



Co-occurrence and distribution of organophosphate tri- and di-esters in indoor dust from different indoor environments in Guangzhou and their potential human health risk[☆]

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ABSTRACT

In this study, 45 indoor dust samples and four particulate samples from air-conditioner filters were collected from four different indoor environments in Guangzhou, China, and the concentration and composition of organophosphate tri-esters (OPEs) and organophosphate di-esters (Di-OPs) were determined. Eight of the 10 target OPEs were detected in indoor dust at different detection frequencies (DFs), with tris(2-chloroisopropyl) phosphate and tris(2-chloroethyl) phosphate being the main components. Seven target Di-OPs were detected at different DFs, with diphenyl phosphate being the dominant compound. The total OPEs ($\sum 8$ OPEs) and total Di-OPs ($\sum 7$ Di-OPs) concentrations varied from 726 to 39,312 ng/g and 68.8–14,766 ng/g, respectively. The $\sum 8$ OPEs concentrations in instrumental houses were significantly higher ($p < 0.001$) than in three other indoor environments. The varying strengths of the correlation between Di-OPs and their respective parent OPEs was suggestive of their emission sources (e.g., direct application, impurities in OPE formulas, and OPE degradation). The hazard index (HI) values of individual OPEs in residential house were lower than 1, the results suggested a limited human health risk from individual OPEs. However, the total HI value (\sum HIs) of OPEs was approximately 1 based on a high exposure scenario and suggested a low risk for toddlers.

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1. Introduction

Organophosphate tri-esters (OPEs) are commonly used as flame retardants/plasticizers due to their excellent flame retardancy properties and flexibility. They have been physically incorporated into a range of products, such as upholstery materials, polyurethane foam, furniture, electronic devices, hydraulic fluids, and polyvinyl chloride materials (Wei et al., 2015; van der Veen and de Boer, 2012). Consequently, they are likely to be released to the ambient environment via volatilization, diffusion, and abrasion processes (Marklund et al., 2003; Cao et al., 2014). Combined with their substantial and long-term application, OPEs have been found ubiquitously in various compartments of the environment, including the indoor environment, aquatic systems (e.g., surface

water, groundwater, and sediment), wastewater and sludge, and the atmosphere, as well as in biota samples and the human body. This has been reviewed in detail by Wei et al. (2015) and Hou et al. (2016).

Due to their continuous emission from OPE-containing materials in the enclosed environment (Brommer and Harrad, 2015; Vojta et al., 2017; Wang et al., 2017), OPE concentrations in the indoor environment are generally higher than in the outdoor environment. Most OPEs are accumulated in indoor dust due to their preference for adsorption to particulates (logKoc 1.68–6.35, detailed information about their physicochemical properties was listed in Table S1) (Guardia and Hale, 2015; Persson et al., 2018). A number of studies have investigated OPE contamination in indoor environment and the potential human health risk, the results indicated that dust ingestion acted as an important pathway for human exposure to OPEs, accompanied by air inhalation, intakes from food and water, and absorption and permeation via dermal contact (Boer et al., 2016; Phillips et al., 2018; de la Torre et al., 2020).

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In contrast, there is limited information available regarding organophosphate di-esters (Di-OPs) in the indoor environment (Björnsdotter et al., 2018; Tan et al., 2019; Wang et al., 2020). Diphenyl phosphate (DPHP) was detected widely from different indoor environment from Spain and Netherland and the resultant health risk has been assessed (Björnsdotter et al., 2018). The co-occurrence of OPEs and Di-OPs has been found from residential indoor dust samples collected from Southern China and the mid-western USA (Tan et al., 2019). Similarly, residential indoor dust and outdoor dust across China also contained OPEs and Di-OPs exhibiting obviously regional difference, and significantly high concentration of the target chemicals have been found from urbanized area (Wang et al., 2020). However, little was known about co-occurrence of OPEs and Di-OPs in indoor environment other than residential environment, such as in office where computer, printer and office equipment were used extensively, or in instrumental houses where a large amount of analytical instrument were used.

Generally, organophosphate di-esters are commonly considered as OPE degradation products or as the metabolites of OPEs in organisms and humans (Hou et al., 2016). Their occurrence in human urine and breast milk, biota samples (Choo et al., 2018; Kim et al., 2019; Ma et al., 2019), as well as in wastewater and sludge (Fu et al., 2017; Zeng et al., 2014; Quintana et al., 2006) have been reported and proving their possible degradation and metabolism. In our previous study, we have found that OPEs, even those persistent chlorinated OPEs, could be degraded to their corresponding Di-OPs during industrial processes manufacturing OPE-containing materials (Xu et al., 2019).

As well known, some Di-OPs, such as di-*n*-butyl phosphate (DnBP), bis-(2-ethylhexyl) phosphate (BEHP), and DPHP are used directly as industrial additives (Quintana et al., 2006; Björnsdotter et al., 2018). Additionally, DPHP can be an impurity within some aryl OPs in household materials (Björnsdotter et al., 2018). Consequently, we speculated that these Di-OPs might also be released from OPE-containing materials during their application. Considering their range of emission sources, we investigated the co-occurrence of OPEs and Di-OPs in indoor dust from different environments, and then estimated their potential human risk via indoor dust ingestion.

In this study, 10 OPEs and seven Di-OPs were selected as target compounds, and 45 indoor dust samples and four particulate samples were collected from air-conditioner filters in different indoor environments in Guangzhou City, China. The main objectives of this study were to: 1) determine the levels and distribution of the selected OPEs and Di-OPs in the dust samples; 2) compare the different composition profiles among the different indoor environments; and 3) evaluate the human health risk posed by OPE and Di-OP exposure via dust ingestion.

2. Materials and methods

2.1. Standards and reagents

The selected OPEs were purchased from Sigma-Aldrich (St. Louis, MO, USA). The 10 selected OPEs were triethyl phosphate (TEP, 99.8%), tripropyl phosphate (TPrP, 99%), tri-*n*-butyl phosphate (TnBP, 99%), triphenyl phosphate (TPHP, 99%), tris(methylphenyl) phosphate (TMPP, 90%), tris(2-butoxyethyl) phosphate (TBOEP, 94%), tris(2-ethylhexyl) phosphate (TEHP, 97%), tris(2-chloroethyl) phosphate (TCEP, 97%), tris(2-chloroisopropyl) phosphate (TCIPP, 99.5%), and tris(1,3-dichloroisopropyl) phosphate (TDCIPP, 97%). Two Di-OPs, diethyl phosphate (DEP) and DnBP, were purchased from ChemService Inc. (West Chester, PA, USA), while four others, bis(2-chloroethyl) phosphate (BCEP), bis(1-chloro-2-propyl)

phosphate (BCIPP), DPHP, and bis(butoxyethyl) phosphate (BBOEP) were obtained from Toronto Research Chemicals Inc. (Toronto, Ontario, Canada). Bis(1,3-dichloro-2-propyl) phosphate (BDCIPP) was purchased from Wellington Laboratories (Guelph, Ontario, Canada). The details of the target compounds are given in Table S1.

Four deuterated OPE standards were obtained from C/D/N Isotopes Inc. (Quebec, Canada) and used as surrogates in OPE analyses: d₁₅-TEP (99.1%), d₂₇-TnBP (98%), d₁₅-TPHP (98%), and d₁₂-TCEP (98%). Three deuterated Di-OPs (d₈-BCEP, d₁₂-BCIPP, and d₁₀-DPHP) were purchased from Toronto Research Chemicals Inc. and used as surrogates in Di-OP analyses. The internal standard hexamethylbenzene (HMB, 99.5%) was obtained from Ehrenstofer-Schäfer Bgm-Schlosser (Augsburg, Germany). All solvents were of chromatographic grade. Acetone, *n*-hexane, and dichloromethane (DCM) were purchased from Merck Co. (Darmstadt, Germany), and ethyl acetate (EtOAc) was purchased from CNW Technologies GmbH (Düsseldorf, Germany). Oasis WAX cartridge (150 mg, 6 mL) were purchased from the Waters Corporation (Milford, MA, USA).

Silica gel (70–230 mesh) was obtained from Merck Co. (Darmstadt, Germany), activated at 180 °C for 12 h, and deactivated with 3% (w/w) redistilled water. Neutral alumina (100–200 mesh, purchased from Wusi Chemical Factory, China), was continuously Soxhlet-extracted with methanol and dichloromethane for 48 h, then activated at 250 °C for 12 h, and deactivated with 3% (w/w) redistilled water. The treated silica and alumina were kept in *n*-hexane before use. Anhydrous sodium sulfate was baked at 450 °C for 4 h prior to use.

2.2. Sample collection

The dust samples were collected according to the standardized sampling technique described in the Verein Deutscher Ingenieure (Zeng et al., 2018a). Forty-five indoor dust samples were collected from different indoor environments (residential house, office, chemical laboratory, and instrumental house) from May 2015 to July 2017 in Guangzhou City, China, and four particulate samples were simultaneously collected from air-conditioner filters (AC dust). Eleven indoor dust samples were obtained from residential house, 22 were obtained from offices, nine were obtained from instrumental houses in which many analytical instrument were placed, and three were obtained from laboratories used for the pretreatment of environmental samples. Dust samples were wrapped in aluminum foil and sealed in PVC bags after sampling, and then stored at –20 °C until analysis. The details of the four microenvironments are given in Table S2.

2.3. Sample preparation

Prior to extraction, the dust was sieved using a stainless steel sieve (60 mesh) to obtain the fraction with a particle size <250 μm. The procedure for the extraction and clean-up of OPEs has been published previously (Zeng et al., 2018b), and the extraction and enrichment of Di-OPs was conducted according to a method published previously, with some modification (Li et al., 2017). A detailed description of the analytical methods is provided in the Supporting Information. A brief description is provided here.

Indoor dust and AC dust samples of about 200 mg were spiked with 200 ng each of surrogate (d₁₅-TEP, d₂₇-TnBP, d₁₅-TPHP, and d₁₂-TCEP) and Soxhlet-extracted with DCM for 72 h. The extracts were concentrated and separated via a chromatographic column packed with neutral alumina and silica gel (1:2). The fraction containing OPEs was evaporated to almost dryness under a gentle N₂ stream and re-dissolved in 200 μl *n*-hexane. Finally, 100 ng HMB was added as an internal standard before a gas chromatography -

mass spectrometry (GC-MS) analysis.

Indoor dust and AC dust samples of approximately 200 mg were spiked with 40 ng each of surrogate (d_8 -BCEP, d_{12} -BCIPP, and d_{10} -DPHP), extracted twice by ultrasonic-assistance with MeOH for 30 min, and subjected to solid phase extraction (SPE) after the solvent was exchanged into 1% MeOH/water and the pH was adjusted to 5 using a NaAC-HAC buffer. The target Di-OPs were recovered and concentrated, and then reconstituted in the 400 μ L MeOH/ultrapure water mixture (1:1, v/v).

Identification and determination of OPEs and Di-OPs was achieved by GC-MS (GC-MS-QP 2010; Shimadzu Corp., Kyoto, Japan) and high performance liquid chromatography (HPLC) using a liquid chromatography unit coupled with an 6460 triple quad mass spectrometer (LC-MS-MS, Agilent Technologies, Santa Clara, CA, USA). The details of the instrumental analyses are given in the Supporting Information.

The limits of detection (LODs) for target OPE compounds, calculated as the standard deviation of seven repeat injections, with a low concentration approximately equal to a blank sample, were in the range of 1.15–6.09 ng/g (Table S3). The LODs for the target Di-OP compounds, defined as a signal-to-noise ratio of 3, varied from 2.68 to 34.5 ng/g (Table S4). The limits of quantification (LOQs) were defined as twice the background values for those compounds detected in blanks, or as twice the LOD for those compounds not found in blanks. Those target compounds without a signal response during instrumental analyses were defined as not detected (ND), and those compounds with a signal response lower than LOQs were defined as LOQs.

2.4. Quality assurance and quality control

During the analytical procedure, strict quality assurance and quality control measures were adopted. Procedural blanks ($n = 8$), spiked blanks (standards spiked into the solvent), spiked matrix (standards spiked into pre-extracted dust), and duplicate samples were analyzed as real samples. In all blanks, TCIPP was found with an average concentration of 44.9 ng/g, TCEP was found in six blanks, with an average concentration of 26.7 ng/g, and TnBP, TDCIPP, and TPHP were detected at their LOQs, but no other OPEs were detected in any blank samples. It has been reported that DnBP was widely detected in the sorbent of Oasis WAX cartridge (Li et al., 2017; Van den Eede et al., 2013), which could not be removed by 2 mL of 5% NH_4OH in methanol (Van den Eede et al., 2013). In the present study, much more solvents (e.g., 4 mL of methanol, 4 mL of 5% NH_4OH in methanol and 6 mL of NaAC-HAC buffer) were used to condition the cartridge and remove DnBP from the sorbent. In the procedural blanks, DPHP was detected with an average concentration of 13.1 ng/g, but the other five Di-OPs were not found in any blanks. The recovery rate of d_{15} -TEP ($22.8 \pm 9.22\%$) was low due to its high volatility (Please see Table S1), but acceptable recovery rates were achieved for d_{27} -TnBP, d_{12} -TCEP, d_{15} -TPHP, d_8 -BCEP, d_{12} -BCIPP, and d_{10} -DPHP at $93.2 \pm 17.0\%$, $116 \pm 14.4\%$, $77.4 \pm 15.0\%$, $98.6 \pm 17.6\%$, $101 \pm 18.6\%$, and $101 \pm 11.1\%$, respectively. In the present study, all the reported values were background-subtracted for those chemicals present in the blanks, but were not corrected with recovery rates.

2.5. Statistical analysis

Statistical analyses were conducted using the OriginPro 9.1 and SPSS 20 software packages. For any target compounds showing DFs higher than 60%, measured values below the LOQs were replaced by 1/2 LOQs, and all original data were log-transformed to approximate a normal distribution before analysis using SPSS 20 (Tan et al., 2019). Spearman's correlation analyses were used to determine the

correlations between individual Di-OPs and their respective parent OPEs (Tan et al., 2019). A one-way analysis of variance and nonparametric tests were performed to determine the statistically significant differences among different indoor environments (Vojta et al., 2017). A statistical significance was reported when $p < 0.05$. No attempt was made to determine the relationship between BCEP and TCEP because of the low DF of BCEP.

3. Results and discussion

3.1. Concentrations and composition profiles of OPEs in indoor dust

The OPE concentrations in indoor dust from the different indoor environments is summarized in Table 1. In this study, TEP and TPrP were not found in any sample, which might be ascribed to their limited usage or high volatilities (Table S1), as indicated by the low recovery of d_{15} -TEP. They were therefore excluded from Table 1.

As can be seen from the table, TCEP (105–19,511 ng/g), TCIPP (192–34,662 ng/g), TDCIPP (27.0–10,747 ng/g), TMPP (7.24–4948 ng/g), TPHP (114–9779 ng/g), and TBOEP (LOQ–23,526 ng/g) were detected in all samples. Forty-two samples contained TnBP at concentrations in the range of LOQ–305 ng/g, and TEHP was detected in 44 samples at concentrations in the range of 30.5–3122 ng/g. The total concentrations of the eight detected OPEs ($\Sigma 8$ OPEs) were in the range of 726–39,312 ng/g, with an average value of 9442 ng/g. Based on the detection frequency (DF) and average concentration, TCIPP (average concentration 4329 ng/g) was the dominant compound, followed by TCEP (average 2232 ng/g). Generally, the total chlorinated OPEs (ΣCl -OPEs) concentration (369–38,141 ng/g, average value of 7219 ng/g) was higher than that of non-chlorinated OPEs (ΣNCl - OPEs, 208–28,554 ng/g, average value of 2223 ng/g). This might reflect the historical fact that Cl-OPEs have been produced and used in larger quantities than NCl-OPEs (Zhou et al., 2017), as well as their long persistence in the environment (van der Veen and de Boer, 2012).

Recently, extensive studies of OPEs in indoor dust have been conducted worldwide, and some of the results are listed in Table S5. It can be seen from the table that the OPE concentrations in this study could be considered to be at an intermediate-level, with a different composition profile compared to results published worldwide. The dominant OPE in residential indoor dust in this study was TCEP, which was in accordance with previous results, in Guangzhou (He et al., 2015; Tan et al., 2019), Wuhan (Zeng et al., 2018a), and Beijing (Wu et al., 2016). In most countries, especially the USA, Japan, and several European countries, TCEP is a minor component accounting for less than 15% of the total Σ OPEs (Schreder and Guardia, 2014; Brommer and Harrad, 2015; Mizouchi et al., 2015; Zhou et al., 2017; Cristale et al., 2018). This phenomenon might be ascribed to the fact that developed countries such as the USA, European countries, and Japan have taken the lead in replacing TCEP with TCIPP (Zeng et al., 2018a).

It was interesting that different OPE concentrations and composition profiles were recorded in the different indoor environments. As indicated in Table 1, OPE concentrations in indoor dust from the instrumental house (8667–39,312 ng/g, average value of 23,885 ng/g) were significantly ($p < 0.001$) higher than those in the residential house (1042–29,900 ng/g, average 8000 ng/g), office (726–16,652 ng/g, average 5241 ng/g), and chemical laboratory (1436–3179 ng/g, average 2205 ng/g). In the instrumental houses, the windows were shut to keep the humidity and temperature constant, and a range of analytical instruments and computers were installed. Large amounts of OPEs might have been released from these equipment and then absorbed on particulate, resulting in very high OPE concentrations in indoor dust (van der

Table 1
Organophosphate tri-ester concentrations (ng/g) in indoor dust from different micro-environments.

	Residential House			Office			Chemical Laboratory			Instrumental House		
	Median	average	range	median	average	range	median	average	Range	median	average	range
TCEP	712	2770	176–19,511	552	1158	105–5199	597	629	312–980	3733	4734	824–10,953
TCIPP	555	970	375–3847	1719	2607	192–8486	546	601	321–938	6790	13,886	943–34,662
TDCIPP	131	352	27.0–1735	192	247	57.5–1038	118	214	112–412	980	2187	232–10,747
TPHP	906	903	114–1849	647	744	120–1715	347	429	204–734	836	1758	200–9779
TMPP	43.7	45.2	7.24–98.1	61.4	77.5	8.98–260	99.7	82.1	34.4–116	57.3	927	29.6–4948
TnBP	21.6	58.1	LOQ–305	26.0	38.5	ND–235	37.3	51.2	32.9–83.4	58.7	64.8	27.4–118
TBOEP	88.2	2215	LOQ–23526	59.3	85.5	LOQ–266	47.5	34.3	LOQ–55.5	61.8	88.8	LOQ–202
TEHP	513	687	ND–3122	213	284	83.5–1442	170	164	91.3–231	145	240	30.5–926
∑OPEs	4798	8000	1042–29,900	3935	5241	726–16,652	2000	2205	1436–3179	21,418	23,885	8667–39,312

ND: not detected; LOQ: below the limit of quantification.

Veen and de Boer, 2012; He et al., 2016). Compared to the other microenvironments, the chemical laboratories had more space, with excellent ventilation, in which the necessary experimental tables and limited electronic devices were installed. As a consequence, it was not surprising that the lowest OPE concentrations were measured in the chemical laboratories (Zhou et al., 2017).

Generally, Cl-OPEs dominated over NCl-OPEs in all indoor dust samples (51–87%). In addition, the Cl-OPEs concentration in instrumental house dust was significantly ($p < 0.05$) higher than in the other three indoor environments, which might be ascribed to the extensive array of instruments and computers that were installed (He et al., 2016). Higher levels of TBOEP were found in the residential house samples than in the other indoor environments, which was possibly due to the regular use of floor polishes and waxes or PVC and rubber products (Abdallah and Covaci, 2014).

We also found different OPE composition profiles in the different indoor environments, as shown in Fig. 1. In the office and instrumental house samples, TCIPP contributed about 50% and 58% of the ∑8 OPEs, respectively, followed by TCEP (22% and 20%, respectively). These results suggest similar emission sources in these environments, especially electrical devices and building materials (Zhou et al., 2017). In contrast, TBOEP accounted for 28% of the ∑8OPEs in residential indoor dust, but only a very limited amount (<3%) in the other indoor environments, suggesting the importance of TBOEP emissions from wooden floors due to the applications of floor polishes and/or floor wax, as well as TBOEP-containing building and decoration materials in the residential house (Zeng et al., 2018a; Wang et al., 2017). The concentrations and composition profiles of OPEs in indoor dust were concluded to

be dependent on the use of OPE-containing products in the indoor environment.

3.2. Concentrations and composition profiles of Di-OPs in indoor dust

The concentration and distribution of Di-OPs in indoor dust from the different indoor environments are summarized in Table 2. It was found that DPHP and DnBP were detected in all indoor dust samples at levels of 26.4–6646 ng/g (average 585 ng/g) and 28.8–1076 ng/g (average 163 ng/g), respectively. In the dust samples DEP (ND–1967 ng/g) and BBOEP (ND–936 ng/g) were found at similar DFs of 88.6%. Among the chlorinated Di-OPs, BCEP, BCIPP, and BDCIPP were detected in the ranges of ND–1892 ng/g, ND–1741 ng/g, and ND–11,832 ng/g, respectively. The DF of BDCIPP (90.9%) was higher than that of BCEP (43.2%) and BCIPP (63.6%), and the highest level of BDCIPP (11,832 ng/g) was one or more orders of magnitude higher the highest levels of BCEP (1892 ng/g) and BCIPP (1741 ng/g). The total concentrations of the seven Di-OPs (∑Di-OPs) ranged from 68.8 ng/g to 14766 ng/g (average 1987 ng/g), with DPHP and DnBP predominant over the other Di-OPs. Based on the DFs and average concentrations, DPHP was the dominant Di-OPs in indoor dust.

The highest ∑Di-OPs concentration was observed in the instrumental houses, with a range of 91.7–14,766 ng/g (average 4657 ng/g), followed by the chemical laboratories (444–3863 ng/g, average 1812 ng/g), office (342–3895 ng/g, average 1473 ng/g), and residential house (68.8–2312 ng/g, average 888 ng/g). Concentrations of BCIPP and BDCIPP in instrumental house dust were significantly ($p < 0.05$) higher than those in the other indoor environments, which was in accordance with the compositional characteristics of TCIPP and TDCIPP. This could be explained that their respective impurities and degradation products that constituted the main sources of BCIPP and BDCIPP in indoor dust.

In contrast to the extensive studies of OPE contamination, only limited data is available regarding Di-OPs in indoor dust. In Australian household dust, DPHP was detected at concentrations ranging from 75 to 190 ng/g (Van den Eede et al., 2015), with other studies reporting levels from 106 to 79,660 ng/g in Spain and the Netherlands (Björnsdotter et al., 2018). Tan et al. (2019) investigated the levels and composition of seven Di-OPs in house dust from South China and the midwestern United States: BCEP, BCIPP, BDCIPP, BBOEP, DPHP, bis(2-ethylhexyl) phosphate (BEHP), and bis(2-methylphenyl) phosphate (BMPP). The authors reported that DPHP and BBOEP were found with DFs of 100% and 90%, and concentration ranges of 31.24–4070 ng/g and LOQ–12,880 ng/g in South China and 903–27,460 ng/g and 96.0–85,950 ng/g in USA, respectively. These results were similar to ours.

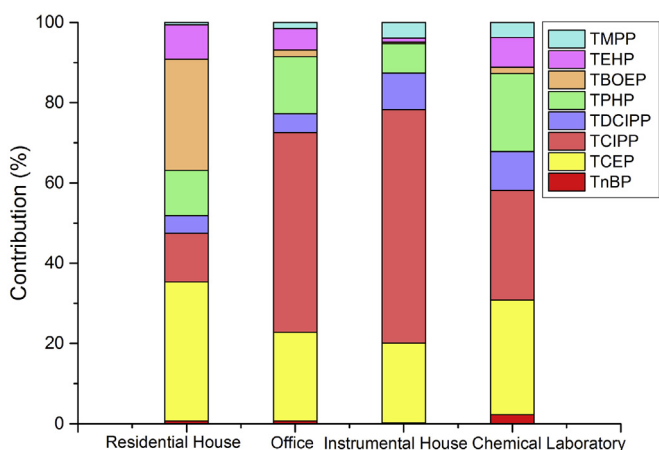


Fig. 1. Congener profiles of organophosphate tri-esters (OPEs) in four micro-environments.

Table 2
Organophosphate di-ester concentrations (ng/g) in indoor dust from different micro-environments.

	Residential House			Office			Chemical Laboratory			Instrumental House		
	Median	average	range	median	average	range	median	average	Range	median	average	range
DEP	29.6	122	ND-562	247	451	14.5–1967	166	593	93.1–1521	116	176	ND-672
DnBP	119	138	28.8–288	108	171	31.9–766	121	416	51.0–1076	86.3	88.4	30.3–151
BBOEP	9.16	103	ND-936	5.22	11.0	ND-55.9	2.20	12.5	ND-35.2	4.96	5.08	ND-12.0
BCEP	139	122	ND-351	ND	129	ND-464	200	213	ND-440	ND	399	ND-1892
BCIPP	ND	9.62	ND-78.0	118	149	ND-611	ND	1.92	ND-5.77	883	729	ND-1741
BDCIPP	11.9	119	ND-922	84.5	105	ND-329	111	112	104–122	302	1840	20.2–11832
DPHP	198	275	26.4–855	395	456	89.8–1261	533	463	193–663	563	1419	40.5–6646
∑Di-OPs	628	888	68.8–2312	1078	1473	342–3895	1131	1812	444–3863	1851	4657	91.7–14766

ND: not detected.

3.3. Relationships between OPEs and Di-OPs and their possible emission sources

The measured concentrations of Di-OPs largely reflected their original abundance in indoor dust due to the limited photo-degradation, hydrolysis, and microbiological degradation in the indoor environment (Tan et al., 2019).

Statistically significant positive correlations were observed between BCIPP and TCIPP ($r = 0.729$, $p < 0.01$), BDCIPP and TDCIPP ($r = 0.545$, $p < 0.01$), and DPHP and TPHP ($r = 0.559$, $p < 0.01$). The results suggested a similar emission source in the indoor environment (Tan et al., 2019). However, no statistical correlations were observed between DnBP and TnBP, and BBOEP and TBOEP.

The ratio of each Di-OP to its corresponding OPE (R) was calculated. As indicated in Table 3, a low $R_{BCIPP/TCIPP}$ was obtained (range of 0.005–0.213, average 0.048), and together with its statistically significant correlation ($r = 0.729$, $p < 0.01$), the results suggested their similar emission source from materials in indoor environment. As we reported previously, chlorinated OPEs could be degraded to their respective Di-OPs during manufacturing procedure of OPEs-containing materials (Xu et al., 2019). Consequently, we speculated that the resultant Di-OPs were mixed into these materials and released into indoor environment during application of the materials. Based on above discussion, we speculated that BCIPP might be an impurity in commercial TCIPP formulas and/or degradation products of TCIPP during rigorous industrial manufacturing procedures. The results were similar to those reported by Tan et al. (2019), who calculated similar $R_{BCIPP/TCIPP}$ (0–0.11) in residential indoor dust in Guangzhou, and considered that BCIPP in indoor dust being an impurity in commercial TCIPP formulas and/or degradation products of TCIPP (Tan et al., 2019).

For the pairing of BDCIPP and TDCIPP, a higher R value (0.022–1.39) and lower correlation ($r = 0.545$, $p < 0.01$) than that of BCIPP and TCIPP was determined, suggesting that BDCIPP was emitted mainly from sources other than as TDCIPP impurity. In addition BDCIPP is not a commercial chemical. Consequently we considered that BDCIPP was largely a degradation product that was mixed into OPE-containing materials during the manufacturing process (Xu et al., 2019), and was then released from materials

Table 3
Concentration ratios and correlation values of each organophosphate di-ester to its respective parent OPE in indoor dust.

Di-OP/OPE pairs	correlation value	Concentration ratio min-max (average)
TnBP/DnBP	$r = 0.052$, $p > 0.05$	0.671–28.9 (4.29)
TCEP/BCEP	$r = 0.112$, $p > 0.05$	0–1.63 (0.210)
TCIPP/BCIPP	$r = 0.729$, $p < 0.01$	0.005–0.214 (0.048)
TDCIPP/BDCIPP	$r = 0.545$, $p < 0.01$	0.022–1.39 (0.498)
TPHP/DPHP	$r = 0.559$, $p < 0.01$	0.036–2.23 (0.676)
TBOEP/BBOEP	$r = 0.073$, $p > 0.05$	0–0.429 (0.101)

alongside TDCIPP during application.

High values of $R_{DPHP/TPHP}$ were obtained, ranging from 0.036 to 2.23, which suggested that aryl OPE impurities might not be the main source of DPHP in indoor dust. Instead, degradation products from aryl OPEs during the industrial process (Xu et al., 2019), as well as its direct application as an industrial additive, for example as a catalyst in polymerization or an additive in paints and coatings (Björnsdotter et al., 2018; Tan et al., 2019; Wang et al., 2020), were likely to be the main reasons for its presence in indoor dust. A strong correlation ($r = 0.559$, $p < 0.01$) was found between DPHP and TPHP, which was similar to that reported by Tan et al. (2019) and Wang et al. (2020), suggesting that DPHP as an impurity or degradation product might mainly be associated with TPHP, rather than ethylhexyl diphenyl phosphate and resorcinol bis(diphenyl-phosphate) (Mitchell et al., 2019).

In contrast, no correlation ($p > 0.05$) was observed between DnBP and TnBP, with a very high $R_{DnBP/TnBP}$ value (0.671–28.9, average 4.29). The results indicated that DnBP might be originated from its industrial application as a plasticizer and metal extractant (Quintana et al., 2006), as well as being a degradation product of TnBP during industrial processes (Xu et al., 2019).

Although there is growing scientific evidence for the adverse effects of OPEs on ecosystems and human health, little is known about the toxicity of Di-OPs. Mitchell et al. (2019) demonstrated that DPHP impacted on the cardiac development of zebra fish in a similar way to TPHP. Further studies should be conducted to determine the occurrence and potential toxicity of Di-OPs, as well as the geochemical processes that lead to their presence in the environment.

3.4. Levels of OPEs and Di-OPs in AC dust

Four paired samples from four sites were analyzed to compare the levels and composition of OPEs and Di-OPs between indoor dust and AC dust. In general, AC dust had higher \sum OPEs (3421–199,640 ng/g) and \sum Di-OPs (201–4620 ng/g) concentrations than their respective indoor dust (OPEs at 1845–29,900 ng/g, Di-OPs at 211–2669 ng/g) (Fig. 2a), suggesting a different adsorption behavior that was dependent on dust particle size due to their different physicochemical properties (Yang et al., 2014). In addition, different composition profiles were also found between these paired samples (Fig. 2b). As can be seen from the Fig, compounds with low vapor pressure exhibited preference on AC dust, such as TPHP (log Koc 4.7), TBOEP(log Koc 5.66) (detailed information about the physicochemical properties were listed in Table S. The AC dust was a complex matrix of smaller particles from the air, which presented a large surface area that would have a strong binding capacity toward organic contaminants (Kang et al., 2012; Cequier et al., 2014). Yang et al. (2014) have found that OPEs with low vapor pressure are inclined to absorb on small size particles, for

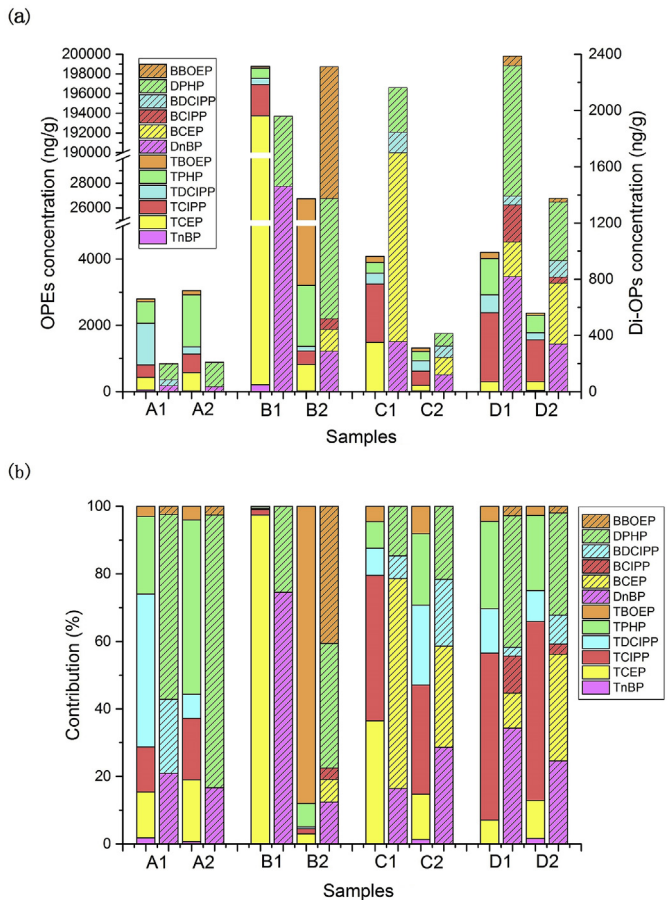


Fig. 2. Concentrations (a) and Congener profiles (b) of OPEs and Di-OPs between AC dust and surface dust. 1 referred to AC dust, 2 referred to surface dust.

example, TMPP, TPHP and TEHP were mainly located on ultrafine particles ($\leq 1 \mu\text{m}$), TnBP was on fine particles ($\leq 2.5 \mu\text{m}$). Consequently, it was rational that higher OPE loading on AC dust than those on indoor dust. Consequently, elevated OPE concentrations would accumulate on AC dust as the amount of particulate retained on the filters increased, if the air-conditioner was not cleaned regularly (Yu et al., 2013).

3.5. Human exposure assessment

Based on the measured OPEs and Di-OPs concentration from residential indoor dust, we estimated the daily intake of OPEs and Di-OPs via indoor dust ingestion using the following equation (Van den Eede et al., 2011; Ali et al., 2013):

$$EDI = C \times D_{\text{dust}} \times I_R / \text{Body weight}$$

where, EDI (ng/kg body weight/d) is the estimated daily intake, C is the OPE or Di-OP (ng/g) concentration in indoor dust, D_{dust} is the daily intake of dust (mg/day), and I_R is the dust ingestion. We assumed 100% absorption of OPEs and Di-OPs from the ingestion of dust, with an average dust intake of 20 and 50 mg/day, and a high dust intake of 50 and 200 mg/day for adults and toddlers, respectively (Van den Eede et al., 2011). We assumed an average body weight of 63 kg for adults and 13.8 kg for toddlers, according to a previous study (Zeng et al., 2018a). Then, the hazard index (HI) value of each OPE, i.e., the ratio of the estimated daily intake (EDI, listed in Table S6) to its corresponding reference dose (RfD, listed in

Table S7), was used to assess the human exposure risk. No reference dose was available for TEHP and Di-OPs (Van den Eede et al., 2011), and therefore HI values for the remaining seven OPEs were measured and then listed in Table 4. The EDI values of the seven Di-OPs are listed in Table 5.

The EDI of OPE via dust ingestion for adults and toddlers was 0–7.47 ng/kg bw/day and 0–85.2 ng/kg bw/day, respectively, under the average scenario, and 0–18.7 ng/kg bw/day and 0–341 ng/kg bw/day, respectively, under the high exposure scenario. The EDI of Di-OPs via dust ingestion for adults was 0.055–1.84 ng/kg bw/day (average 0.704 ng/kg bw/day) and 0.218–7.34 ng/kg bw/day (average 2.82 ng/kg bw/day) under the average and high exposure scenarios, respectively. An elevated exposure was found for toddlers, with values in the range of 0.100–3.35 ng/kg bw/day (average 1.29 ng/kg bw/day) and 0.249–8.38 ng/kg bw/day (average 3.22 ng/kg bw/day) due to their lower body weight, higher dust ingestion dose, and more frequent hand-to-mouth contact.

For the average dust exposure for adults and toddlers, HI values varied from 0 to 4.98×10^{-03} and from 0 to 5.68×10^{-02} , respectively. For the high dust exposure scenario, the higher HI of TBOEP was determined to be $\sim 1.24 \times 10^{-02}$ for adults and $\sim 2.27 \times 10^{-01}$ for toddlers. Toddlers had a higher health risk than adults under the same conditions because of their higher dust ingestion, which resulted from their activity on the ground and more frequent hand-to-mouth contact (Stapleton et al., 2009; Wu et al., 2016). In the present study, the HI values of the individual OPEs were below 1 for adults and toddlers, indicating a limited human health risk through dust ingestion for local inhabitants. However, it was notable that under the worst scenario (the highest concentration of TCEP and TBOEP detected in the present study), the HI of TCEP (1.29×10^{-01}) and TBOEP (2.27×10^{-01}) indicated a possible risk to toddlers.

Until recently, limited data regarding the reference dose of Di-OPs was available, therefore no HI values have been calculated to assess the potential human health risk. However, the results indicated that more attention should be given to the occurrence, transformation, and toxicity of these Di-OPs, especially those ubiquitously present in the environment at high concentrations. Dermal uptake via contact with dust and air inhalation also represented important exposure pathways in addition to dust ingestion (Abdallah et al., 2016; Schreder et al., 2016), and further studies should be conducted to determine the human health risks through various exposure pathways.

4. Conclusion

In summary, OPEs were widely detected in different indoor environments with total concentrations in the range of 726–39,312 ng/g (average 9442 ng/g). Two chlorinated OPEs, TCIPP and TCEP, dominated over aryl OPEs and alkyl OPEs, suggesting their being in use and potential human health exposure risk. The HI values of individual OPEs were lower than 1, suggesting a limited health risk of OPEs via dust ingestion for adults and toddlers. However, the total HI value of OPEs based on a high exposure was approximately 1 for toddlers. Further study should be carried out for their occurrence in gaseous phase due to their higher vapor pressure, and the resultant potential human health risk, for comprehensive assessment of OPEs risk in indoor environment.

Simultaneously, Di-OPs were widely detected in different indoor environments with total concentrations of 68.8–14,766 ng/g (average 1987 ng/g). High levels of DPHP and DnBP were measured in all samples, with an overall range of 26.4–6646 ng/g and 28.8–1076 ng/g, respectively. The results suggested their commercial application. It was notable that BECP and BCIPP were found showing DFs >40%, suggesting their similar emission sources to OPEs from items installed in indoor dust. Intake Di-OPs via dust

Table 4
Hazard index values by estimated daily human exposure to OPE reference doses.

	Adults					Toddlers				
	Mean	Minimum	Maximum	25th	75th	Mean	Minimum	Maximum	25th	75th
HI values based on high exposure										
TCEP	9.99×10^{-04}	6.35×10^{-05}	7.04×10^{-03}	2.17×10^{-04}	6.48×10^{-04}	1.82×10^{-02}	1.16×10^{-03}	1.29×10^{-01}	2.79×10^{-03}	1.18×10^{-02}
TCIPP	9.62×10^{-05}	3.72×10^{-05}	3.82×10^{-04}	8.30×10^{-05}	9.56×10^{-05}	1.76×10^{-03}	6.80×10^{-04}	6.97×10^{-03}	8.36×10^{-04}	1.75×10^{-03}
TDCIPP	1.86×10^{-04}	1.43×10^{-05}	9.18×10^{-04}	7.47×10^{-05}	1.39×10^{-04}	3.40×10^{-03}	2.61×10^{-04}	1.68×10^{-02}	1.10×10^{-03}	2.54×10^{-03}
TPHP	1.02×10^{-04}	1.30×10^{-05}	2.10×10^{-04}	6.41×10^{-05}	1.46×10^{-04}	1.87×10^{-03}	2.37×10^{-04}	3.83×10^{-03}	9.34×10^{-04}	2.67×10^{-03}
TMPP	2.76×10^{-05}	4.42×10^{-06}	5.99×10^{-05}	1.87×10^{-05}	3.67×10^{-05}	5.04×10^{-04}	8.07×10^{-05}	1.09×10^{-03}	2.60×10^{-04}	6.71×10^{-04}
TnBP	1.92×10^{-05}	0	1.01×10^{-04}	4.89×10^{-06}	2.17×10^{-05}	3.51×10^{-04}	0	1.84×10^{-03}	8.93×10^{-05}	3.96×10^{-04}
TBOEP	1.17×10^{-03}	1.61×10^{-06}	1.24×10^{-02}	3.11×10^{-05}	6.19×10^{-05}	2.14×10^{-02}	2.94×10^{-05}	2.27×10^{-01}	5.39×10^{-04}	1.13×10^{-03}
HI values based on average exposure										
TCEP	4.00×10^{-04}	2.54×10^{-05}	2.82×10^{-03}	6.12×10^{-05}	2.59×10^{-04}	4.56×10^{-03}	2.90×10^{-04}	3.21×10^{-02}	6.99×10^{-04}	2.96×10^{-03}
TCIPP	3.85×10^{-05}	1.49×10^{-05}	1.53×10^{-04}	1.83×10^{-05}	3.82×10^{-05}	4.39×10^{-04}	1.70×10^{-04}	1.74×10^{-03}	2.09×10^{-04}	4.36×10^{-04}
TDCIPP	7.44×10^{-05}	5.72×10^{-06}	3.67×10^{-04}	2.41×10^{-05}	5.57×10^{-05}	8.49×10^{-04}	6.53×10^{-05}	4.19×10^{-03}	2.76×10^{-04}	6.36×10^{-04}
TPHP	4.09×10^{-05}	5.18×10^{-06}	8.38×10^{-05}	2.05×10^{-05}	5.84×10^{-05}	4.67×10^{-04}	5.92×10^{-05}	9.57×10^{-04}	2.34×10^{-04}	6.67×10^{-04}
TMPP	1.10×10^{-05}	1.77×10^{-06}	2.40×10^{-05}	5.71×10^{-06}	1.47×10^{-05}	1.26×10^{-04}	2.02×10^{-05}	2.73×10^{-04}	6.51×10^{-05}	1.68×10^{-04}
TnBP	7.68×10^{-06}	0	4.03×10^{-05}	1.96×10^{-06}	8.67×10^{-06}	8.77×10^{-05}	0	4.60×10^{-04}	2.23×10^{-05}	9.90×10^{-05}
TBOEP	4.69×10^{-04}	6.44×10^{-07}	4.98×10^{-03}	1.18×10^{-05}	2.48×10^{-05}	5.35×10^{-03}	7.35×10^{-06}	5.68×10^{-02}	1.35×10^{-04}	2.83×10^{-04}

Table 5
Estimated daily intake of Di-OP via dust ingestion (ng/kg bw/day).

	Adults					Toddlers				
	Mean	Minimum	Maximum	25th	75th	Mean	Minimum	Maximum	25th	75th
EDI values based on high exposure										
DEP	0.386	0	1.78	0	0.649	0.441	0	2.04	0	0.741
DnBP	0.439	0.091	0.913	0.175	0.711	0.501	0.104	1.04	0.200	0.811
BBOEP	0.327	0	2.97	0.006	0.057	0.373	0	3.39	0.007	0.065
BCEP	0.386	0	1.11	0	0.571	0.440	0	1.27	0	0.652
BCIPP	0.031	0	0.248	0	0	0.035	0	0.283	0	0
BDCIPP	0.377	0	2.93	0.002	0.217	0.430	0	3.34	0.002	0.247
DPHP	0.873	0.084	2.72	0.430	0.885	0.996	0.096	3.10	0.491	1.01
∑Di-OPs	2.82	0.218	7.34	0.833	4.76	3.22	0.249	8.38	0.950	5.44
EDI values based on average exposure										
DEP	0.097	0	0.446	0	0.162	0.176	0	0.814	0	0.296
DnBP	0.110	0.023	0.228	0.044	0.178	0.200	0.042	0.417	0.080	0.325
BBOEP	0.082	0	0.743	0.001	0.014	0.149	0	1.36	0.003	0.026
BCEP	0.096	0	0.278	0	0.143	0.176	0	0.508	0	0.261
BCIPP	0.008	0	0.062	0	0	0.014	0	0.113	0	0
BDCIPP	0.094	0	0.732	0.001	0.054	0.172	0	1.34	0.001	0.099
DPHP	0.218	0.021	0.679	0.108	0.221	0.398	0.038	1.24	0.196	0.404
∑Di-OPs	0.704	0.055	1.84	0.208	1.19	1.29	0.100	3.35	0.380	2.17

ingestion might act as an important pathways for residents. However, little was known about their toxicities to human health, much more attention should be paid to the occurrence, toxicities, and ultra-fate in indoor environment as well as their potential human health risk.

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.

CRedit authorship contribution statement

Qiongpu Hu: Data curation, Formal analysis, Writing - original draft, Writing - review & editing, Formal analysis. **Liang Xu:** Data curation, Formal analysis. **Yi Liu:** Formal analysis. **Xiangying Zeng:** Conceptualization, Writing - review & editing. **Zhiqiang Yu:** Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

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