^4$	100
	TCIPP	8.42×10^{6}	$3.84 imes 10^5$	2.90×10^{6}	6.79×10^3	$8.38 \times 10^2 - 1.80 \times 10^5$	100	4.40×10^3	$5.83 imes 10^{1}$ -4.14 $ imes 10^{4}$	100	1.63×10^2	6.30×10^{1} -4.14 × 10^{4}	100
	TDCIPP	$1.77 imes 10^5$	$8.99 imes 10^3$	$6.58 imes10^4$	$1.51 imes 10^2$	$3.56 imes 10^{1}$ -4.55 $ imes 10^{2}$	100	$8.41 imes10^1$	$2.78 - 1.82 \times 10^3$	100	2.93×10^1	$1.59 imes 10^{1}$ -2.79 $ imes 10^{2}$	100
	TPhP	$9.57 imes 10^7$	$2.77 imes10^{6}$	$2.63 imes 10^7$	$2.79 imes10^4$	$2.03 \times 10^3 - 3.13 \times 10^5$	100	4.57×10^3	$2.18 imes 10^2 - 1.00 imes 10^5$	100	$2.77 imes10^2$	$1.43 imes 10^2$ – $5.10 imes 10^4$	100
4	EDP	6.11×10^3	1.42×10^{3}	$5.24 imes10^3$	$9.49 imes 10^1$	4.81×10^{1} -7.74 $\times 10^{2}$	100	$4.18 imes 10^1$	$0.68 - 3.87 \times 10^3$	100	$5.51 imes10^1$	1.52×10^{1} -2.33 $\times 10^{2}$	100
	p-TCP	$1.86 imes 10^6$	$4.75 imes 10^4$	$3.15 imes 10^5$	2.22×10^2	$ m n.d2.30 imes10^3$	77.8	$1.21 imes 10^1$	$n.d1.44 \times 10^{2}$	67.7	n.d.	$ m n.d2.08 imes10^2$	50.0
	m-TCP	$1.13 imes 10^5$	3.61×10^{3}	$3.19 imes10^4$	2.31	${ m n.d1.08 imes10^2}$	61.1	n.d.	$n.d2.15 \times 10^1$	44.5	0.27	$ m n.d2.04 imes10^{1}$	50.0
-	o-TCP	6.92×10^{5}	$2.21 imes 10^4$	1.56×10^5	$7.63 imes 10^1$	$ m n.d7.81 imes10^2$	88.9	$1.30 imes10^1$	$n.d2.69 \times 10^2$	94.5	1.54	$ m n.d9.93 imes10^{1}$	75.0
	Tippp	$8.90 imes 10^4$	2.29×10^{3}	4.86×10^{1}	$2.14 imes 10^1$	$ m n.d1.36 imes10^2$	100	2.39	n.d6.35	84.4	0.68	$ m n.d2.53 imes10^1$	93.8
	\sum opes	$1.30 imes10^8$	$4.60 imes10^{6}$	4.01×10^7	$7.40 imes 10^4$	9.09×10^3 -7.09 $\times 10^5$		2.37×10^4	$1.44 \times 10^3 - 1.91 \times 10^5$		3.68×10^3	$1.29 \times 10^3 - 1.35 \times 10^5$	
-	di-OPEs												
-	BCEP	1.07	n.d.	0.71	0.44	n.d2.52	72.2	0.46	n.d1.47	83.3	0.23	n.d.–1.10	87.5
-	BCIPP	$3.75 imes 10^2$	1.84×10^{2}	1.49×10^{2}	3.50	$ m n.d1.34 imes10^{1}$	94.4	0.64	0.11-3.66	100	0.79	$0.28 - 3.27 imes 10^{1}$	100
-	DPhP	7.06×10^2	8.46×10^2	1.82×10^{2}	2.31×10^{1}	$2.59{-}1.26 imes 10^{2}$	100	2.78	0.77-9.30	100	2.56	$0.71{-}1.43 imes10^{1}$	100
-	DBP	7.05	4.75	2.33	2.04	0.84-4.43	100	0.32	0.14-0.77	100	0.40	0.17-2.71	100
-	BDCIPP	5.72	1.50	1.24	0.97	0.43-2.06	100	0.25	n.d1.09	94.4	0.29	n.d0.59	93.8
	mDCP	2.39×10^{1}	3.08×10^{1}	4.73	0.25	0.04-2.25	100	0.04	n.d0.15	88.9	0.02	n.d0.20	81.2
-	BBOEP	1.95	1.00	0.94	0.16	n.d1.11	83.3	0.09	n.d0.69	88.9	0.06	n.d0.46	87.5
	∑ di-OPEs	$1.14 imes 10^3$	$1.10 imes 10^3$	3.46×10^{2}	3.16×10^{1}	$8.27 - 1.41 imes 10^2$		4.51	$1.36-1.43 imes 10^{1}$		5.23	$2.13-4.85 \times 10^{1}$	
-	^a n.d. = Not c	letected. $DF = \Gamma$ v one sampling s	betection frequen-	cies. e dismantling par	k. so there is no n	nedian concentration.							
				5									

Table 1 Concentrations (pg/m^3) of tri-OPEs and di-OPEs in atmosphere samples from an e-waste dismantling park and its surrounding area.

m³) (Clark et al., 2017). Besides, relatively higher concentrations of \sum tri-OPEs were detected in air particulate matter in offices of Hangzhou, China (5.0×10^3 – 1.48×10^6 pg/m³) (Yang et al., 2014), which may be related to tri-OPEs are widely used in household products and electronic appliances. The variation of tri-OPEs levels between different reports may be related to specific sources, and needs more studies to clarify.

For individual congeners, TPhP concentration was the highest in the e-waste dismantling park, followed by Cl-tri-OPEs, such as TCPP and tris (2-chloropropyl) phosphate (TCIPP). These two compounds accounted for 73–99% of \sum tri-OPEs, and concentration of alkyl-tri-OPEs was the lowest. This may be related to the fact that TPhP is widely used as flame retardants, plasticizer additives, and polyvinyl chloride in electronic and industrial products (Lu et al., 2017; Wang et al., 2020a, 2020b), and Cl-tri-OPEs are persistent in the environment and has a wide application in electronic products (Li et al., 2019a, 2019b; Liu et al., 2016). This result was consistent with surface soil samples collected in the same area, where TPhP had the highest content followed by Cl-tri-OPEs (Ge et al., 2020). TPhP was also found to be the major organic constituent of particulate matters released during printed circuit board recycling process, suggesting that it may act as a marker for ewaste dismantling (Bi et al., 2010). In addition, TPhP content was the highest in an e-waste region, but TCIPP was the most dominant compound in urban region (Wang et al., 2018). TPhP concentration was significantly higher compared to other tri-OPEs in e-waste area. Therefore, TPhP could be used as an indicator of the e-waste dismantling process.

Among the detected di-OPEs, DPhP was the most predominant congener, accounting for 62%, 77%, and 53% of \sum di-OPEs in the e-waste dismantling park in 2017, 2018, and 2019, respectively. BCIPP was the second-highest contributing congener, accounting for 33%, 17%, and 43% of \sum di-OPEs in 2017, 2018, and 2019, respectively. Relatively higher contributions of DPhP and BCIPP were also found in the surrounding area, indicating that these congeners of di-OPEs might diffuse from the e-waste dismantling park. However, DBP contributed only 1% in e-waste dismantling park while it was as high as 21% in surrounding area. One possible reason was that besides e-waste dismantling, other sources also contributed DBP. For instance, DBP is widely used in commercial products and in metal extraction (Quintana et al., 2006). TBP, the parent compound of DBP, is predominantly used as plasticizer in lubricants and plastic (Veen and Boer, 2012). The emission of TBP from private plastic recycling workshops also makes a large contribution (Ge et al., 2020), as TBP may be degraded to DBP during the plastic recycing processs. On the other hand, it might be attributed to the half-life times of different compounds in atmosphere were different (Wu et al., 2020). Nevertheless, the predominance of DPhP (accounting for $\geq 60\%$ of \sum di-OPEs) found in air particles within the e-waste dismantling park further indicated that DPhP was derived from e-waste dismantling activities.

3.2. Gas-particle partitioning of tri-OPEs and di-OPEs

Gas-particle partitioning results of tri-OPEs and di-OPEs in atmosphere from surrounding area and the e-waste dismantling park are illustrated in Figs. 1 and S2. Tri-OPEs were mainly distributed in particulate phase, accounting from 70% to 100% at different sampling sites. Specifically, aryl-tri-OPEs were mainly deposited in particulate phase, with a contribution of 70-100%. For Cl-tri-OPEs, the contributions of gaseous-phase accounted for <21%, except at site S11 (accounting for 40%). The sampling site S11 is close to a densely populated living area, and other unknown sources may exist since Cl-tri-OPEs are frequently used in paint, lacquer, glue, and industrial processes (Wei et al., 2015). Cl-tri-OPEs were also found to be the most dominant compounds in office air particulate matter in Hangzhou, China (Yang et al., 2014). Therefore, further research is needed to clarify. However, for alkyl-tri-OPEs, the gas-particle partitioning varied significantly at different sampling sites, which might be related to the direct emissions of alkyl-tri-OPEs from other non-e-waste sources. As previously reported, alkyl-tri-OPEs are also used as hydraulic fluid and lubricant additives (Shi et al., 2020), which can be easily released in gaseous form. In addition, aryl-tri-OPEs and Cl-tri-OPEs were exclusively detected in particulate phase (>99%) for air sampled from e-waste dismantling park, while more tri-OPEs components were volatized into the gaseous phase in the surrounding area. This might be ascribed to lower vapor pressure and higher octanol/air partition coefficient (K_{OA}) values (Wang et al., 2019) of aryl-tri-OPEs and Cl-tri-OPEs compared to alkyl-tri-OPEs, which tend to bind to particulate matter. For aryl- and Cl-tri-OPEs, the



Fig. 1. Gas-particle partitioning of tri-OPEs ((a) alkyl-tri-OPEs; (b) Cl-tri-OPEs; (c) aryl-tri-OPEs) and di-OPEs ((d) alkyl-di-OPEs; (e) Cl-di-OPEs; (f) aryl-di-OPEs) in atmospheric samples from the e-waste dismantling park and the surrounding area.

gaseous phase contributions in the surrounding area were also dramatically higher than those in e-waste dismantling park. As the major tri-OPEs components emitted from e-waste dismantling park, diffusion velocity of particle-bonded aryl- and Cl-tri-OPEs was not as fast as that of the gaseous phase. The proportion of gaseous-phase might be increased during diffusion and transmission of pollutants.

As reported, tri-OPEs were also exclusively found in the particulate phase in an indoor environment (Carlsson et al., 1997) and e-waste recycling plant (Sjödin et al., 2001), with a contribution \geq 99% of the total tri-OPEs, which was consistent with the results for the e-waste dismantling park in this study. The gas-particle partitioning could differ widely because of the uncertainty in predicted saturation vapor pressure (P_S) (of the subcooled liquid) (An et al., 2011) and K_{OA} (Salthammer and Schripp, 2015). Flame retardants, which typically possess low Ps and high K_{OA}, prefer binding with particles (Veen and Boer, 2012). However, the gas-particle partitioning of individual compounds of tri-OPEs differed widely, rather than absorbed onto atmospheric particles due to their different values of K_{OA} (Wolschke et al., 2016).

To simulate gas-particle partitioning, Pankow defined partitioning constant (K_p) as $K_p = F/A/TSP$, where F (ng/m³) and A (ng/m³) are particulate-associated and gas-associated levels, respectively; and TSP is the level of TSP ($\mu g/m^3$) (Pankow, 1988). Moreover, the relationship between K_p and subcooled steam pressure (p_L^0) was also proposed as: $\log K_{\rm p} = m_{\rm r} \log p_{\rm L}^0 + b_{\rm m}$. For a balanced distribution, m_r is close to -1(Pankow and Bidleman, 1992). To explore the gas-particle partitioning equilibrium of tri-OPEs, the relationship between log $K_{\rm P}$ and log $p_{\rm L}^0$ of tri-OPEs was analyzed at three atmospheric sampling points: e-waste dismantling park, upwind area, and downwind area. As Fig. S3 show, the gas-particle partitioning in the upwind direction was closer to the equilibrium state, followed by the downwind direction, while the gasparticle partitioning in the e-waste dismantling park was the most unbalanced (the values of m_r for e-waste dismantling park, upwind area, and downwind area were -0.2889, -0.92194, and -0.44678, respectively). The possible reason was that there was a constant input of tri-OPEs in the e-waste dismantling area, and the downwind area was influenced by e-waste dismantling. Therefore, the gas-particle partitioning in e-waste dismantling area and the downwind area did not reach the equilibrium state, while the upwind point was not influenced by e-waste recycling and was close to the equilibrium state. This information further demonstrated that e-waste dismantling is a key source of tri-OPEs.

For di-OPEs, gas-particle partitioning of Cl-di-OPEs and aryl-di-OPEs showed similar trends as for tri-OPEs (Fig. 1). Both congeners were also exclusively found in particulate phase in e-waste dismantling park, but their proportions in gaseous phase in the surrounding area increased due to the diffusion and transport of these pollutants (Fig. S2). Their formation mechanism might be similar to that of tri-OPEs discussed above. Specifically, DPhP was more likely to evaporate into gaseous phase than BCIPP and other di-OPEs (Fig. S4). The reason for higher concentration of DPhP in the gaseous phase remains unknown. Theoretically, DPhP has a higher K_{OA} than BCIPP (Tan et al., 2019), which would favor its deposition in particulate phase. Since DPhP was the most dominant compound of di-OPEs, gas-particle partitioning of di-OPEs could also be determined by DPhP distribution. Besides, compared with alkyl-tri-OPEs, alkyl-di-OPEs were more likely to distribute in particulate phase, and variations in their gas-particulate distribution among different sampling sites inside and outside the e-waste dismantling park were smaller. These results indicated that other non-e-waste sources might determine the gas-particle partitioning of alkyl-di-OPEs, and more future research is required to clarify this issue.

3.3. Source appointment of tri-OPEs and di-OPEs

To reveal potential sources of di-OPEs, correlations of di-OPEs and their parent tri-OPEs were analyzed. Significant linear correlations were found between TPhP and DPhP ($R^2 = 0.53$, p < 0.01), TCIPP and BCIPP ($R^2 = 0.49$, p < 0.01), as well as TBP and DBP ($R^2 = 0.53$, p < 0.01) (Fig. 2), indicating that DPhP, BCIPP and DBP in the atmosphere might come from the degradation of their parent tri-OPEs or share a similar source. As is known, the oligomeric organophosphorus flame retardants (o-PFRs) of resorcinol bis(diphenylphosphate) (RBDPP) and bisphenol A bis(diphenylphosphate) (BPA-BDPP) include both TPhP and DPhP. Commercial diethylene glycol bis[di(2chloroisopropyl) phosphate] (DEG-BDCIPP) includes TCIPP and BCIPP (Matsukami et al., 2015). However, no significant correlation between TCEP and BCEP ($R^2 = 0.096$, P = 0.10) was observed, indicating that they might have different sources or environmental behaviors. As reported, TCEP has a longer half-life time in atmosphere than TCIPP and thus might not easily be degraded, although these two chemicals are structurally similar (Wang et al., 2019). Therefore, TCEP does not readily convert to BCEP in air, as well as in urine (He et al., 2018). Researchers also suggested that the relative importance of the different sources impacted the variation of different di-OPEs (Tan et al., 2019).

To further understand the sources of di-OPEs and tri-OPEs, principal component analysis (PCA) was performed (Fig. S5) and the rotated component matrix for loads of di-OPEs and tri-OPEs in principal component are shown in Table S8. Two principal components were responsible for 76.9% of the total variance for all samples, which can basically explain the data. The first principal component (PC1) was responsible for 68.6% of the total variance, which was predominantly weighted by most of the di-OPEs and tri-OPEs. It has been reported that Cl-tri-OPEs are used as alternatives for penta-BDE (Stapleton et al., 2012) and nonchlorinated tri-OPEs are employed as plasticizer additives in electronic products (Lu et al., 2017). In addition, RBDPP and BPA-BDPP are used as alternatives for BDE-209 in electronic consumer products, and TPhP is often added to RBDPP and BPA-BDPP products (Brandsma et al., 2013). The concentration analysis in this study showed that ewaste dismantling produced a large quantity of tri-OPEs and di-OPEs. Therefore, PC1 might represent the source from e-waste dismantling activities. The second principal component (PC2) accounted for 8.3% of total variance and there was a larger load on di-OPEs than tri-OPEs. This was because di-OPEs could originate not only from tri-OPEs degradation, but also directly from commercial application. For example, DPhP is a chemical additive and industrial catalyst (Mitchell et al., 2019). Triethyl phosphate (TEP) is used as a plasticizer in polyvinylchloride, polyester resins, and polyurethane foam (Wei et al., 2015). Thus, PC2 might be related to local industries, such as recycling old hardware and electrical appliances, and plastics.

3.4. Spatial and temporal distribution characteristics

To explore the influence of the emission of tri-OPEs and di-OPEs from e-waste dismantling park on the surrounding area, the geographical distributions of the logarithmic concentrations of \sum tri-OPEs and \sum di-OPEs were investigated for three consecutive years (Fig. 3). The pollution in e-waste dismantling park was much more severe than that in the surrounding area, and the pollution was generally significant in the southern area downwind of e-waste dismantling park, which might be affected by the wind direction at that time and spread from the e-waste dismantling park. Our previous report on emission of VOCs from the same e-waste dismantling park also found that wind could affect the transport of VOCs (Zhang et al., 2020).

Furthermore, it was found that the trends of the spatial spread of tri-OPEs and di-OPEs differed from 2017 to 2019. In 2017, tri-OPEs were released in a narrow space but their pollution was relatively severe, particularly the southern area of the e-waste dismantling park. Comparatively, a wider geographical range was observed in 2018. In addition, although the levels in 2018 were lower than those in 2017, the pollution of tri-OPEs in the residential area in the northern part of ewaste dismantling park was also seriously polluted. This could be ascribed to the plastic recycling activity without permission, since some



Fig. 2. Concentration associations of tri-OPEs with their respective di-OPEs in the atmospheric samples. (a) TPhP-DPhP; (b) TBP-DBP; (c) TCIPP-BCIPP; (d) TCEP-BCEP (P < 0.05 indicates significant associations).

(b) 2018-tri-OPEs

tri-OPEs are also used as plasticizers (Wei et al., 2015). The impact range of pollution in 2019 was similar to that in 2017, but the levels of pollution were reduced. Unlike tri-OPEs, the pollution degree and pollution

range of di-OPEs in 2018 and 2019 were far lower than those in 2017 (Fig. 3). In general, the contamination of tri-OPEs, as well as di-OPEs around the e-waste dismantling park, reduced year by year.

(c) 2019-tri-OPEs

(a) 2017-tri-OPEs



Fig. 3. Spatial and temporal distribution of tri-OPEs ((a) 2017-tri-OPEs; (b) 2018-tri-OPEs (c) 2019-tri-OPEs) and di-OPEs ((d) 2017-di-OPEs; (e) 2018-di-OPEs; (f) 2019-di-OPEs). Data used was the logarithm of the total concentrations (Log10).

To better understand the spatial and temporal distribution characteristics of tri-OPEs, the spatial distribution of the main tri-OPEs compounds, TPhP and Cl-tri-OPEs, was further studied (Fig. S6). TPhP pollution in e-waste dismantling park was the most severe, followed by the southern area downwind of the e-waste dismantling park, which was consistent with the pollution characteristics of \sum tri-OPEs. Different from TPhP, alkyl-tri-OPEs and Cl-tri-OPEs had lower pollution concentrations and had a more ubiquitous distribution (Fig. S6). It might be mainly because alkyl-tri-OPEs and Cl-tri-OPEs originated not only from e-waste dismantling but also from other non-e-waste sources. To further clarify the pollution characteristics of di-OPEs, spatial distributions of specific isomers were also analyzed, including DPhP, BCIPP, DBP, and BDCIPP (Fig. S7). It was found that the geographical distribution of DPhP was similar to that of TPhP, the result further indicated that DPhP mainly originated from TPhP degradation or the impurities of TPhP products.

Although the concentrations varied, the compositions were similar for different sampling years. Similarly, no significant difference existed in the composition of homologs between surrounding area and e-waste dismantling park (Fig. 4). Different from this study, previous studies found that TCIPP was the dominant compound in the outdoor air of urban region, followed by TPhP (Wang et al., 2018), while \sum TCPP (tris-(2-chloroisopropyl)-phosphate) was the dominant compound in the urban atmosphere of Pakistan (Syed et al., 2020). These results indicated that the pollutants in the surrounding area mainly diffused from the e-waste dismantling park. A clear downward trend in concentration was observed for these chemicals in the surrounding area, and the total concentrations of both tri-OPEs and di-OPEs in 2019 were 10 times lower than those in 2017. These results indicated



Fig. 4. Composition profiles of tri-OPEs (a) and di-OPEs (b) in the atmosphere samples from e-waste dismantling area.

that the amounts of pollutants released into the surrounding areas of the e-waste dismantling park decreased, since local government has strengthened the prevention and control of pollution.

3.5. Non-carcinogenic risk assessment via inhalation exposure

According to the characteristics of different ages, we divided into five different age groups, included infants (0-2 year), the first years of children (2-6 year), the last years of children (6-11 year), youth (11-16 year) and adults (16-70 year). Non-carcinogenic risks to different age groups via inhalation exposure were evaluated to assess the adverse effects of tri-OPEs on local residents. As the ADD of di-OPEs was much lower than that of tri-OPEs and the recommended RfD of di-OPEs is unknown, the health risks of di-OPEs are not discussed here. In this study, it was assumed that in the worst case, all particle-bound and gaseous tri-OPEs were absorbed and utilized, that was, IF was 100%. The hazard index (HI) values of tri-OPEs are shown in Fig. 5, BW, IR, RfD, etc. would cause differences in HIs for different life-stages (Guida et al., 2021). The HI values of all tri-OPEs in e-waste dismantling park were higher than the surrounding area, indicating that people in the e-waste dismantling park had higher exposure risk than those in the surrounding area. HI values of both areas were below the safe thresholds (HI = 1), indicating that there was no potential noncarcinogenic risk of these chemicals to human health. In the e-waste dismantling park, the non-carcinogenic risk of tri-OPEs was the highest in 2017, decreased in 2018, and then increased again in 2019. However, the non-carcinogenic risk of tri-OPEs decreased year by year in the surrounding area. The non-carcinogenic risk decreased with age in both ewaste dismantling park and surrounding area, which was mainly related to inhalation rate and body weight.

Since tri-OPEs are mainly composed of Cl-tri-OPEs and TPhP, the non-carcinogenic risks of TCPP, TCIPP, TDCP and TPhP were further analyzed (Fig. S8). The non-carcinogenic risk of TPhP was the highest, followed by TCPP and TCIPP, while TDCIPP had the lowest risk. The non-carcinogenic risks of TCPP, TCIPP, TDCP and TPhP in e-waste dismantling park were the highest in 2017, decreased in 2018, and then increased in 2019. In the surrounding area, the non-carcinogenic risks of TCPP and TCIPP were equivalent in 2017 and 2018, and decreased in 2019, while the non-carcinogenic risks of TDCIPP and TPhP decreased year by year. These results might be mainly related to their concentrations in the atmosphere and their RfD.

From the above results, it is evident that more attention should be given to the non-carcinogenic risk of TPhP, TCPP and TCIPP to the



Fig. 5. Non-carcinogenic risk of inhalation exposure to tri-OPEs with consecutive three years (Including five age groups of people: 0–2 years old; 2–6 years old; 6–11 years old; 11–16 years old; 11–70 years old).

lower age groups (0–16 years old). Although there was no noncarcinogenic risk of these chemicals via inhalation exposure in this study, considering their potential toxicity, more studies are still needed to accurately assess their health risk. For example, the risk contribution via dermal contact, inhalation, and ingestion together can be studied in the future.

4. Conclusions

Pollution profiles of thirteen tri-OPEs and seven di-OPEs were analyzed in air of an e-waste dismantling park and surrounding area in South China. The target analytes were widely detected, the concentrations of tri-OPEs were higher than those of di-OPEs, and the pollution in e-waste dismantling park was more serious compared to the surrounding area. Tri-OPEs and di-OPEs were primarily affected by ewaste recycling, while di-OPEs were more affected by other factors than tri-OPEs, which should be studied further. TPhP and DPhP were the predominant congeners of tri-OPEs and di-OPEs, and TPhP could be used as an indicator of the e-waste dismantling activity. Finally, although the non-carcinogenic risk of these chemicals via inhalation exposure to human health was acceptable in this study, human exposure risk should also be given more attention in the future.

CRediT authorship contribution statement

Congcong Yue: Methodology, Formal analysis, Writing – original draft. **Shengtao Ma:** Methodology, Formal analysis. **Ranran Liu:** Methodology, Data curation. **Yan Yang:** Visualization, Investigation. **Guiying Li:** Writing – review & editing. **Yingxin Yu:** Visualization, Investigation. **Taicheng An:** Conceptualization, 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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Appendix A. Supplementary data

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