

Occurrence and Distribution of Organophosphate Ester Flame Retardants in Indoor Dust and Their Potential Health Exposure Risk

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Abstract: The occurrence and distribution of 10 organophosphate ester (OP) flame retardants/plasticizers were studied in indoor dust collected in 2 districts of Wuhan City. Total concentrations of the 10 OPs (Σ OPs) varied from 86.5 to 6389 ng/g in 26 dust samples in Caidian District and from 300 to 10 186 ng/g in 27 samples in Jiang'an District. In most dust samples tris(2-chloroethyl) phosphate was dominant over the other OPs, with concentrations of 9.14 to 2722 ng/g (mean 388 ng/g) in Caidian District and 57.3 to 3718 ng/g (mean 616 ng/g) in Jiang'an District. The calculated hazard indices, based on estimated exposure dose via dust ingestion to the reference dose, were much lower than 1. The results suggested that the inhabitants in the 2 regions were at low risk of exposure through dust ingestion. *Environ Toxicol Chem* 2018;37:345–352. © 2017 SETAC

Keywords: Organophosphate ester flame retardant; Dust; Wuhan City; Human health risk assessment

INTRODUCTION

Organophosphate esters (OPs) are a group of phosphoric acid derivatives. Depending on their substituent group, OPs can be divided into 3 subgroups of chlorinated OPs, alkyl OPs, and aryl OPs, each of which exhibits different physicochemical properties, such as water solubility; log octanol–water partition coefficient and vapor pressure, which could affect their occurrence; distribution; and ultimate fate in the environment (van der Veen and de Boer 2012; Wei et al. 2015). Because of their fire resistance potential and flexibility, OPs are widely used as flame retardants and plasticizers in electrical/electronic equipment, furniture, textiles, and polyurethane foam. In general, chlorinated OPs, including tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), are used as flame retardants and alkyl/aryl OPs are used as plasticizers and industrial additives. For example, triphenyl phosphate (TPHP) is used as a plasticizer in polyvinyl chloride (PVC) cable, whereas tris(2-butoxyethyl) phosphate (TBEOP) is added to floor wax and rubber. Detailed information about their production

and application has been provided (van der Veen and de Boer 2012). Consumption of OPs has increased recently because of the ban on the use of penta- and octa-polybrominated diphenyl ethers (PBDEs). The global consumption of OPs was 500 000 metric tons in 2011 and was estimated to be 680 000 metric tons in 2015 (van der Veen and de Boer 2012; Wei et al. 2015).

These compounds are physically mixed into the products being protected and can easily enter the ambient environment during their production, usage, and disposal via volatilization, abrasion, and leaching (Keimowitz et al. 2016; Stapleton et al. 2012). After emission, these chemicals are distributed worldwide and can be found in indoor air and dust (Abdallah and Covaci 2014; Brommer and Harrad 2015; Yang et al. 2014); the atmosphere (Salamova et al. 2014); surface water, groundwater, seawater, and drinking water (Ding et al. 2015; Hu et al. 2014; Postigo and Barceló 2015); sediment (Cao et al. 2012); and soil (Mihajlovic and Fries 2012), as well as in biota and the human body (Santín et al. 2016; Sundkvist et al. 2010). Many studies have demonstrated that OPs have a range of adverse effects on aquatic organisms and the human body, including impacts on the reproductive and endocrine systems, the expression of transcriptional regulators, and endocrine-disrupting activity. Chlorinated OPs have been proved to be neurotoxic and carcinogenic, and these toxicities have been reviewed in detail (van der Veen and de Boer 2012; Wei et al. 2015). In addition, it has been demonstrated that OPs in the indoor environment can

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affect the hormone levels and semen quality of inhabitants (de Boer et al. 2016).

There are several exposure pathways of OPs to the human body, including inhalation from air (including fine particles), ingestion from dust, absorption, permeation via dermal contact, and ingestion from food and water (Wei et al. 2015). Despite this, until recently no data were available regarding the relative contribution from different exposure pathways (Abdallah and Covaci 2014; de Boer et al. 2016). Some studies have reported that OP intakes from water and diet pose a limited human health risk. For example, low levels of OPs were detected at the nanograms per liter level in drinking and bottled water in eastern China, with ignorable risks for local inhabitants (Ding et al. 2015). Exposure doses to OPs through fish and dietary ingestion are of minor importance because of their limited bioconcentration and metabolism in biota (Santín et al. 2016; Sundkvist et al. 2010). There is mounting evidence that dust ingestion is an important pathway for human exposure because people spend most of their time in indoor environments, and OPs are frequently detected in indoor dust because of their direct and continuous emission from OP-containing products in dwellings (Brommer and Harrad 2015). Based on the published research data, de Boer et al. (2016) have speculated that dust ingestion might be the main exposure pathway for the human body.

Until recently, most studies have focused on the occurrence and distribution of OPs in indoor dust, as well as the human exposure risk (Abdallah and Covaci 2014; Cao et al. 2014; Cequier et al. 2014). However, OPs might be physically added to various products; therefore, studies are still needed to determine their concentrations and distributions in different microenvironments, such as indoor air and dust. In the present study, we collected indoor dust in central China. The aims of the present study were to 1) determine the levels of OPs in dust, 2) investigate the compositional profiles of OPs in indoor dust, and 3) assess the human exposure risk of OPs via indoor dust ingestion.

MATERIALS AND METHODS

Standards and reagents

Ten OP standards were purchased from Sigma-Aldrich: triethyl phosphate (TEP, 99.8%), tripropyl phosphate (TPPrP, 99%), tri-*n*-butyl phosphate (TNBP, 99%), TPHP (99%), tris-(methylphenyl) phosphate (TMPP, 90%), TBEOP (94%), TCEP (97%), TCIPP (99.5%), TDCIPP (97%), and tris(2-ethylhexyl) phosphate (TEHP, 97%). Four deuterated OPs were purchased from C/D/N Isotopes and used as surrogate standards. Their purities were as follows: d15-TEP (99.1%), d27-TNBP (98%), d15-TPHP (98%), and d12-TCEP (98%). The internal standard hexamethylbenzene (HMB, 99.5%) was obtained from the laboratories of Ehrenstofer-Schäfer Bgm-Schlosser.

All solvents used were of chromatographic grade. Dichloromethane, acetone, and *n*-hexane were purchased from Merck; ethyl acetate was purchased from CNW Technologies. ENVI-Florisil solid-phase extraction tubes (1 g, 6 mL) were purchased from Supelco.

Sample collection

In 2013, 53 indoor dust samples were collected in 2 districts (Jiang'an District and Caidian District) in Wuhan City, the provincial capital of Hubei Province. Jiang'an District, the old residential area, is densely inhabited, with more than 780 000 people within an area of 62.24 km², whereas Caidian District, a developing suburb, has approximately 480 000 inhabitants in an area of 1100 km². Detailed data regarding the sampling location, sampling processes, and sample information have been published elsewhere (Liu 2014). According to a standardized sampling technique (Verein Deutscher Ingenieure 2001), indoor dust samples were swept from the floor of living rooms and bedrooms and from the surface of furniture using a wool brush previously cleaned with acetone, dichloromethane, and *n*-hexane. The samples represented 1 wk of deposition, and the house was not cleaned during this period. Simultaneously, 4 outdoor dust samples were collected from the floor underneath corridor railing and the surface of the balcony floor. After sampling, all of the dust was stored in aluminum foil, sealed in PVC zip bags, and stored at -20 °C prior to analysis. Approximately 1 g of anhydrous sodium sulfate (*n* = 4) wrapped in aluminum foil was brought to the sampling sites, sealed in PVC zip bags after sampling, and then analyzed as field blanks.

Sample analyses

Before extraction, according to guidance released by the US Environmental Protection Agency (2008), the samples were sieved through a stainless steel 60-mesh sieve (250 μm) to remove large debris, hair, and so on. Approximately 0.5 g of sample was spiked with 10 ng of the surrogates (d15-TEP, d12-TCEP, d27-TNBP, and d15-TPHP) and then Soxhlet-extracted using dichloromethane for 48 h. The extract was concentrated with an evaporator rotator to approximately 1 mL; then, the solvent was exchanged as *n*-hexane and reduced to 0.5 to 1 mL. The extracts were then loaded on ENVI-Florisil cartridges for further cleanup and separation according to a published method (Van den Eede et al. 2012). Polar and nonpolar solvents were used for eluting different flame organic compounds, and the OPs were collected in 10 mL ethyl acetate. The collected fraction was evaporated to dryness under a gentle N₂ stream and redissolved in 200 μL *n*-hexane. Prior to instrumental analyses, 100 ng HMB was added as an internal standard.

The target analytes were determined using a QP2010 gas chromatograph (Shimadzu) coupled with a quadrupole mass spectrometer operated in electron impact ionization mode. The OPs were separated on a TG-5MS column (30 m × 0.25 mm × 0.25 μm film; Thermo Fisher Scientific) with helium as the carrier gas at a flow rate of 1 mL/min. A 1-μL sample was injected using the splitless mode (0.75 min). The detailed analytical parameters have been reported (Zeng et al. 2015).

Quality assurance and quality control

For quality assurance and quality control, procedural blanks (*n* = 5), spiked blanks (*n* = 6, spiked standards into solvent),

spiked matrix ($n = 6$, spiked standards into preextracted dust), and duplicate samples ($n = 4$) were analyzed with real samples in each batch of 10 samples. In addition, field blanks ($n = 4$) were all analyzed as real dust samples.

In the procedural blanks, TCEP, TCIPP, and TBEOP were found at concentrations lower than 2 ng, which were 1 to 3 orders of magnitude lower than those in the indoor dust samples, except for TCIPP in 2 dust samples; their concentrations were comparable with procedural blanks, so we assigned them as the limit of detection (LOD). In addition, TCEP and TCIPP were found at concentrations lower than 3 ng in the field blanks. The recovery rates of the 4 surrogates were 62 ± 14 , 85 ± 12 , 106 ± 35 , and $94 \pm 32\%$, for d9-TEP, d27-TNBP, d12-TCEP, and d15-TPHP, respectively. All reported OP concentrations in dusts had background values subtracted and were not corrected with recovery rates.

Health risk assessment

In the present study, we made a preliminary assessment of the human exposure risk via indoor dust ingestion and estimated the daily intake of OPs using the following equation with limited modification, published previously (Ali et al. 2013; Van den Eede et al. 2011), without consideration of other exposure pathways, such as inhalation, food intake, and dermal permeation (de Boer et al. 2016):

$$\text{Exposure dose (ng/body weight/d)} = C \times D_{\text{dust}} \times I_{\text{R}}/\text{Body weight}$$

In the equation, C is the measured concentration of an individual OP in indoor dust, D_{dust} is the daily intake of dust, and I_{R} is the dust ingestion rate. We assumed 100% absorption of the intake of OPs via dust ingestion, using average dust ingestion doses of 20 and 50 mg/d and high doses of 50 and 200 mg/d for adults and children, respectively. The average body weights for adults and children were 63 and 13.8 kg, respectively, according to He et al. (2015). Then, the hazard index values, the ratio of daily intake of OPs to its corresponding reference dose, were calculated based on the estimated exposure dose. However, no reference dose values for TEP, TPrP, and TEHP were found (Van den Eede et al. 2011), and their hazard index values were not included in the present study.

All statistical analyses were performed using SPSS software Ver 19.0 (IBM).

RESULTS AND DISCUSSION

Concentration of OPs in indoor dust

The occurrence and distribution of OPs in the indoor dust samples collected in the present study are summarized in Table 1. Of the 10 target analytes, TCEP and TCIPP were found in all dust samples, with concentrations varying in the range of 9.14 to 2722 ng/g (mean, 588 ng/g) with an LOD of 5474 ng/g (mean, 660 ng/g) in Caidian District and 57.3 to 3718 ng/g (mean, 856 ng/g) and LOD 1718 ng/g (mean, 245 ng/g) in Jiang'an District. The other 8 OPs were detected in some of

the samples at different levels. The occurrence and distribution of individual OPs in the 2 study regions are plotted in Figure 1. In Caidian District, TCEP (mean, 588 ng/g) and TCIPP (mean, 660 ng/g) were the predominant components, followed by TDCIPP (mean, 289 ng/g), TPHP (mean, 265 ng/g), and TBEOP (mean, 244 ng/g). In Jiang'an District, TBEOP (mean, 885 ng/g) and TCEP (mean, 856 ng/g) were the predominant chemicals, followed by TPHP (mean, 613 ng/g), TEHP (mean, 278 ng/g), and TCIPP (mean, 245 ng/g). We found that the TBEOP concentration in Jiang'an District was significantly higher than that in Caidian District ($p < 0.05$), whereas the other 9 OPs were found at different levels without any significant differences.

Depending on the different substituent groups, there are more than 10 OPs being used that have been detected in the environment (van der Veen and de Boer 2012). Figure 1 shows the 7 most widely detected OPs (TNBP, TBEOP, TPHP, TMPP, TCEP, TCIPP, and TDCIPP) in the present study, with TEP and TPrP excluded because of their low concentrations and TEHP excluded because of its low detection frequency in previous studies. Figure 2 and Supplemental Data, Table S1, summarize the published data for indoor dust worldwide. As Figure 2 shows, low levels of these $\sum 7$ OPs were found in Pakistan (Ali et al. 2013) and Egypt (Abdallah and Covaci 2014). Similarly, mean concentrations of the 7 individual OPs and the resultant $\sum 7$ OPs in the 53 indoor dust samples in the present study were lower than those in previously reported data. For example, TBEOP (406 ng/g) in the present study was comparable to levels reported in Guangzhou (Ali et al. 2013), Saudi Arabia (Ali et al. 2016), and Germany (Brommer et al. 2012), although it was much lower than levels found in Beijing (8544 ng/g; Wu et al. 2016), Kuwait (10 685 ng/g; Ali et al. 2013), Norway (12 800 ng/g; Cequier et al. 2014), Sweden (5700 ng/g; Luongo and Östman 2016), and the United States (11 000 ng/g; Dodson et al. 2012). To the best of our knowledge, significantly high levels of TBEOP were found in Japan (248 521–508 320 ng/g; Araki et al. 2014; Mizouchi et al. 2015), which were 2 to 3 orders of magnitude higher than in other countries. Similarly, TPHP concentrations in the present study were clearly lower than those reported in European countries (Brommer and Harrad 2015; Luongo and Östman 2016), the United States (Dodson et al. 2012), and an e-waste recycling workshop in China (He et al. 2015). For the 3 chlorinated OPs, the average concentrations for each chemical were lower than those found in Guangzhou and Beijing (except for TDCIPP; He et al. 2015; Wu et al. 2016). The TCEP concentration (725 ng/g) was similar to levels reported in Saudi Arabia (Ali et al. 2016), Kuwait (Ali et al. 2013), Belgium (Van den Eede et al. 2011), and Romania (Dirtu et al. 2012) but lower than the levels in the United States (Dodson et al. 2012) and several European countries (Bergh et al. 2011; Brommer and Harrad 2015; Cristale et al. 2016; Luongo and Östman 2016). The TCIPP concentration (432 ng/g) was comparable to levels reported in New Zealand (Ali et al. 2012) and Germany (Brommer et al. 2012), whereas the TDCIPP concentration was comparable to that reported in Romania (Dirtu et al. 2012) and The Netherlands (Brandsma et al. 2014) but lower than concentrations in most of the countries mentioned in this paragraph. Comparatively, low

TABLE 1: Occurrence and distributions of organophosphate esters in dust from Wuhan City (nanograms per gram)

	CD District				JA District			
	Range	Mean	Median	DF (%)	Range	Mean	Median	DF (%)
TEP	ND–197	35.4	14.3	76.9	ND–782	94.3	17.8	51.9
TPrP	ND–37.2	14.3	8.79	30.8	ND–915	147	19.1	48.1
TNBP	ND–77.0	24.0	18.4	61.5	ND–220	39.7	23.7	88.9
TBEOP	ND–1307	244	158	46.2	ND–5252	885	254	77.8
TEHP	ND–675	155	111	96.2	ND–2696	278	146	92.6
TPHP	ND–770	265	220	80.8	ND–2819	613	350	81.5
TMPP	ND–161	64.3	32.5	23.1	ND–76.2	29.0	20.8	48.1
TCEP	9.14–2722	588	387	100	57.3–3718	856	616	100
TCIPP	LOD–5474	660	189	100	LOD–1718	245	142	100
TDCIPP	ND–1514	289	132	92.3	ND–951	156	81.5	81.5
ΣCl-OPs	23.6–6144				83.9–5221			
ΣNon-Cl-OPs	30.9–2048				61.3–5571			

Cl-OP = chlorinated organophosphate; DF = detected frequency; LOD = limit of detection; ND = not detected; TBEOP = tris(2-butoxyethyl) phosphate; TCEP = tris(2-chloroethyl) phosphate; TCIPP = tris(2-chloroisopropyl) phosphate; TDCIPP = tris(1,3-dichloro-2-propyl) phosphate; TEHP = tris(2-ethylhexyl) phosphate; TEP = triethyl phosphate; TMPP = tris(methylphenyl) phosphate; TNBP = tri-n-butyl phosphate; TPHP = triphenyl phosphate; TPrP = tripropyl phosphate.

levels of these OPs were found in household dust from the Philippines (Kim et al. 2013).

As discussed in the *Introduction*, OPs are found ubiquitously in indoor dust worldwide because their consumption has increased as PBDEs have been gradually phased out (Stapleton et al. 2012). This increase has attracted increased concern regarding indoor pollution by OPs and potential impacts on human health, especially with regard to their occurrence in indoor dusts. It could be that the different levels of OPs exhibiting different composition characteristics occurred in indoor dust from the mentioned countries. The phenomenon might be attributed to the following. The United States, some European countries, and Japan have taken the lead in using OPs as alternatives to PBDEs, and more strict fire regulations were required in these countries (Araki et al. 2014; Dodson et al. 2012; Mizouchi et al. 2015; Stapleton et al. 2012; Sühring et al. 2016) than in some less developed countries such as Pakistan (Ali et al. 2013). Consequently, high concentrations of OPs, even higher than the concentrations of PBDEs, have been found in dust samples from these countries (Araki et al. 2014; Brandsma et al. 2014; Cequier et al. 2014; Luongo and Östman 2016). In China, an increasing number of OPs are manufactured and used, but the flame retardant market is still dominated by traditional chlorinated/brominated flame retardants (China Market Research Reports 2017). It is therefore reasonable that relatively low concentrations of OPs were found in the dust samples from China, even lower than the concentrations of PBDEs (He et al. 2015; Wu et al. 2016). In a related study, we measured levels and distribution of PBDEs in the same indoor dust and found that BDE 209 (230–19 276 ng/g) dominated over tri-nano BDE (18.3–826 ng/g) by 1 to 3 orders of magnitude and was higher than OPs in the present study (Liu 2014), indicating that PBDEs are still used in China. Also, the sampling method could affect the occurrence and distribution of OPs in indoor dust (Ali et al. 2013); researchers collected dust by wiping with a brush or using a vacuum cleaner and treated samples without sieving or through different sieves, such as 100 μm (He et al. 2015), 250 μm (Mizouchi et al. 2015), and 500 μm (Van den Eede et al. 2011; Wu

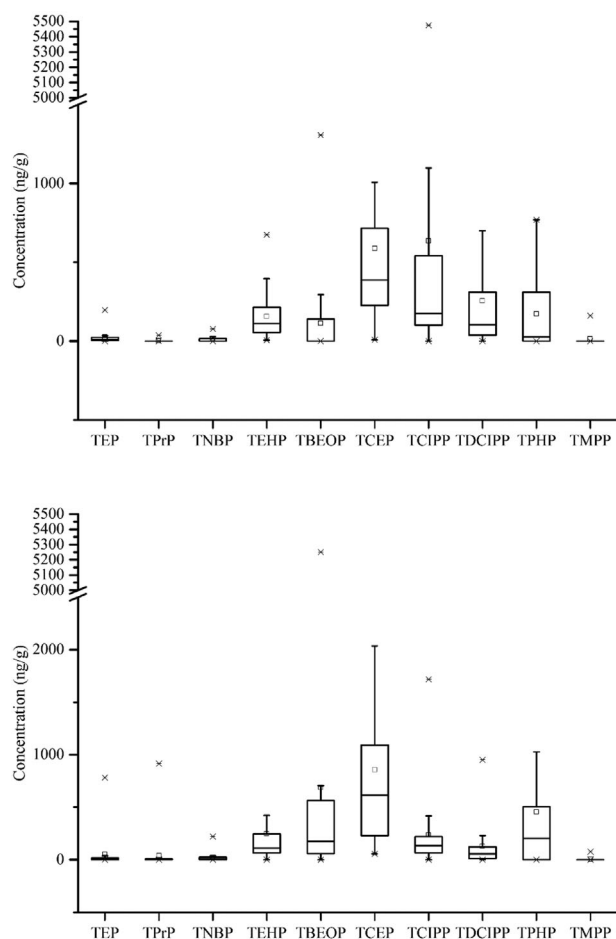


FIGURE 1: Box plot of the organophosphate ester concentrations in indoor dust from Caidian District (upper) and Jiang'an District (lower). The lower, middle, and upper lines in the box indicate the 25th, 50th, and 75th percentile values, respectively; the square symbol and lower and upper bars represent the mean, minimum, and maximum values, respectively. TBEOP = tris(2-butoxyethyl) phosphate; TCEP = tris(2-chloroethyl) phosphate; TCIPP = tris(2-chloroisopropyl) phosphate; TDCIPP = tris(1,3-dichloro-2-propyl) phosphate; TEHP = tris(2-ethylhexyl) phosphate; TEP = triethyl phosphate; TMPP = tris(methylphenyl) phosphate; TNBP = tri-n-butyl phosphate; TPHP = triphenyl phosphate; TPrP = tripropyl phosphate.

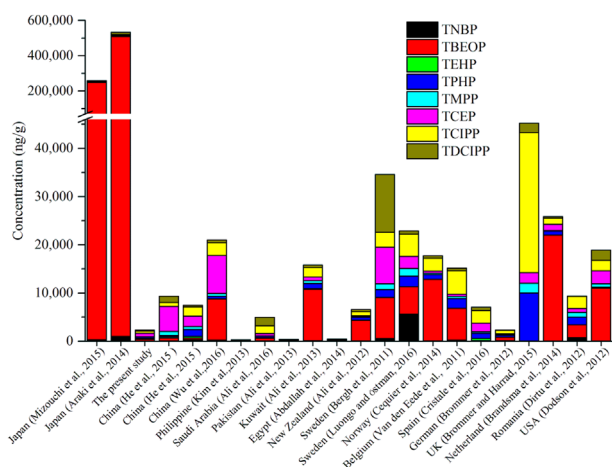


FIGURE 2: Levels of 7 widely used organophosphate esters (OPs) in indoor dust in some published references. (Tris[2-ethylhexyl] phosphate [TEHP] is not considered widely used because of its low detection frequency in previous studies.) TNBP = tri-n-butyl phosphate; TBEOP = tris(2-butoxyethyl) phosphate; TCEP = tris(2-chloroethyl) phosphate; TCIPP = tris(2-chloroisopropyl) phosphate; TDCIPP = tris(1,3-dichloro-2-propyl) phosphate; TTP = tris(trimethylsilyl) phosphate.

et al. 2016). As we know, OPs would be distributed in particles with different sizes depending on their physicochemical properties (Yang et al. 2014). Furthermore, specific individual OPs were widely used in different products (van der Veen and de Boer 2012), resulting in a different OP composition in the surrounding environment (Brommer and Harrad 2015; Mizouchi et al. 2015; Wu et al. 2016). For example, most of the studied Japanese houses have wooden flooring and/or PVC wallpaper; significantly high levels of TBEOP were found in these house dust samples because of the wide application of floor polish and of plasticizers in PVC (Araki et al. 2014; Mizouchi et al. 2015).

Composition profile of OPs in indoor dust

The composition profiles of OPs in Caidian District and Jiang’an District are shown in Figure 3. As can be seen in the figure, in most of the samples from Caidian District, TCEP and TCIPP were the predominant components, accounting for approximately 46% of $\sum 10\text{OPs}$ on average, whereas in Jiang’an District, TBEOP (average 34%) and TCEP (average 19%) were the predominant components, contributing >50% to $\sum 10\text{OPs}$.

The different composition and concentration of individual OPs revealed their possible emission sources in the regions studied. Because of its toxicity, TCEP has been gradually replaced by TCIPP and is forbidden in baby products in developed countries (Hoffman et al. 2015). However, in China, TCEP is still in use, with the high amounts used resulting in its ubiquitous presence in water/sediment, sludge, and the indoor environment (Cao et al. 2012; Ding et al. 2015; He et al. 2015; Yang et al. 2014; Zeng et al. 2014). In the present study, TCEP was found at high levels and with 100% frequency of detection, indicating its continued usage.

As TBEOP is an important additive of wax, floor polish, and paper coating, the TBEOP concentration was shown to be

strongly related to wooden flooring in houses in Japan (Araki et al. 2014), and in the present study, a few samples with high levels (e.g., Jiang’an District samples 12, 17, 18, 23, and 27) were also found in homes with wooden floors. However, no obvious correlation could be established between wooden floors and TBEOP levels in the regions studied. In general, TCEP and TCIPP are used in polyurethane foam, and TECP and TDCIPP are added to polyurethane foam, PVC, and textiles (van der Veen and de Boer 2012). Similar to TBEOP, no obvious coefficient relationship was found between these materials (type and amounts) and TCEP ($p = 0.134$), TCIPP ($p = 0.449$), and TDCIPP ($p = 0.488$). These phenomena might be explained by 1) various types of furniture/electronic equipment being used in specific dwellings, with different modes of use and additive doses, resulting in a broad range of emission loads, and 2) different

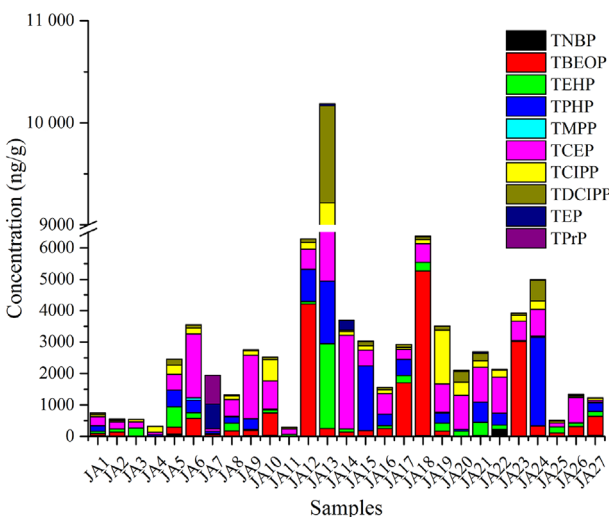
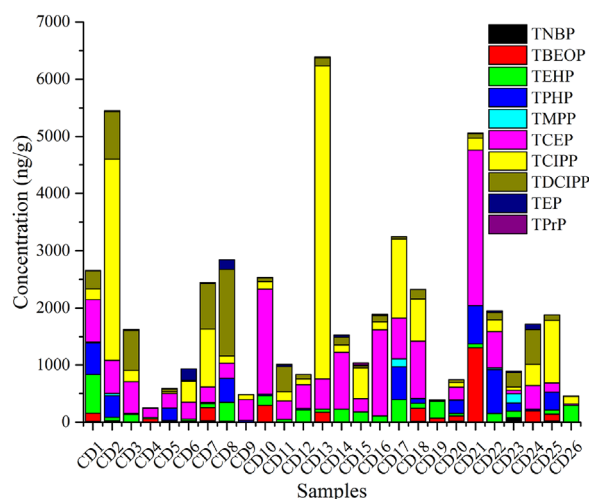


FIGURE 3: Composition profile of the 10 organophosphate esters (OPs) in dust from Caidian District (upper) and Jiang’an District (below). CD = Caidian District; JA = Jiang’an District; TBEOP = tris(2-butoxyethyl) phosphate; TCEP = tris(2-chloroethyl) phosphate; TCIPP = tris(2-chloroisopropyl) phosphate; TDCIPP = tris(1,3-dichloro-2-propyl) phosphate; TEHP = tris(2-ethylhexyl) phosphate; TEP = triethyl phosphate; TMPP = tris(methylphenyl) phosphate; TNBP = tri-n-butyl phosphate; TPHP = triphenyl phosphate; TPrP = tripropyl phosphate.

TABLE 2: Hazard index values by estimated daily human exposure (nanograms per kilogram bodyweight per day) to organophosphate ester reference doses

	Adults					Children				
	Mean	Minimum	Maximum	25th	75th	Mean	Minimum	Maximum	25th	75th
HI based on average exposure										
TNBP	1.99×10^{-06}	0.00	2.91×10^{-05}	0.00	2.73×10^{-06}	2.27×10^{-05}	0.00	3.32×10^{-04}	0.00	3.11×10^{-05}
TBEOP	8.59×10^{-05}	0.00	1.11×10^{-03}	0.00	5.13×10^{-05}	9.81×10^{-04}	0.00	1.27×10^{-02}	0.00	5.86×10^{-04}
TPHP	1.43×10^{-05}	0.00	1.28×10^{-04}	0.00	1.76×10^{-05}	1.64×10^{-04}	0.00	1.46×10^{-03}	0.00	2.01×10^{-04}
TMPP	2.58×10^{-06}	0.00	3.93×10^{-05}	0.00	0.00	2.94×10^{-05}	0.00	4.49×10^{-04}	0.00	0.00
TCEP	1.05×10^{-04}	1.32×10^{-06}	5.37×10^{-04}	3.28×10^{-05}	1.30×10^{-04}	1.19×10^{-03}	1.51×10^{-05}	6.12×10^{-03}	3.75×10^{-04}	1.48×10^{-03}
TCIPP	1.71×10^{-05}	0.00	2.17×10^{-04}	3.20×10^{-06}	1.30×10^{-05}	1.95×10^{-04}	0.00	2.48×10^{-03}	3.65×10^{-05}	1.49×10^{-04}
TDCIPP	4.02×10^{-05}	0.00	3.21×10^{-04}	4.23×10^{-06}	3.72×10^{-05}	4.59×10^{-04}	0.00	3.66×10^{-03}	4.82×10^{-05}	4.24×10^{-04}
HI based on high exposure										
TNBP	4.97×10^{-06}	0.00	7.28×10^{-05}	0.00	6.82×10^{-06}	9.08×10^{-05}	0.00	1.33×10^{-03}	0.00	1.25×10^{-04}
TBEOP	2.15×10^{-04}	0.00	2.78×10^{-03}	0.00	1.28×10^{-04}	3.92×10^{-03}	0.00	5.07×10^{-02}	0.00	2.34×10^{-03}
TPHP	3.58×10^{-05}	0.00	3.20×10^{-04}	0.00	4.40×10^{-05}	6.54×10^{-04}	0.00	5.84×10^{-03}	0.00	8.03×10^{-04}
TMPP	6.45×10^{-06}	0.00	9.83×10^{-05}	0.00	0.00	1.18×10^{-04}	0.00	1.80×10^{-03}	0.00	0.00
TCEP	2.61×10^{-04}	3.30×10^{-06}	1.34×10^{-03}	8.21×10^{-05}	3.24×10^{-04}	4.77×10^{-03}	6.02×10^{-05}	2.45×10^{-02}	1.50×10^{-03}	5.91×10^{-03}
TCIPP	4.28×10^{-05}	0.00	5.43×10^{-04}	8.00×10^{-06}	3.26×10^{-05}	7.82×10^{-04}	0.00	9.92×10^{-03}	1.46×10^{-04}	5.95×10^{-04}
TDCIPP	1.01×10^{-04}	0.00	8.01×10^{-04}	1.06×10^{-05}	9.29×10^{-05}	1.84×10^{-03}	0.00	1.46×10^{-02}	1.93×10^{-04}	1.70×10^{-03}

HI = hazard index; TBEOP = tris(2-butoxyethyl) phosphate; TCEP = tris(2-chloroethyl) phosphate; TCIPP = tris(2-chloroisopropyl) phosphate; TDCIPP = tris(1,3-dichloro-2-propyl) phosphate; TMPP = tris(methylphenyl) phosphate; TNBP = tri-n-butyl phosphate; TPHP = triphenyl phosphate.

levels of volatilization and/or abrasion during their life span. This explanation is supported by 2 published reports, which have demonstrated that OPs in indoor dust originate mainly from mechanical abrasion from used furniture rather than volatilization from newly purchased/obtained items (Keimowitz et al. 2016; Wu et al. 2016).

Ingestion exposure to OPs and the potential health risk

The hazard index values of 7 OPs (except for TEP, TPrP, and TEHP) for adults and children under different scenarios in Wuhan City are listed in Table 2. Concerning adults with average indoor ingestion dose (20 mg/d), hazard index values varied from 2.91×10^{-05} (for TBP) to 1.11×10^{-03} (for TBEOP), all significantly lower than 1. Even at a high dust ingestion dose of 50 mg/d, the maximum value of the hazard index varied from 7.28×10^{-05} to 2.78×10^{-03} , also significantly lower than 1. The results indicated that OPs in residential dust from Wuhan City posed limited human health risk through dust ingestion. As for children, because of their higher dust dose and lower body weight, a comparatively higher risk was found than that for adults. Under the worst-case scenario of high dust ingestion (200 mg/d), hazard index values ranged from 1.33×10^{-03} to 5.07×10^{-02} , which were much less than 1, suggesting limited health risk for children.

However, the potential risk of indoor OP exposure might be underestimated if estimates are based only on dust OP concentrations. As mentioned in the preceding paragraph, the presence of OPs in indoor dust suggests that OP-containing materials were used in the houses of the present study, and these could be important emission sources of OP pollution in the indoor environment. Depending on the exact chemicals used, a certain percentage of the OPs that escape from these materials might be partitioned into the gaseous phase as well as in fine particles in air. In particular, higher levels of chlorinated OPs have been found in the gaseous phase and fine particles than in dust, and this could be an important exposure pathway to the human body, resulting in a significant risk for human health (Schreder et al. 2016). In addition, OPs could be transformed into hydroxylated metabolites in the human liver, and these products might be more toxic than their parent compounds (Kojima et al. 2016; Van den Eede et al. 2013). Consequently, OP contamination and the resulting risk to human health should be given more attention in future.

CONCLUSION

In the present study, 53 indoor dust samples were analyzed for the occurrence and distribution of 10 OP flame retardants/plasticizers. In these samples, TCEP, TCIPP, and TBEOP were identified as the main OP components, although the composition was inconsistent with published data from Japan, the United States, and the United Kingdom. The results indicated different modes of application of flame retardants and PBDEs that are still in use in China. A limited human health risk was calculated based on the measured dust OP concentrations. Further studies should be conducted to determine the airborne concentrations of OPs

and dust concentrations for accurate risk assessment via inhalation and respiration, combined with the risk via dust ingestion.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3996.

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Data availability—Data, associated metadata, and calculation tools are available from the corresponding author (zhiqiang@gig.ac.cn).

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