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Occurrence of two novel triazine-based flame retardants in an E-waste recycling area in South China: Implication for human exposure

Mingjie Shen [a], Jiali Ge [a], James C.W. Lam [b], Mingshan Zhu [a], Juan Li [a], Lixi Zeng [a],*

[a] *School of Environment, Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, China*
[b] *Department of Science and Environmental Studies, The Education University of Hong Kong, Hong Kong, China*

HIGHLIGHTS

- TDBP-TAZTO was detected with high levels in dust from e-waste recycling area.
- TTBP-TAZ was also found in dust from e-waste recycling area in China.
- TDBP-TAZTO exhibits significantly higher levels in e-waste dust than legacy HBCDD.
- Occupational and general dust exposure to TDBP-TAZTO and TTBP-TAZ was assessed.
- Dust exposure to TDBP-TAZTO was significantly higher for occupational workers.

GRAPHICAL ABSTRACT

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ABSTRACT

The recent increase in the use of alternative flame retardants (FRs) in consumer products has led to emerging contaminants in the environment. Identification of novel FRs is urgently needed because the potential threat posed by these chemicals has provoked considerable attention, but the details of the threat are not yet widely understood. In this study, two novel triazine-based FRs, tris(2,3-dibromopropyl) isocyanurate (TDBP-TAZTO) and 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ), were identified in dust samples from an e-waste recycling area in China. Two legacy FRs, namely, tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD), were also analyzed for comparison. The mean level of TDBP-TAZTO in the e-waste dust samples was found to be much higher (2060 ng g^{-1}) than that of HBCDD (526 ng g^{-1}), while the mean level of TTBP-TAZ in residential dust samples was moderately higher (119 ng g^{-1}) than that of HBCDD (35.7 ng g^{-1}). A comparison of the TDBP-TAZTO and TTBP-TAZ concentrations with those of other alternative and legacy FRs indicated that TDBP-TAZTO is a major FR that is currently used in China. The estimated daily intake of TDBP-TAZTO via dust ingestion for occupational workers was much higher than that of HBCDD and was also much higher than for local adults and children. Exposure to TDBP-TAZTO poses a potentially high risk to the health of the local population, especially for the occupational workers, when the multicomponent chemical 'cocktail' effects are taken into account. More investigations on the environmental behaviors and risk factors of TDBP-TAZTO and TTBP-TAZ in various environmental matrices, as well as their toxicological effects, should be performed in the future.

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* Corresponding author at: School of Environment, Jinan University, China.
E-mail address: lxzeng@jnu.edu.cn (L. Zeng).

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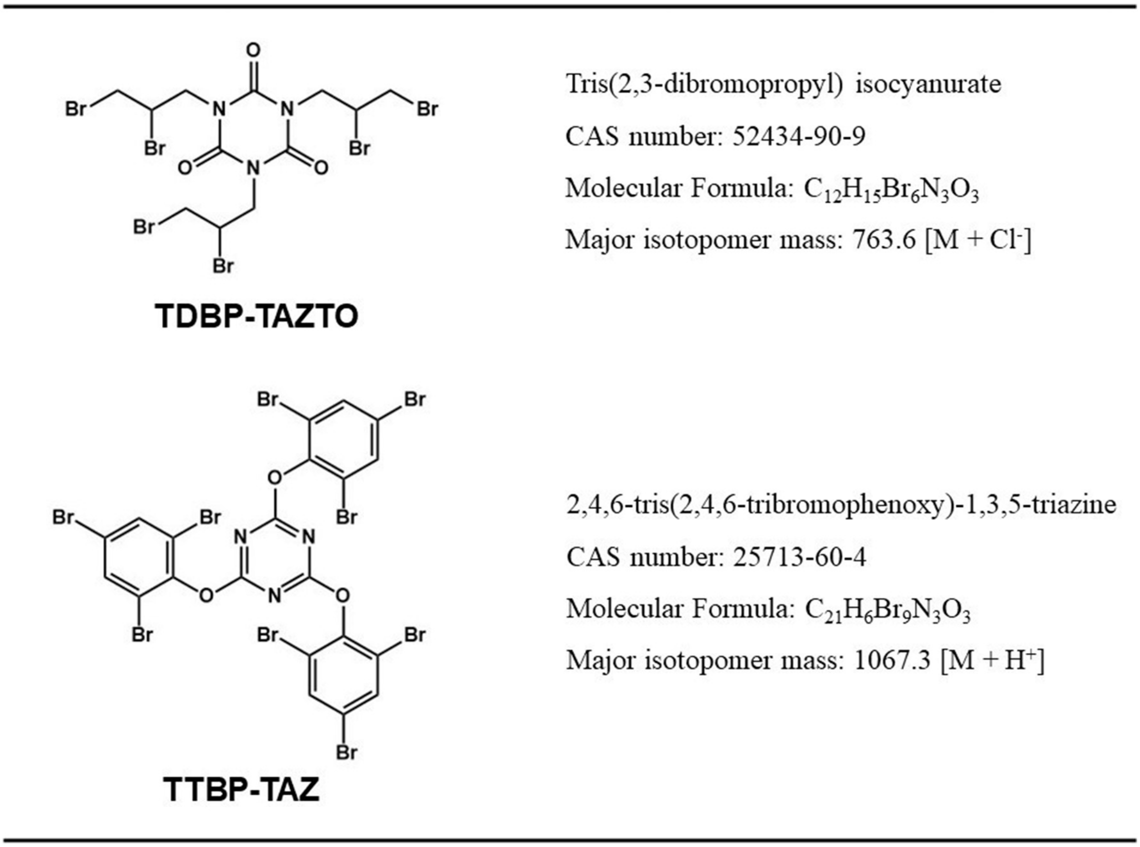
1. Introduction

Brominated flame retardants (BFRs) are widely added to various commercial products such as plastic, textiles, and electric and electronic equipment (Bergman et al., 2012). Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA) are traditionally the three most widely used BFRs and have high production volumes (Larsson et al., 2018). PBDEs and HBCDD have been found to be toxic, persistent and bioaccumulative in many studies (Besis and Samara, 2012; Dingemans et al., 2011; Marvin et al., 2011; Vonderheide et al., 2008). Given the environmental and health hazards of pentaBDE, octaBDE, decaBDE and HBCDD, they were classified as persistent organic pollutants (POPs) by the Stockholm Convention on POPs during 2009–2017. Thus far, the use of commercial PBDEs and HBCDD is banned or restricted worldwide. TBBPA is an endocrine disruptor of concern (Lilienthal et al., 2008; Van der Ven et al., 2008). However, unlike for PBDEs and HBCDD, there are no regulatory restrictions on the use of TBBPA in Asia or other countries and regions (Barghi et al., 2017).

Bans or restrictions on the use of PBDEs and HBCDD have led to their replacement with novel flame retardants (FRs). Accordingly, triazine structure-based polymers as a group of novel alternative FRs are currently being used in various electronic products (Ballesteros-Gómez et al., 2014). Tris(2,3-dibromopropyl) isocyanurate (TDBP-TAZTO; alternative acronym: TBC) and 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) (Fig. 1) are two widely used triazine FRs that are replacing the banned or regulated FRs (Ballesteros-Gómez et al., 2014; Guo et al., 2018; Ruan et al., 2009).

TDBP-TAZTO is a novel triazine-based additive FR. Owing to its excellent abilities as a flame retardant, TDBP-TAZTO is widely used in polymer products. China has begun to produce and use TDBP-TAZTO extensively since the mid-1980s (Ruan et al., 2009). It was reported that the annual production of TDBP-TAZTO in China was approximately 500 t in 1996, but, to date, there is a lack of information on its global production volume (Ruan et al., 2009). Despite this, increasing production is expected due to a huge demand for its use in electronic products. TDBP-TAZTO was first identified by Ruan et al. (2009) in different environment matrices at a manufacturing plant in South China. Other studies have found that TDBP-TAZTO can accumulate in biota, sediment and soil (Tang et al., 2014; Wang et al., 2017; Wang et al., 2016; Wang et al., 2013; Zhu et al., 2012). Another recent study found an unexpectedly high concentration of TDBP-TAZTO in curtains (Miyake et al., 2017). Toxicological studies indicated that TDBP-TAZTO can result in endocrine toxicity and neurotoxicity in animals (Li et al., 2011; Li et al., 2015; Ye et al., 2015; Zhang et al., 2011). TDBP-TAZTO is now listed as a high-priority hazardous chemical by the UK Environmental Agency. Given its potential hazards and lack of restrictive regulations on its use, the release of TDBP-TAZTO into the environment could become a concern. Even though TDBP-TAZTO has been found in different environmental samples and is present in consumer products, there is no information on the levels of TDBP-TAZTO in indoor or outdoor dusts. There is an urgent need to provide the necessary knowledge on the occurrence, distribution, human exposure, and potential health risks of this novel FR.

TTBP-TAZ is another novel triazine-based BFR that is used as a substitute for the currently banned PBDEs and HBCDD (Ballesteros-Gómez et al., 2014). Until now, only a few studies (Ballesteros-Gómez et al., 2014; Guo et al., 2018) have reported the occurrence of TTBP-TAZ in the environment. TTBP-TAZ was first identified in the plastic casings of electronic products and in indoor dust samples from the Netherlands (Ballesteros-Gómez et al., 2014). Recently, a study reported that TTBP-TAZ was identified in selected samples from North America (Guo et al., 2018). It is estimated that TTBP-TAZ has a long persistence of ~17 years (Liagkouridis et al., 2015). To our knowledge, information



Tris(2,3-dibromopropyl) isocyanurate
CAS number: 52434-90-9
Molecular Formula: $C_{12}H_{15}Br_6N_3O_3$
Major isotopomer mass: 763.6 $[M + Cl^-]$

2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine
CAS number: 25713-60-4
Molecular Formula: $C_{21}H_6Br_9N_3O_3$
Major isotopomer mass: 1067.3 $[M + H^+]$

Fig. 1. Structures of TDBP-TAZTO and TTBP-TAZ.

on the occurrence and distribution of TTBP-TAZ in the environment of China is lacking.

China is one of the largest processors of e-waste in the world (Labunska et al., 2014). Domestic e-waste is the main source for resource recycling at present. Many previous studies (Li et al., 2019; Luo et al., 2014; Tue et al., 2013; Wang et al., 2010; Zheng et al., 2015) have substantially confirmed that e-waste is a main source of many legacy and alternative FRs. However, the occurrence of triazine-based BFRs, such as TDBP-TAZTO and TTBP-TAZ, and human exposure to these novel FRs in an e-waste recycling area still remain largely unknown.

The present study attempted to address the abovementioned knowledge gaps. A mega e-waste recycling industrial park and adjacent communities were selected as a case study. Indoor dust samples were collected from e-waste recycling workshops and local residential homes; meanwhile, outdoor dust samples were collected from exterior street surfaces. Legacy BFRs, HBCDD and TBBPA were also analyzed for comparison. The occupational and general exposures were comprehensively evaluated. These results provide new information on the occurrence and distribution of two novel triazine-based FRs and their potential health risks from dust exposure in a heavily contaminated environment.

2. Methods and materials

2.1. Background of the study area

The study area (N 23.5°, E 113.0°) is located in Shijiao Town, Qingyuan City, Guangdong Province, and the map of study area can be found in our previous study (Chen et al., 2018). Qingyuan City is one of the largest e-waste recycling areas, with the most intensive dismantling activity, in China since the 1980s. Over 1300 recycling workshops and 80,000 workers are engaged in e-waste recycling activities in Qingyuan only. It is estimated that approximately 1.7 million tons of e-waste are dismantled annually. Before the 2010s, the recycling was done by many dispersed family workshops, and primitive recycling methods, including unprotected manual dismantling, open burning and acid washing, were pervasive. Light e-waste (cellphones, video recorders, cable and circuit boards) and heavy e-waste (computers, electrical machines, capacitors and transformers) are manually dismantled in these family-run workshops aiming for the recycling of the metal materials. Since the 2000s, legislative regulative measures have been implemented by local government, and industrial centralization has been developed to minimize the severe environmental pollution (Zhang et al., 2017). After the 2010s, the traditional family-run workshops were transferred to the local e-waste recycling industrial parks. The recycling methods were changed and now mainly rely on mechanical and thermal dismantling with the help of manual dismantling, while open burning and acid washing were banned. In this study, the selected typical e-waste recycling industrial park mainly recycles plastics that encased electric or electronic componentry as the major recycling activities in recent years.

2.2. Field sample collection

Sampling campaigns were conducted in the study area between September 2016 and July 2017. Three types of dust samples ($n = 86$) were sampled from e-waste recycling workshops, surrounding residential homes and exterior street surfaces in the study area (within ~8 km). A vacuum cleaner with a paper collector bag was used for the dust sample collection. The vacuum cleaner was carefully cleaned between each sampling. Of the 86 total samples, 43 samples were collected from e-waste recycling workshops in the industrial park. Only one pooled dust sample composed of three to six subsamples was collected from each e-waste recycling workshop. Twenty-five indoor dust samples were obtained from local homes distributed randomly in neighboring residential areas around the industrial park (within ~4 km). Most of the e-waste dismantling workers at the industrial park are local residents and migrant laborers who live in the surrounding residential areas. A composite sample consisting of floor dust and elevated surface dust from electronic/electrical equipment (televisions, computers, etc.) was collected from each residential home. Eighteen outdoor dust samples were collected from the exterior street surfaces of the study area (within 1–8 km). After air drying, all dust samples were sieved using a 100-mesh sieve to remove the plastic or other coarse particles and then stored at −20 °C in amber glass jars.

2.3. Sample preparation, instrumental analysis and quantification

Approximately 20 mg of the sieved sample was spiked with 25 ng of an internal standard (IS) ($^{13}C_{12}$-γ-HBCDD and $^{13}C_{12}$-TBBPA). After vortex mixing and aging for 12 h, the samples were ultrasonically extracted for 15 min using 3 mL of mixed hexane/dichloromethane (DCM)/acetone (v/v/v = 1:1:1) and then centrifuged at 5000 rpm for 8 min. The extraction was repeated at least 3 times, and the combined extract was concentrated to approximately 0.5 mL under gentle N_2 flow. The extract was purified using an SPE cartridge (6 mL, 1 g of activated silica). The cartridge was conditioned using 30 mL of hexane. After the loading, the target compounds were eluted using 5 mL of hexane/DCM (v/v = 1:1) and 10 mL of DCM. The eluents were condensed to near dryness and redissolved in 0.5 mL methanol. A known amount (25 ng) of d_{18}-γ-HBCDD as an injection standard was added before analysis.

Instrumentation analysis was performed using a high-performance liquid chromatography coupled with a triple-quadrupole mass spectrometer (HPLC-MS/MS, Quad™ 5500, SCIEX, Redwood City, CA, USA) and operated in the negative electrospray ionization mode with multiple reaction monitoring. TDBP-TAZTO, HBCDD and TBBPA were analyzed according to a previously developed method with some optimizations (Feng et al., 2010). Briefly, for each extract, 5 μL was injected into an Eclipse Plus C_{18} column (2.1 × 100 mm, 1.8 μm, Agilent) for chromatographic separation. The selected transitions were m/z 763.6 → 78.9/80.9 for TDBP-TAZTO; 640.9 → 78.9/80.9 for α-, β- and γ-HBCDD; and 542.6 → 78.9/80.9 for TBBPA. For the labeled standards, m/z 652.7 → 78.9/80.9 for $^{13}C_{12}$-γ-HBCDD, 657.7 → 78.9/80.9 for d_{18}-γ-HBCDD and 554.8 → 78.9/80.9 for $^{13}C_{12}$-TBBPA were selected. The mobile phase consisted of water (A) and methanol (B) at a flow rate of 0.2 mL min^{-1}. The gradient elution program was as follows: the initial condition was 30% B, ramped to 80% B at 1.0–4.5 min, ramped to 100% B at 4.5–12 min, held until 14 min, returned to the initial condition in 1.0 min and then equilibrated until 19 min.

The analysis of TTBP-TAZ was developed for our study using HPLC-MS/MS operating in the positive electrospray ionization mode with multiple reaction monitoring. The transitions m/z 1067.3 → 313/355 were selected. More details about the MS parameters are given in Table S1 in Supporting Information (SI). The mobile phase consisted of water (A) and methanol (B) containing 0.2% formic acid at a flow rate of 0.2 mL min^{-1}. The gradient elution program was as follows: the initial condition was 20% B, ramped to 80% B at 0–1.0 min, ramped to 100% B at 1.0–3.5 min, held until 12 min, returned to the initial condition in 1.0 min and then equilibrated until 18 min.

The chromatograms of the standard chemicals are provided in Fig. S1. For TDBP-TAZTO, HBCDD and TBBPA, an internal standard was used for quantification ($^{13}C_{12}$-γ-HBCDD for α-, β- and γ-HBCDD and TDBP-TAZTO, and $^{13}C_{12}$-TBBPA for TBBPA). For TTBP-TAZ, an external standard was used for the quantification. Calibration curves were set up in the range of 1–500 ng mL^{-1} with a regression coefficient (r^2) of >0.996.

2.4. Quality assurance and quality control

All glassware was ultrasonic rinsed with solvent and heated at 450 °C overnight before use. Each batch of six samples included one procedure blank to monitor the contamination of the blank. To prevent cross-contamination during analysis, we injected methanol into each batch of samples. Field blanks were prepared by suction of anhydrous sodium sulfate with a vacuum cleaner in the same way as collecting field samples. No target compounds were detected in all the procedure and field blanks. The matrix spike ($n = 6$) recoveries were, on average, 83% ± 9% for TDBP-TAZTO, 84% ± 10% for TTBP-TAZ, 87% ± 7% for TBBPA, 85% ± 5% for α-HBCDD, 79% ± 8% for β-HBCDD and 90% ± 6% for γ-HBCDD. Recoveries for the internal standards $^{13}C_{12}$-γ-HBCDD and $^{13}C_{12}$-TBBPA in the dust samples were between 69% and 114% and between 73% and 112%, respectively. All reported concentrations were on a dry weight (dw) basis in this study. The limits of detection (LODs) were defined as a signal-to-noise ratio of 3 and were 0.90 ng g^{-1} dw for TDBP-TAZTO, 3.8 ng g^{-1} dw for TTBP-TAZ, 0.64 ng g^{-1} dw for TBBPA and 0.30 ng g^{-1} dw for α-, β- and γ-HBCDD.

2.5. Calculation of the daily intake

The estimated daily intakes (EDIs, ng kg^{-1} day^{-1}) of TDBP-TAZTO, TTBP-TAZ, TBBPA and HBCDD via dust ingestion and dermal absorption were calculated using the following equations (Chen et al., 2018):

$$\mathrm{EDI}_{\text{ingestion}} = \sum \frac{C_{\text{dust}} \times IR \times EF}{BW}$$

$$\mathrm{EDI}_{\text{dermal absorption}} = \sum \frac{C_{\text{dust}} \times SA \times AF \times ABS \times EF}{BW}$$

$$\mathrm{EDI}_{\text{total dust}} = \mathrm{EDI}_{\text{ingestion}} + \mathrm{EDI}_{\text{dermal absorption}}$$

where C_{dust} is the concentration of the target contaminant in the dust samples in a certain type of environment (ng g^{-1}), IR is the daily ingestion of dust (mg day^{-1}), EF is the exposure fraction (hours spent over a day in a certain environment), BW is the body weight (kg), SA is the exposed body surface area in contact with dust (cm^2 day^{-1}), AF is the adherence factor of dust on the skin (mg cm^{-2}), and ABS is the dermal absorption factor. Detailed parameter values used in the calculations are presented in Table S2. The daily activity patterns and the time spent per day in various types of living environment for the e-waste dismantling plant workers and local residents, based on our field survey, are given in Table S3.

2.6. Statistical analysis

The mean, geomean, median, 95th percentile (P95), range and detection frequency (DF) were used to describe the detection results of the target compounds in dust. Descriptive statistical and Spearman's correlation analyses were performed using SPSS version 20.0. Concentrations below the LODs were replaced with half of the LODs for statistical analysis. A two-tailed t-test was used to determine the significant differences between the concentrations of the target compounds in dust samples. Statistical significance was accepted if $p < 0.05$.

3. Results and discussion

3.1. Widespread occurrence and high levels of TDBP-TAZTO and TTBP-TAZ in dust

The descriptive statistics of the TDBP-TAZTO and TTBP-TAZ concentrations (mean, geomean, median, P95, range and DF) in three types of dust samples obtained from e-waste workshops, surrounding residential houses and exterior street surfaces are summarized in Table 1. The box-whisker plots of the TDBP-TAZTO and TTBP-TAZ concentrations in the three types of dust samples are illustrated in Fig. S2. TDBP-TAZTO was detected in all dust samples, and its concentrations in e-waste recycling workshops were at much higher levels than those from surrounding residential homes and exterior street surfaces. According to the statistical analysis, the average TDBP-TAZTO concentration (2060 ng g^{-1}) in dust samples from e-waste recycling workshops was found to be approximately two orders of magnitude higher than those from surrounding residential homes (33.2 ng g^{-1}) and exterior street surfaces (18.8 ng g^{-1}). However, the median or geomean of the TDBP-TAZTO concentration in dust samples collected from e-waste workshops was approximately 35–50 times higher than that from two surrounding sampling locations. The ranges of the TDBP-TAZTO concentrations in dust samples from e-waste recycling workshops, surrounding residential houses and exterior street surfaces were between 26.9 and 18,200, 3.37 and 145, and 2.96 and 32.7 ng g^{-1}, respectively. The maximum value of 18,200 ng g^{-1} was found in one e-waste workshop, whereas the minimum value of 2.96 ng g^{-1} was observed in one street surface, approximately 8 km away from the industrial park. The results indicated that TDBP-TAZTO was widely detected in a typical e-waste recycling area, with unexpectedly high levels in workshop dust in particular, suggesting a largely fugitive emission of TDBP-TAZTO from the indoor environmental matrices, including dust or suspended particles. A previous study suggested that TDBP-TAZTO could be transported regionally via dust deposition (Ruan et al., 2009). The widespread occurrence of TDBP-TAZTO at relatively lower levels in the dust samples from surrounding residential homes and exterior street surfaces indicated its regional transport potential.

Until now, information on the environmental occurrence of TDBP-TAZTO in dust is very scarce. Only one study (Guo et al., 2018) reported that TDBP-TAZTO was analyzed in dust samples from North America, but it was not detected. Thus, to our knowledge, this is the first report on the detection of the presence of TDBP-TAZTO in dust. However, TDBP-TAZTO detection in other environmental matrices, such as soils and sediments, has been frequently reported in Asian regions (Tang et al., 2014; Wang et al., 2017; Wang et al., 2016; Wang et al., 2013). As an important additive-type fire retardant, TDBP-TAZTO is being widely used in plastics that encase electric or electronic componentry (Report, 2019). Therefore, like the emissions from the manufacturing processes that lead to the release of large amounts of TDBP-TAZTO (Ruan et al., 2009), the emissions from e-waste dismantling/recycling processes may also be an important source of TDBP-TAZTO in the environment.

TTBP-TAZ was detected in 38 of 43 e-waste dust samples, all residential dust samples, and 14 of 18 street dust samples, with concentration ranging between 5.82 and 374, 4.60 and 431, and 4.00 and 16.2 ng g^{-1}, respectively. The maximum value of 431 ng g^{-1} was found in a residential dust sample. Unlike TDBP-TAZTO, significantly higher levels of TTBP-TAZ were detected in dust samples from local residential homes than from e-waste workshops and exterior street surfaces (Fig. S2A). Currently, information about TTBP-TAZ is quite scarce. There are few studies that have reported on the environmental occurrence of TTBP-TAZ. Ballesteros-Gómez et al. (2014) first reported that TTBP-TAZ was present in plastic consumer products of electronic/electrical equipment from the Netherlands, with concentrations ranging from 0.01 wt% to 1.9 wt%. Furthermore, TTBP-TAZ could be detected in 9 of 17 household dust samples, with much higher concentrations in the dust on ($n = 4$, range 1070–22,150 ng g^{-1}) and around ($n = 4$, range 220–3950 ng g^{-1}) the electronic/electrical equipment than on the floor ($n = 1$, concentration 160 ng g^{-1}). Their findings indicated that TTBP-TAZ may be mainly released from the electronic/electrical equipment into the ambient environment. Guo et al. (2018) recently reported high concentrations of TTBP-TAZ detected in all seven e-waste dust samples collected (range 1170–42,000 ng g^{-1}, median 5540 ng g^{-1}), but relatively low concentrations were detected in 21 of 30 residential dust samples (range 0.43–92 ng g^{-1}, median 6.76 ng g^{-1}) in North America.

In the present study, the levels of TTBP-TAZ in the e-waste dust samples collected in China were much lower than those collected in North America (Guo et al., 2018). This suggested that, unlike in North

Table 1
Descriptive statistics of concentrations of TDBP-TAZTO, TTBP-TAZ, TBBPA and HBCDDs in dust samples collected from e-waste recycling workshops, local residential homes and exterior street surfaces.

Sampling site	Statistical parameter	Concentration (ng g^{-1} dw)						
		TDBP-TAZTO	TTBP-TAZ	TBBPA	α-HBCDD	β-HBCDD	γ-HBCDD	ΣHBCDD
E-waste recycling workshops ($n = 43$)	Mean	2060	53.5	3020	242	34.5	250	526
	Geomean	706	24.1	1620	69.6	12.6	39.6	139
	Median	871	23.2	1330	42.3	8.86	29.6	83.5
	P95[a]	9780	226	10,400	806	145	1560	1970
	Range	26.9–18,200	<LOD–374	44.9–19,600	7.80–3920	1.18–285	2.50–4940	12.4–5640
	DF[b]	100%	88%	100%	100%	100%	100%	100%
Local residential homes ($n = 25$)	Mean	33.2	119	509	21.7	3.23	10.8	35.7
	Geomean	20.2	74.9	328	14.0	2.01	5.46	23.2
	Median	18.7	72.6	259	12.9	1.97	3.63	19.4
	P95	118	379	1570	77.3	10.7	49.2	116
	Range	3.37–145	4.60–431	56.9–1870	1.09–95.3	0.50–16.0	1.28–72.4	3.47–132
	DF	100%	100%	100%	100%	100%	100%	100%
Exterior street surfaces ($n = 18$)	Mean	18.8	7.17	74.2	8.91	1.68	3.59	14.2
	Geomean	14.3	5.34	50.0	7.84	1.43	2.25	12.1
	Median	20.7	6.03	85.4	9.69	1.75	1.61	14.9
	P95	30.8	15.5	132	13.9	2.42	8.91	23.6
	Range	2.96–32.7	<LOD–16.2	5.57–135	2.22–15.2	0.30–2.49	0.42–9.28	2.91–26.5
	DF	100%	78%	100%	100%	100%	100%	100%

[a] P95: the 95th percentile.

[b] DF: detection frequency.

America and the Netherlands, TTBP-TAZ has not been used on a large scale in China as a substitute for PBDEs and HBCDD after these FRs were phased out, although its use may have started recently. However, in the e-waste recycling areas in China, the level of TTBP-TAZ in residential dust samples, which were a mix of floor and electronic equipment dust, was comparable to that in the Netherlands (Ballesteros-Gómez et al., 2014) but obviously higher than that in North America (Guo et al., 2018). The higher levels of TTBP-TAZ detected in the residential dust samples compared to those in the e-waste dust samples in this study might have been due to its long-term release from the electronic equipment and to its accumulation in indoor dust. Furthermore, TTBP-TAZ was not detected in any of the outdoor environment matrices in a previous study (Guo et al., 2018) but could be frequently detected and was prevalent in the exterior street dust samples in the present study. This suggests that TTBP-TAZ may also be transported regionally via dust deposition. More monitoring studies of TTBP-TAZ in various outdoor sources should be conducted to obtain relevant information in the near future.

As shown in Fig. S2B, TDBP-TAZTO in e-waste dust samples exhibited significantly higher concentrations than TTBP-TAZ, suggesting that TDBP-TAZTO is more commonly used in China as a major substitute for legacy FRs compared to TTBP-TAZ. Given that no TDBP-TAZTO, but very high levels of TTBP-TAZ, was detected in the e-waste dust samples from North America (Guo et al., 2018), we can deduce that there are different production and usage patterns for alternative FRs between China and other countries, such as North America. It is surprising that relatively higher levels of TTBP-TAZ than TDBP-TAZTO were found in local residential dust samples, implying that TTBP-TAZ is more easily released from home electronic equipment or originated from other indoor sources, and this merits further investigations. No significant correlation was found between the concentrations of TDBP-TAZTO and TTBP-TAZ in all three types of dust samples (Tables 2, S4 and S5), suggesting different sources and/or environmental factors for these two novel FRs.

3.2. Comparison of two novel FRs with HBCDD, TBBPA and other well-known FRs

HBCDD and TBBPA were also analyzed in dust samples for comparison with the newly identified TDBP-TAZTO and TTBP-TAZ. As shown in Table 1, three diastereomers, α-, β- and γ-HBCDD, were detected in 100% of the e-waste, residential and street dust samples, with ΣHBCDD (sum of the three isomers) in the range of 12.4–5640, 3.47–132 and 2.91–26.5 ng g^{-1}, respectively. Like with TDBP-TAZTO, significantly higher concentrations of ΣHBCDD were found in e-waste dust samples than in residential and street dust samples (Fig. S2A). α-HBCDD was identified as the major diastereomer in all dust samples, which was consistent with the findings of previous studies (Abdallah et al., 2008a; Fromme et al., 2014). ΣHBCDD concentrations in the e-waste dust samples in the present study were comparable to the previously reported levels in surface particulates from e-waste recycling workshop floors in the same region but were lower than those found in two other Chinese e-waste recycling areas, Taizhou and Guiyu (Zeng et al., 2016). Comparing the concentrations of ΣHBCDD in the residential dust samples with those reported for other countries (Fig. S3), ΣHBCDD in the present study was apparently lower than reported in the general home dust samples collected in Germany (Fromme et al., 2014), Belgium (D'Hollander et al., 2010), New Zealand (Ali et al., 2012), Canada, USA, UK (Abdallah et al., 2008a; Abdallah et al., 2008b; Tao

Table 2
Spearman's correlation coefficients for the target compound concentrations in dust from e-waste recycling workshops.

Compounds	TDBP-TAZTO	TTBP-TAZ	TBBPA	α-HBCDD	β-HBCDD	γ-HBCDD
TTBP-TAZ	0.266					
TBBPA	0.457**	0.371*				
α-HBCDD	0.709**	0.358*	0.649**			
β-HBCDD	0.649**	0.371*	0.613**	0.976**		
γ-HBCDD	0.551**	0.393**	0.683**	0.871**	0.893**	
ΣHBCDD	0.629**	0.344*	0.657**	0.958**	0.969**	0.954**

* Correlation is significant at the 0.05 level (two-tailed).

** Correlation is significant at the 0.01 level (two-tailed).

et al., 2016), Japan (Takigami et al., 2009) and Korea (Barghi et al., 2017) and was much lower than that in office dust samples collected from South China (Ni and Zeng, 2013). In China, control measures for HBCDD have been implemented since it was listed as a POP by the Stockholm Convention in 2013, and further regulations of HBCDD by the government have taken effect since 2016. Thus, the effectiveness of controls and regulations has reduced the concentrations of HBCDD in dust. As shown in Fig. S2B, ΣHBCDD showed significantly lower levels than those of TDBP-TAZTO (e-waste dust) and TTBP-TAZ (residential dust), suggesting that HBCDD may be replaced by emerging novel FRs such as, TDBP-TAZTO. A more significant correlation was observed between ΣHBCDD and TDBP-TAZTO than between ΣHBCDD and TTBP-TAZ (Table 2), implying that HBCDD and TDBP-TAZTO have similar applications, sources and environmental factors owing to their similar physicochemical properties (Wang et al., 2013).

Among the four detected target BFRs, TBBPA was identified to be the most dominant BFR in all dust samples with the highest concentration and percent abundance (Fig. 2). The concentration of TBBPA in the e-waste, residential and street dust samples ranged from 44.9 to 19,600, 56.9 to 1870 and 5.57 to 135 ng g^{-1}, respectively. Like TDBP-TAZTO and HBCDD, significantly higher levels of TBBPA were detected in e-waste dust samples than in residential and street dust samples. The TBBPA levels in the e-waste dust samples in the present study were slightly lower than the levels previously reported for surface particulates from e-waste recycling workshop floors in the same region but were much lower than those found in the Chinese e-waste recycling areas of Taizhou and Guiyu (Zeng et al., 2016). The TBBPA levels in the residential dust samples in the present study were also lower than those in the e-waste recycling area of Taizhou (Wu et al., 2016) but were apparently higher than in the general home dust samples collected from urban areas in Germany (Abb et al., 2011; Fromme et al., 2014), UK (Abdallah et al., 2008a), Belgium (D'Hollander et al., 2010; Geens et al., 2009), South Africa (Abafe and Martincigh, 2016), Japan (Takigami et al., 2009), Korea (Barghi et al., 2017), USA, Greece, Romania, Colombia, Pakistan, Kuwait, India, Saudi Arabia, Vietnam, and China (Wang et al., 2015) (Fig. S4). The significantly higher levels of TBBPA than TDBP-TAZTO, TTBP-TAZ and HBCDD in China could be attributed to the lack of regulatory restrictions on the use and production of TBBPA. A more significant correlation was also observed between TBBPA and TDBP-TAZTO than between TBBPA and TTBP-TAZ (Table 2), implying that TBBPA and TDBP-TAZTO may have similar applications and emission sources as well.

Legacy BFRs including PBDEs, polybrominated biphenyls (PBBs) and other alternative BFRs, such as decabromodiphenyl ethane (DBDPE), dechlorane plus (DP), bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HBB), pentabromotoluene (PBT) and pentabromoethylbenzene (PBEB), were not measured in the present study. Given that these legacy and alternative BFRs have been previously detected in surface particulates from e-waste workshop floors in the same region (Zeng et al., 2016), further comparisons of the concentrations of TDBP-TAZTO and TTBP-TAZ with those of these well-known BFRs were conducted. We found that the concentrations of TDBP-TAZTO in e-waste dust samples were only lower than those of PBDEs (sum of 18 PBDE congeners, 130–1,100,000 ng g^{-1}) and DBDPE (140–170,000 ng g^{-1}) but were slightly higher than those of PBBs and much higher than those of DP, BTBPE, HBB, PBT and PBEB (Zeng et al., 2016). The concentrations of TTBP-TAZ in the e-waste dust samples were higher than those of PBT and PBEB but were still lower than those of other well-known BFRs (Zeng et al., 2016). It should be noted that, by the above comparison, TDBP-TAZTO was identified as the fourth most dominant FR detected in e-waste dust samples, next only to PBDEs, TBBPA and DBDPE. With the start of the global ban on decaBDE in 2017 by the Stockholm Convention, TDBP-TAZTO, like DBDPE, may be used to replace decaBDE, and increasing production volume and use in the region are expected in the future. However, TDBP-TAZTO has always been ignored and seldom been investigated in the environment. Given its unexpectedly high levels in dust and its known toxicological effects (Li et al., 2011; Li et al., 2015; Wang et al., 2014; Ye et al., 2015; Zhang et al., 2011), TDBP-TAZTO should be of concern and deserves further investigations.

3.3. Estimation of daily intake of novel and legacy FRs via dust ingestion and dermal absorption for the occupational and general populations

The EDIs for the occupational and general exposures in the e-waste recycling area were evaluated on the basis of the concentrations of the novel and legacy FRs measured in different dust samples. Two exposure routes, namely dust ingestion and dermal absorption, were considered for calculating the total EDIs via dust exposure. The exposure assessments were conducted under two scenarios: median and high-end exposure. The median and high-end estimates of the daily intakes of FRs were calculated according to the median and 95th percentile (P95) concentrations in dust samples, respectively. Fig. 3 illustrates the combined estimates of the daily median and high-end exposure to TDBP-TAZTO, TTBP-TAZ, TBBPA, and ΣHBCD via dust ingestion and dermal absorption for occupational workers and local residents (adults and children). Detailed EDI values are given in Table S6.

The estimated median exposure to TDBP-TAZTO via combined dust ingestion and dermal absorption was 0.91 ng kg^{-1} day^{-1} for occupational e-waste workers, which was approximately 30 times higher than that for local adults and over five times higher than that for local children. It is noted that, for occupational exposure, the median EDI of TDBP-TAZTO was nine times higher than that of ΣHBCDD but was just slightly lower than that of TBBPA. This suggests severe occupational exposure of TDBP-TAZTO in the e-waste recycling area. For the general exposure of local adults and children, the median EDIs of TDBP-TAZTO were comparable to those of ΣHBCDD. Local children suffered from higher exposure dose than local adults. The estimated median exposure

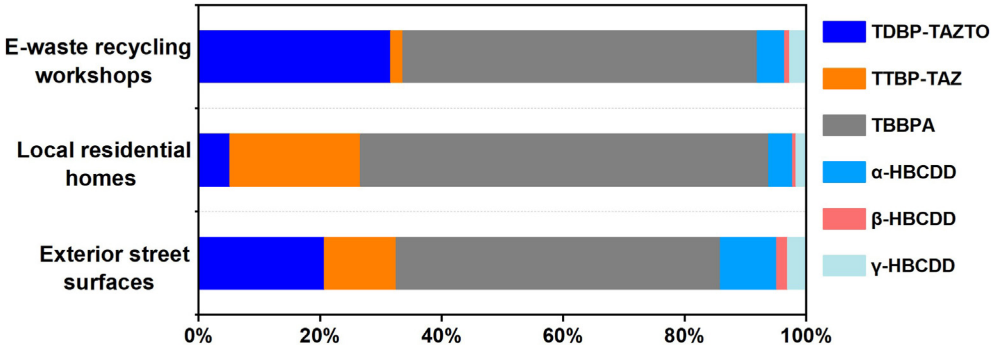


Fig. 2. Average abundance profiles of TDBP-TAZTO, TTBP-TAZ, TBBPA and α-, β-, and γ-HBCDD in three types of dust samples.

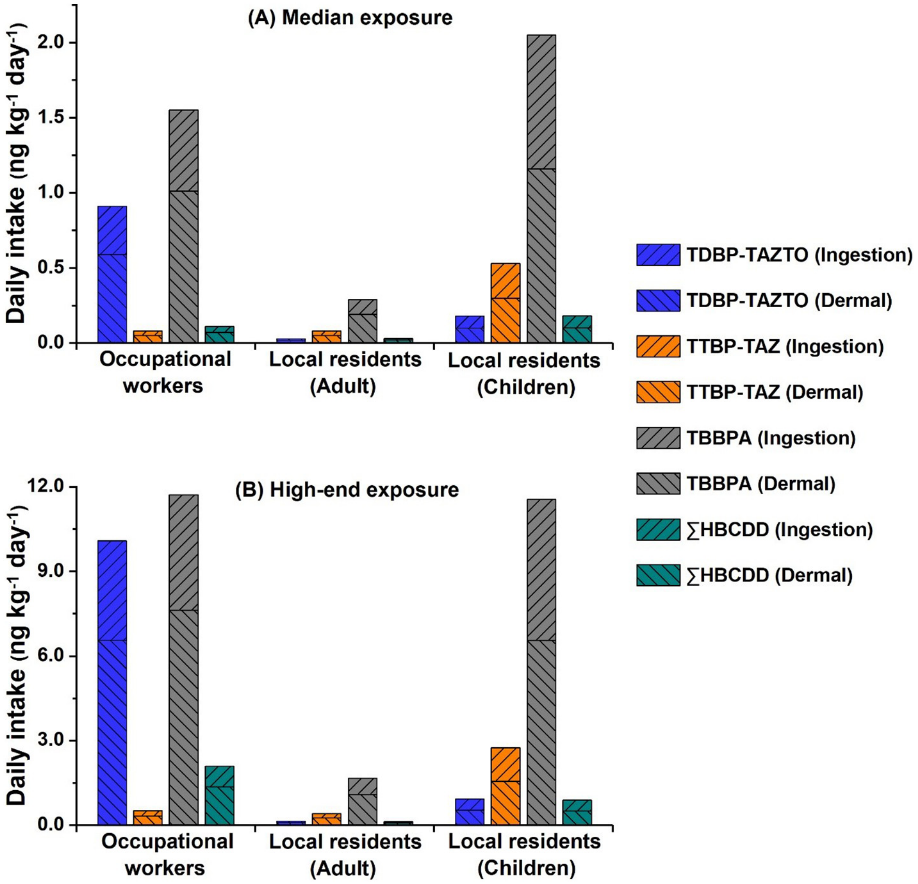


Fig. 3. Estimated daily intakes of TDBP-TAZTO, TTBP-TAZ, TBBPA and ΣHBCDD via dust ingestion and dermal absorption for occupational workers and local residents (adults and children) under median (A) and high-end (B) exposure scenarios, respectively.

to TTBP-TAZ was 0.08, 0.08 and 0.53 ng kg^{-1} day^{-1} for occupational workers, local adults and children, respectively. Obviously, a significantly higher EDI of TTBP-TAZ was found for local children than for local adults and occupational workers. Moreover, compared with adults, a significantly higher EDI of TBBPA was observed for children, implying that children are the population most susceptible to FR exposure. The occupational exposure of e-waste workers to TTBP-TAZ was similar to that of ΣHBCDD and lower than that of TDBP-TAZTO; however, the general exposure of local residents to TTBP-TAZ was significantly higher than those of ΣHBCDD and TDBP-TAZTO. The results indicated that, even in the residential environment near the e-waste recycling area, dust exposure to TDBP-TAZTO and TTBP-TAZ should not be overlooked compared with legacy FRs.

The estimated high-end exposure to TDBP-TAZTO, TTBP-TAZ, TBBPA and ΣHBCDD for occupational workers, local adults and children showed a similar exposure profile (Fig. 3B) to that of the median exposure. The estimated high-end exposure to TDBP-TAZTO was as high as 10.1 ng kg^{-1} day^{-1} for occupational workers, which was approximately two orders of magnitude higher than for local adults and one order of magnitude higher than for local children. The EDI of TTBP-TAZ for the high-end occupational exposure was 0.50 ng kg^{-1} day^{-1}, which was approximately 20 times lower than that of TDBP-TAZTO. Moreover, by comparison, the high-end exposure levels for TDBP-TAZTO and TTBP-TAZ were at least 4–10 times higher than the corresponding median exposure levels.

To our knowledge, this is the first report on the daily intakes of TDBP-TAZTO and TTBP-TAZ via dust ingestion, and no available data can be used for comparison. However, from a global comparison perspective, the EDIs of HBCDD and TBBPA under the median exposure scenario in the present study were at the low end and the upper end of the global range, respectively. It is important to point out that, under both exposure scenarios, the contribution of dermal absorption to the EDIs was higher than that of ingestion. A recent study (Lao et al., 2018) confirmed that dermal absorption is responsible for the greater exposure to particulate polycyclic aromatic hydrocarbons in barbecue smoke than that of inhalation. The impact of dermal absorption of FRs still needs to be verified to improve our understanding of the human exposure pathways.

3.4. Implications of potential health risk

The health risk from dust exposure of legacy HBCDD and TBBPA can be evaluated using the hazard quotient (HQ) and comparing the EDI value with a reference dose (RfD) (HQ = EDI / RfD) (Ruan et al., 2018). An HQ < 1 indicates little or no health concerns. The US National Research Council (NRC, 2000) proposed an RfD for ΣHBCDD of 200 μg kg^{-1} day^{-1}, derived from a no-observed-adverse-effect-level (NOAEL) based on increased liver weights and abnormal fatty accumulation in rats. Wikoff et al. (2015) suggested an RfD for TBBPA of 600 μg kg^{-1} day^{-1}, based on uterine hyperplasia in rats. If compared only with the RfDs mentioned above, all the calculated HQs of ΣHBCDD and TBBPA, even under a high-end exposure scenario, were still much lower than these suggested RfDs. In this case, it appears that current exposure levels of HBCDD and TBBPA would not raise health concerns for the occupational workers and local residents in the e-waste recycling area. However, these preliminary assessments have limitations. There is still a lack of sufficient toxicological studies, and the RfDs could be further refined once more toxicity data become available. For example, a sensitive RfD for ΣHBCDD of 1.67 ng kg^{-1} day^{-1} was derived from a NOAEL based on impaired lipid and glucose homeostasis in mice fed a high-fat diet (Ruan et al., 2018; Yanagisawa et al., 2014). If this RfD was used for comparison, the calculated HQ (1.25) of ΣHBCDD for occupational workers under the high-end exposure scenario would be substantially >1, implying a potential risk of HBCDD exposure for e-waste workers via dust ingestion. As a class of novel FRs, both TDBP-TAZTO and TTBP-TAZ lack available RfD data, and therefore, risk assessments cannot be directly conducted at present regarding these two novel triazine FRs. Given the similar physicochemical properties of TDBP-TAZTO and HBCDD, if a RfD value for TDBP-TAZTO was similar to that of HBCDD, it could also pose a potential risk to the health of e-waste workers.

It is noteworthy that, in addition to dust exposure, food consumption and air inhalation are important human exposure pathways of these individual FRs. Consequently, the health risks might have been severely underestimated in the present study for the occupational workers and local residents. Moreover, dust from an e-waste recycling area accumulates a large amount of conventional organic pollutants and heavy metals other than the newly identified contaminants. Therefore, as mentioned in our recent work (Chen et al., 2018), if the multicomponent chemical ‘cocktail’ effects were considered, the calculated HQs would increase substantially and pose a potentially high risk not only to the e-waste workers but also to the local residents. Given the more frequent usage and faster replacement of electronic products now, e-waste recycling is highly associated with the circular economy of the world. Many toxic substances, including the newly identified TDBP-TAZTO and TTBP-TAZ in raw electronic materials or products, will ultimately end up as e-wastes to be recycled, which will pose a potentially high risk to the health of the local population, especially of e-waste workers. Our results here highlight the potentially high health risk from the combined exposure to novel and conventional FRs as well as from multiple other chemicals, which should raise concerns about their effects on the environment and human health. Further investigations on the exposure routes of novel FRs in humans and on the individual and combined toxicological effects of these FRs on human health are urgently needed to allow a more accurate risk assessment.

4. Conclusions

This study has demonstrated that two novel triazine-based FRs, namely, TDBP-TAZTO and TTBP-TAZ, are prevalent in dust from indoor and outdoor environments in an e-waste recycling area in China. TDBP-TAZTO was found for the first time in e-waste dust at unexpectedly higher levels than HBCDD. TDBP-TAZTO was significantly correlated with HBCDD and TBBPA, suggesting their similar sources. A comparison of the TDBP-TAZTO concentrations with those of other alternative and legacy FRs indicated that TDBP-TAZTO is a major FR in present use, only behind PBDEs, TBBPA and DBDPE. TTBP-TAZ was first detected in dust samples from China at relatively lower concentrations than in dust samples from North America and the Netherlands. The estimated daily intake of TDBP-TAZTO via dust ingestion for occupational workers was much higher than that of HBCDD and was also much higher than for local adults and children. TDBP-TAZTO exposure may pose a potentially high risk to the health of the local population, especially for e-waste workers, if the multicomponent chemical ‘cocktail’ effects are considered. More investigations on the behavior and risk factors for TDBP-TAZTO and TTBP-TAZ in various environmental matrices, as well as their toxicological effects, should be performed in the future.

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Appendix A. Supplementary data

Optimized parameters for TTBP-TAZ analysis (Table S1); parameters and data for EDI calculations (Tables S2 and S3); Spearman's correlation coefficients for the target compounds in residential home and street dust samples (Tables S4 and S5); Detailed EDI data (Table S6); Chromatogram of the standard chemicals (Fig. S1); Box-whisker-plots of concentrations in dust (Fig. S2); Worldwide comparison of ∑HBCDD and TBBPA concentration in dust (Figs. S3 and S4). Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.05.264.

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