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Occurrence and distribution of typical semi-volatile organic chemicals (SVOCs) in paired indoor and outdoor atmospheric fine particle samples from cities in southern China[☆]

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ABSTRACT

Interest in the potential human health of semi-volatile organic chemicals (SVOCs) in indoor and outdoor environments has made the exposure assessment and source appointment a priority. In this study, paired indoor and outdoor atmospheric fine particle ($PM_{2.5}$) samples were collected from 15 homes representing five typical urban cities in southern China. Four typical SVOCs, including 16 congeners of polycyclic aromatic hydrocarbons (PAHs), 13 congeners of organophosphorus flame retardants (OPFRs) and 8 congeners of polybrominated diphenyl ethers (PBDEs), as well as tetrabromobisphenol A (TBBPA) and its three debrominated congeners were analyzed. The highest total concentrations were found for OPFRs, followed by PAHs, PBDEs, and TBBPA. The indoor concentrations of two alkyl-OPFR isomers, tributylphosphate (TBP) and tris (2-butoxyethyl) phosphate (TBEP), were 4.3 and 11 times higher, respectively, than those of outdoors ($p < 0.05$). Additionally, the ratios of indoor to outdoor concentrations of alkyl-OPFR isomers varied greatly, suggesting that these compounds originated mainly from different household goods and products used in individual homes. The outdoor concentrations of PAHs and highly brominated PBDEs (BDE-209) typically exceeded the indoor concentrations. Significant correlations were also found between indoor and outdoor $PM_{2.5}$ samples for PAHs and BDE-209, indicating that outdoor sources such as vehicle exhausts and industrial activities strongly influence their atmospheric occurrence. Additionally, the concentrations of debrominated TBBPA derivatives were higher than those of TBBPA in over 33% of both indoor and outdoor air particle samples. Nevertheless, our results indicated that inhalation exposure to typical SVOCs posed no non-carcinogenic risks to the human body. Although we observed notable differences in the sources, occurrences, and distributions of typical SVOC congeners, more studies using matched samples are still needed to unambiguously identify important indoor and outdoor sources in order to accurately assess the contributions of different sources and the associated human exposure risks.

Author statement

Shengtao Ma: Methodology, Formal analysis, Writing – original draft, Congcong Yue: Methodology, Formal analysis, Jian Tang: Methodology, Data curation, Meiqing Lin: Methodology, Formal analysis, Meihui Zhuo: Methodology, Formal analysis, Yan Yang: Visualization, Investigation, Guiying Li: Writing- Reviewing and Editing, Taicheng An: Conceptualization, Supervision, Editing.

1. Introduction

Semi-volatile organic compounds (SVOCs) are important indoor and outdoor organic contaminants that are of great concern owing to their wide occurrence and adverse effects on human beings'

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health (Besis and Samara, 2012; Chen et al., 2019). SVOCs can be released into the ambient environment via various anthropogenic activities. For example, polycyclic aromatic hydrocarbons (PAHs) are widely recognized as anthropogenic carcinogenic compounds that originate from vehicle emissions, incomplete combustion of coal and fossil fuel, and industrial and chemical manufacturing (Wang et al., 2019; Zhang et al., 2019a, 2020). Flame retardants (FRs), including organophosphorus flame retardants (OPFRs) and brominated flame retardants (BFRs) are compounds added to polymers that are widely used in various electronics, foams, textiles, and plastics. Over the lifetime of such products, the embedded FRs may be volatilized and released into the atmosphere, potentially presenting a risk to human well-being (Ding et al., 2016; Khan et al., 2016; Liu et al., 2016). Some technical products of BFRs, such as polybrominated diphenyl ethers (PBDEs), have recently been regulated as persistent organic pollutants (POPs) due to their potential endocrine-disrupting effects and developmental neurotoxicity (Guo et al., 2018; Ji et al., 2019). However, other BFRs such as tetrabromobisphenol A (TBBPA) and its analogs remain widely used without restrictions, especially in countries heavily involved in their production such as China and Japan (Ma et al., 2019). OPFRs were introduced as alternative FRs and are rapidly gaining market share, resulting in high frequencies of detection in environmental media and an upward trend in detected concentrations (Blum et al., 2019). Evidence from toxicological and epidemiological studies suggests that exposure to OPFRs may disrupt human sphingolipid homeostasis (McGee et al., 2013; Zhao et al., 2016). In addition, reproductive toxicity studies have shown that exposure to triphenyl phosphate (TPhP, a typical technical product of OPFRs) might retard the development of ovarian and greatly reduced the production of egg in Japanese Medaka (*Oryzias latipes*), even at environmental concentrations, and might also impact the wild fish on population level (Li et al., 2019). There have been few studies on the sources, environmental occurrence, and fates of these SVOCs in indoor and outdoor environments, and fewer still that have examined emerging alternative FRs (Khan et al., 2016; Zhou et al., 2017; Khairy and Lohmann, 2019; Wang et al., 2020a). However, recent reports suggest that the atmospheric concentrations of novel OPFRs significantly exceed those of legacy PBDE flame retardants (Liu et al., 2016).

In the atmospheric environment, many factors can influence the distributions and fates of typical SVOCs from indoor and outdoor sources, complicating the assessment of human exposure risks. Most SVOCs originated from indoor sources; in particular, halogen flame retardants are mainly incorporated into household products and electronic/electrical appliances used in daily life (Rudel et al., 2010). Clear indoor–outdoor gradients in atmospheric PBDE concentrations have been observed in studies on indoor and outdoor air samples collected in Ottawa, Canada (Wilford et al., 2004), Stockholm, Sweden (Newton et al., 2015), and Alexandria, Egypt (Khairy and Lohmann, 2018). Indoor concentrations of OPFRs were also significantly higher than outdoor concentrations in both air (Khan et al., 2016; Zhou et al., 2017; Khairy and Lohmann, 2019) and dust (Wang et al., 2020b) samples collected from different regions. Outdoor air levels of PAHs in urban areas were higher than those indoors (Zhang et al., 2020), but the opposite pattern was observed in rural and remote areas where traditional biomass fuels are widely used (Zhang et al., 2019a). In addition, the ratios of indoor to outdoor concentrations differed significantly between congeners. For example, the indoor levels of lower brominated PBDEs in southern China were comparable to or higher than those of outdoors, but outdoor concentrations of deca-BDEs (BDE-209) were apparently higher than those of indoors (Ding et al., 2016). Additionally, the indoor-to-outdoor (I/O) concentration ratios of PAHs increased in proportion to their molecular weights (Naumova et al., 2002). These results highlight the importance of assessing the relative contributions of different indoor and outdoor sources when conducting human exposure studies. The physiochemical properties of target pollutants, air exchange rates, and lifestyle factors may all profoundly influence the distributions and fates of these SVOCs in the atmosphere (Besis and Samara, 2012). Important anthropogenic outdoor sources of these compounds include traffic, fossil fuel combustion and pyrolysis, e-waste recycling activities and industrial processes (An et al., 2011; Chen et al., 2019; Liu et al., 2019). Because of the diverse sources and congener-specific behaviors of SVOCs, there is a clear need for studies using paired indoor and outdoor atmospheric samples to characterize the relative contributions of indoor and outdoor sources to overall emissions of these potentially harmful substances.

The intense anthropogenic activity in the Pearl River Delta (PRD) has led to the release of many emerging organic pollutants into the local atmosphere. For example, elevated atmospheric concentrations of highly brominated flame retardants (BDE-209) were observed in Guangzhou and tentatively attributed to intensive e-waste recycling activities (Liu et al., 2016). In recent decades, pollution monitoring targets and activities in the PRD region have mainly focused on the environmental occurrence and fates of PAHs (Liu et al., 2015; Zhang et al., 2018; Song et al., 2020) and PBDEs (Ding et al., 2018; Peng et al., 2018; Hu et al., 2019) in indoor and outdoor environments; few publications have presented the data on the sources and emissions of OPFRs (Liu et al., 2016; Hu et al., 2019; Chen et al., 2020; Zeng et al., 2020). In particular, little is known about the relative importance of indoor and outdoor sources of these emerging organic pollutants. The aim of the present work is therefore to mainly study the levels of several common SVOCs, including PAHs, OPFRs, PBDEs, and TBBPA, in indoor and outdoor air particles from five cities in the PRD region. Paired indoor and outdoor atmospheric samples were collected from residential homes in each city and their levels of the targeted SVOCs were quantified to distinguish between indoor and outdoor sources of these compounds.

2. Materials and methods

2.1. Sampling

Air fine particles ($PM_{2.5}$) were sampled in indoor and outdoor environments in five typical urban cities in the PRD region between June and August 2017. Details of the sampling methods and sites have been presented previously (Zhuo et al., 2019). Fifteen paired indoor and outdoor samples were examined in this work. These paired samples represent four of the most heavily populated cities of the PRD region - Guangzhou (GZ, $n = 3$), Shenzhen (SZ, $n = 4$), Dongguan (DG, $n = 3$), and Foshan (FS, $n = 3$) as well as another city, Zhaoqing (ZQ, $n = 2$), with a lower level of urbanization and a lower population density.

2.2. Sample analysis

Four common types of SVOCs, including 16 PAH congeners, 13 OPFR isomers, 8 PBDE congeners, and TBBPA as well as its three debrominated congeners were analyzed, and the detailed method description were shown in the Supporting Information (SI). PBDEs and PAHs were analyzed using our previously reported method (Chen et al., 2019; Liu et al., 2019). For the analysis of OPFRs and TBBPA, the method was modified slightly. Briefly, the quartz fiber filters containing the $PM_{2.5}$ samples were cut into pieces and then extracted using a Soxhlet system with a hexane/dichloromethane/acetone mixture (2:2:1, v/v/v) for 48 h after spiking with surrogate standards. The extracts were evaporated to dryness on a rotary evaporator and then dissolved again in 1 mL of hexane. Further purification was performed by passage through florisil solid-phase extraction (SPE) cartridges (2g/12 mL). TBBPA and OPFRs were then eluted with 10 mL of ethyl acetate/dichloromethane (1:1, v/v), and the eluents were dried under a gentle nitrogen stream. Finally, the residues were reconstituted in 200 μL of methanol for the analysis of TBBPA after adding internal standards. Instrumental analysis of PBDEs was performed using a GC–NCI–MS based method (Liu et al., 2019). PAHs and OPFRs were analyzed by GC-MS-MS using the instrumental conditions described previously (Chen et al., 2019; Lin et al., 2019). A comprehensive description of the instrumental conditions used (Table S1) along with typical total ion chromatograms of the standards (Fig. S1) are all presented in the SI. A HPLC-MS-MS-based approach was used to detect and quantify TBBPA and its three debrominated congeners (Liu et al., 2020); the corresponding parameter conditions (Table S2) and a typical ion chromatogram (Fig. S2) are also shown in the SI.

2.3. Quality assurance and quality control

One spiked sample and one procedural blank (clean QFFs) were analyzed for every batch of 10 samples. Only BDE-209 and tributyl phosphate (TBP) were detected in the blanks, at concentrations amounting to less than 3% of those in the sample extracts. The concentrations measured in the samples were blank-corrected accordingly. Reported concentrations were not surrogate-recovery corrected in this work. Recoveries for most PAHs ranged from 70% to 104%, but that of naphthalene (Nap) was only 31%. Recoveries of OPFRs, PDBEs, and TBBPA were 55 ± 23% to 104 ± 3%, 98 ± 3% to 125 ± 2%, and 93 ± 5%, respectively. The method detection limit (MDL) was defined as the mean blank value plus three standard deviations or a signal of five times the noise level, and was between 0.03 and 3 pg/m^3 for PAHs, 0.1 and 6.6 pg/m^3 for OPFRs, and 0.06 and 0.3 pg/m^3 for PBDEs and TBBPA, respectively. The MDLs and the recoveries of the target analytes are presented in full in the SI (Tables S3 and S4).

2.4. Health risk assessment

Estimated daily intakes (EDIs, ng/kg/day) of $PM_{2.5}$-bound PAHs, OPFRs, PBDEs and TBBPA were obtained by considering the time spent on various indoor and outdoor activities in conjunction with the measured indoor and outdoor concentrations of these SVOCs. The same approach was used to evaluate the non-carcinogenic risk via the inhalation exposure for each compound. EDIs were calculated based on a worst-case scenario in which it was assumed that 100% of all particle-bound SVOCs present in the atmosphere were absorbed by the human body. EDIs and hazard index (HI_{svocs}) values for chronic effects caused by the SVOCs were calculated as follows:

$$EDIs = [C_{indoor}F_{indoor} + C_{outdoor}F_{outdoor}] \bullet R_R$$

$$HI_{svocs} = EDIs/RfD$$

Here, C_{indoor} and $C_{outdoor}$ are the $PM_{2.5}$-bound concentrations of the target SVOCs in the indoor and outdoor environment, respectively. F_{indoor} (21 h) and $F_{outdoor}$ (3 h) are the amounts of time spent each day in indoor and outdoor environments, respectively, according to the Exposure Factors Handbook of Chinese Population (EFHCP, Ministry of Environmental Protection, 1st Edition). R_R is the adult respiration rate; its value (15.8 m^3/day) was also taken from the EFHCP. Reference doses (RfDs) for the target compounds are all given in Table S5.

3. Results and discussion

3.1. Pollution levels and profiles of paired indoor and outdoor atmospheric fine particles

The concentrations of different target chemicals in paired indoor and outdoor ($PM_{2.5}$ samples are summarized in Tables 1–3. The highest total concentrations were obtained for OPFRs, followed in decreasing order by PAHs, PBDEs, and TBBPA. The detailed pollution characteristics of these compounds are discussed individually below.

3.1.1. Organophosphate flame retardants

The mean, median, and range of concentrations for OPFRs in indoor and outdoor $PM_{2.5}$ samples from five cities are shown in Table 1. In general, the concentration of total OPFRs in indoor $PM_{2.5}$ (median, 4860 pg/m^3) was slightly higher than that of outdoor particles (median, 4330 pg/m^3), but the difference was statistically non-significant. The highest concentrations were obtained for chlorinated OPFR isomers, which had median concentrations of 3000 and 2180 pg/m^3 in outdoor and indoor $PM_{2.5}$ samples, respectively, and accounted for 67% and 59% of the total OPFRs, respectively. This suggests that chlorinated OPFRs are the OPFRs with the greatest commercial use in the PRD region, which is consistent with the results of previous studies conducted in Guangzhou (Chen et al., 2020; Zeng et al., 2020). The median concentrations of these aryl-substituted OPFRs in indoor environments were similar to those in the outdoor atmosphere. However, the concentrations of non-chlorinated alkyl-OPFRs in indoor $PM_{2.5}$ samples were significantly higher than those of outdoor samples (median, 1330 versus 540 pg/m^3, $p < 0.05$). In particular, the indoor concentrations of TBP and tris(2-butoxyethyl) phosphate (TBEP) were 4.3 and 11.0 times higher than those of the outdoor ($p < 0.05$), suggesting that the indoor sources of these two alkyl-OPFRs contribute significantly to overall air pollution. Alkyl-OPFRs are mainly used in floor polishes and as plasticizers in rubber and plastics, making the indoor environment a major emission source because these compounds are continuously released from domestic products during daily usage (Zeng et al., 2020). Similar results were obtained in a study conducted in Germany: the concentrations of OPFRs in indoor environments were approximately 8 times higher than the outdoor concentrations (Zhou et al., 2017). Additionally, Wang et al. (2020b) reported that indoor dust levels of OPFRs were one order of magnitude higher than those of outdoor dust in Northwestern and Southwestern China.

The composition profiles of the OPFR isomers in indoor particles was similar to that of outdoor particles: in both cases, TPhP and the chlorinated substituted congeners tris(2-iso chlorophenyl) phosphate (TiCPP), tris(1-chloro-2-propyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCP) were the main components. However, the contributions of TBP in indoor air samples were higher than those in outdoor samples, which may be related to the previously mentioned release of TBP from household products; chlorinated and aryl-substituted congeners are the most widely used flame retardants and plasticizers in the Southern Chinese market. The observed OPFR compositional profiles are consistent with those found in other studies conducted in the same region (Hu et al., 2019; Chen et al., 2020; Zeng et al., 2020). Because there is evidence that chlorinated OPFRs have neurotoxic or carcinogenic effects (Hou et al., 2016), further research is needed to more thoroughly assess the occurrence and potential health risk of these compounds.

The mean concentration of total OPFRs in indoor air particle samples from Dongguan (DG) was lower than that of the other four cities, while the outdoor total OPFR concentration of Shenzhen (SZ)

Table 1
Concentrations of OPFRs in indoor and outdoor $PM_{2.5}$ samples (pg/m^3).

Analytes	Outdoor (n = 15)			Indoor (n = 15)		
	Mean	Median	Range	Mean	Median	Range
TPrP	3.5 ± 3.0	2.4	nd–10.6	1.2 ± 1.2	1.5	nd–4.3
TBP	220 ± 142	208	19.1–437	953 ± 552	779	281–2100
TCEP	713 ± 1410	206	104–5670	503 ± 420	368	nd–1660
TCPP	1090 ± 1080	625	30.7–4050	1680 ± 2950	401	nd–9140
TiCPP	933 ± 808	758	120–2460	1090 ± 1320	745	nd–3820
TDCP	523 ± 347	514	nd–989	604 ± 533	512	nd–2110
TPhP	1010 ± 979	684	166–3880	887 ± 490	714	269–2000
TBEP	54.9 ± 121	nd	nd–389	448 ± 536	314	nd–1980
EDP	203 ± 224	169	nd–968	240 ± 145	188	nd–561
TEHP	134 ± 169	91.9	nd–710	135 ± 112	95.0	59.3–459
p-TCP	0.3 ± 0.8	nd	nd–3.0	0.1 ± 0.3	nd	nd–1.2
m-TCP	8.7 ± 6.5	6.7	nd–23.1	3.6 ± 2.9	3.3	nd–9.3
o-TCP	4.7 ± 13.3	nd	nd–50.0	1.2 ± 4.7	nd	nd–18.1
$\sum_{alkyl}$ OPFRs[a]	616 ± 467	540	203–2050	1780 ± 806	1330	860–3120
$\sum_{aryl}$ OPFRs[b]	1030 ± 988	694	168–3900	892 ± 472	714	272–2000
$\sum_{chloro}$ OPFRs[c]	3260 ± 2520	3000	502–8770	3870 ± 3900	2180	806–13900
$\sum_{all}$ OPFRs[d]	4900 ± 2430	4330	1740–9640	6540 ± 3960	4860	2820–15800

[a] $\sum_{alkyl}$ OPFRs = sum of TPrP, TBP,TBEP and TEHP.
[b] $\sum_{aryl}$ OPFRs = sum of TPhP, EDP, p-TCP, m-TCP and o-TCP.
[c] $\sum_{chloro}$ OPFRs = sum of TCEP, TCPP, TiCPP and TDCP.
[d] $\sum_{all}$ OPFRs sum of all alkyl-, aryl- and chloro-OPFRs.

Table 2
Concentrations of PAHs in indoor and outdoor $PM_{2.5}$ samples (pg/m^3).

Analytes	Outdoor (n = 15)			Indoor (n = 15)		
	Mean	Median	Range	Mean	Median	Range
Nap	19.7 ± 20.4	4.0	nd–51.5	13.3 ± 9.5	14.6	nd–27.3
Acy	4.1 ± 3.0	3.8	0.5–9.4	1.4 ± 2.0	0.4	nd–6.4
Ace	7.6 ± 8.0	6.5	0.1–22.2	2.9 ± 5.2	0.7	nd–15.9
Flu	26.2 ± 20.0	19.7	nd–66.9	9.2 ± 10.4	6.7	nd–30.6
Phe	175 ± 104	158	nd–332	81.4 ± 51.9	62.7	11.0–234
Ant	30.3 ± 61.1	7.1	nd–206	4.0 ± 6.9	0.0	nd–24.1
Fluo	169 ± 115	143	nd–386	69.3 ± 68.9	60.5	9.6–284
Pyr	235 ± 144	197	49.6–527	83.1 ± 82.5	63.4	nd–328
BaA	101 ± 87.6	68.5	11.7–329	59.3 ± 76.6	18.1	3.6–279
Chr	187 ± 100	161	59.3–393	57.9 ± 49.8	58.8	7.6–204
BbF	1260 ± 850	1240	129–3090	580 ± 698	325	42.6–2450
BkF	149 ± 119	129	8.4–430	43.0 ± 47.2	25.4	3.6–139
BaP	524 ± 341	428	71.8–1370	191 ± 247	73.6	7.3–939
DBA	45.1 ± 31.2	41.2	3.2–116	26.0 ± 34.9	18.9	1.8–133
InP	359 ± 309	289	13.8–1080	290 ± 396	137	9.4–1230
BP	549 ± 388	397	55.4–1380	301 ± 325	201	29.4–954
$\sum_{all}$ PAHs	3840 ± 2420	3320	786–9160	1810 ± 1920	1280	194–6460

Table 3
Concentrations of PBDEs and TBBPA in indoor and outdoor $PM_{2.5}$ samples (pg/m^3).

Analytes	Outdoor (n = 15)			Indoor (n = 15)		
	Mean	Median	Range	Mean	Median	Range
BDE-28	9.2 ± 10.6	6.4	0.1–25.6	13.5 ± 12.0	9.6	nd–45.3
BDE-47	6.9 ± 8.0	5.1	0.2–13.2	9.3 ± 8.6	7.1	0.5–24.1
BDE-99	5.0 ± 6.0	3.8	nd–9.4	6.1 ± 6.6	4.4	0.6–11.2
BDE-100	1.4 ± 2.0	1.1	nd–5.3	1.5 ± 1.2	1.2	nd–4.0
BDE-153	3.4 ± 2.8	2.1	0.18–7.2	3.4 ± 2.9	3.0	0.1–6.4
BDE-154	1.4 ± 1.6	1.2	nd–4.0	1.4 ± 0.9	1.1	0.1–2.9
BDE-183	1.9 ± 2.1	1.7	0.11–5.0	2.1 ± 1.6	1.7	0.2–4.3
BDE-209	239 ± 210	200	nd–1020	180 ± 152	165	nd–796
$\sum_{3-7}$ PBDEs[a]	29.2 ± 22	23.8	1.0–82.3	37.3 ± 36.0	26.9	1.4–78.1
$\sum_{all}$ PBDEs[b]	268 ± 248	211	1.0–1090	217 ± 185	192	1.4–874
MoBBPA	29.6 ± 91.4	5.0	nd–358	5.6 ± 6.6	3.6	nd–18.8
TriBBPA	2.6 ± 6.6	nd	nd–25.4	0.1 ± 0.6	nd	nd–2.2
TBBPA	49.3 ± 91.8	5.5	nd–326	15.0 ± 37.1	nd	nd–144
$\sum_{all}$ TBBPA[c]	81.5 ± 132	10.4	nd–388	20.7 ± 38.5	4.2	nd–155

[a] $\sum_{3-7}$ PBDEs represents the sum concentrations of BDE-28, -47, −99, −100, −153, −154, and −183.
[b] $\sum_{all}$ PBDEs represents the sum concentrations of $\sum_{3-7}$ PBDEs and BDE-209.
[c] $\sum_{all}$ TBBPA represents the sum concentrations MoBBPA, TriBBPA and TBBPA.

was higher than those of the other cities (Fig. S3). These results may be due to differences in the dominant sources of OPFR emissions in each city. The concentration of outdoor $PM_{2.5}$-bound OPFRs measured as 1740–9640 pg/m^3 in our study was consistent with or slightly higher than that observed in Guangzhou (314–9720 pg/m^3) in early 2013 (Zeng et al., 2020), in Dalian (320–3460 pg/m^3) in 2016–2017 (Wang et al., 2020a), and in the Beijing-Tianjin-Hebei region (gas + particle, 174–5250 pg/m^3) in 2016–2017 (Zhang et al., 2019b). The outdoor concentrations of three major chlorinated OPFRs (TCPP, TCEP, and TDCPP) were also slightly higher than those measured in 10 urban cities across China in 2014 (Liu et al., 2016). However, the concentration of outdoor OPFRs in our study was an order of magnitude lower than that recorded in Guangzhou (4.17–75.2 ng/m^3) in 2016 (Chen et al., 2020). The coupled indoor and outdoor concentrations of OPFRs were also significantly lower than those from Guangzhou in the summer of 2015 (Hu et al., 2019). This variation in reported OPFR concentrations may be largely due to differences in sampling times and non-point source emissions at sampling sites in different studies.

The indoor-to-outdoor ratios of OPFRs varied significantly among the studied congeners, as shown in Fig. 1. TBP and TBEP exhibited comparatively high but also highly variable I/O ratios: the I/O ratios for TBP in all 15 resident homes examined in this work were greater than 1, and those for TBEP were greater than 1 in 13 out of 15 homes. It thus appears that these compounds originate primarily from indoor sources. The high variability of the observed I/O ratios for these compounds suggests that TBP and TBEP may be released from different domestic sources in individual homes. In contrast, the I/O ratios of the chlorinated OPFRs were slightly greater than (TCEP and TiCPP) or close to (TCPP and TDCP) 1 in most of the matched samples, and the ratios of aromatic OPFRs were also close to 1. Indoor and outdoor sources thus both appear to contribute to levels of these pollutants in the environment. Similar conclusions were drawn in an earlier study on paired indoor-outdoor dust samples (Wang et al., 2020b). However, only limited data on the indoor and outdoor distributions of OPFRs exist, and more research using matched samples is needed to identify potential sources of these compounds.

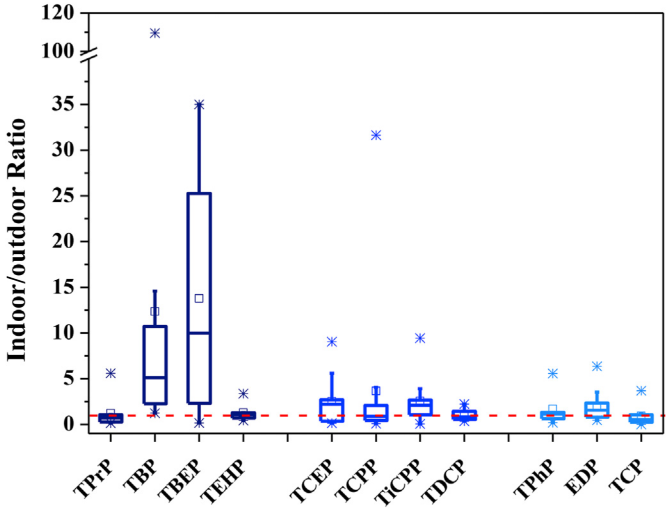

Fig. 1. Indoor/outdoor ratios (I/O) of OPFR concentrations in paired atmospheric particle samples. The reference line indicates an I/O ratio of 1. The horizontal line inside each box indicates the median, the boxes represent the 25th and 75th percentiles, the square represent mean, the whiskers represent the extreme points.

3.1.2. Polycyclic aromatic hydrocarbons

As Table 2 shows, the concentrations of PAHs in outdoor $PM_{2.5}$ samples were significantly higher than those in indoor samples (mean: 3840 pg/m^3 versus 1810 pg/m^3, $p < 0.05$). In outdoor $PM_{2.5}$ samples from different cities, the mean concentrations of total PAHs decreased in the order ZQ > FS > DG > GZ > SZ. Conversely, the mean PAH concentrations in indoor air samples from GZ, DG, and ZQ were very similar, slightly higher than those of FS, and significantly higher than those of SZ (Fig. S3). However, we should note that the samples of the present study were limited. Our results suggest that levels of most indoor PAHs were heavily influenced by outdoor sources. The outdoor concentrations of $PM_{2.5}$-bound PAHs measured in this study were in the same ranges as those measured in Guangzhou in the summers of 2015 (Hu et al., 2018) and 2016 (Song et al., 2020) but slightly lower than those measured earlier in the summer of 2012 (Wang et al., 2016) and in the spring of 2015 (Zhang et al., 2018) in the same geographic regions. This is consistent with the gradual decrease in PAH emissions within China (Shen et al., 2013). The coupled indoor and outdoor levels of PAHs in southern Chinese cities determined in this work were also significantly lower than those reported for Beijing (Zhang et al., 2020), Tianjin (Han et al., 2015), and rural areas of northern China (Zhang et al., 2019a).

The relative contributions of individual PAHs to the total levels of $PM_{2.5}$-bound PAHs did not differ greatly between the studied cities. The similarity of the PAH compositional profiles supported the conclusion that the levels of PAHs in indoor dust samples were heavily influenced by outdoor sources. Benzo[b]fluoranthene (BbF) was found to be the most abundant PAH congener in both indoor and outdoor air particles, and high molecular weight (HMW) five-to-six rings PAHs collectively accounted for 71% and 73% of total PAHs in indoor and outdoor air particles, respectively. Similar results were reported by Song et al. (2020) and Hu et al. (2018), and these findings are consistent with the physicochemical properties of HMW PAHs, which are readily adsorbed onto particulate matter due to their relatively low vapor pressures. HMW PAHs are generally believed to originate from vehicular emissions and fossil fuel combustion, and individual sources can be distinguished by considering diagnostic ratios of individual PAH isomers (Zhang et al., 2020). Diagnostic ratios of fluoranthene/(fluoranthene + pyrene) (Fluo/(Fluo+Pyr)) ranging from 0.4 to 0.5 together with indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene)(InP/(InP+BP)) ratios ranging from 0.2 to 0.4 are indicative of petroleum combustion; the corresponding values observed in our work were obtained as 0.45 and 0.38, respectively.

The average indoor-outdoor concentration ratios of PAHs were all lower than 1, as shown in Fig. 2. Similar results were previously reported by Naumova et al. (2002), who observed I/O ratios below 1 for all PAH isomers with 4 or more rings. Outdoor concentrations of $PM_{2.5}$-bonded PAHs exceeding those measured indoors were also observed in samples collected in a primary school classroom in Beijing (Zhang et al., 2020), and in a community from Tianjin in Northern China (Han et al., 2015), during both heating and non-heating periods. However, PAH concentrations in the kitchen air of rural households using traditional biomass fuels in Northern China were higher than those outdoors (Zhang et al., 2019a). The I/O ratios of PAHs also increased in proportion to their molecular weight (Fig. 2). This is consistent with the observation that outdoor-to-indoor transport of $PM_{2.5}$-bound pollutants has a greater impact on low molecular weight PAHs than that on HMW PAHs (Zhang et al., 2019a).

3.1.3. Brominated flame retardants (PBDEs and TBBPA)

The concentrations of tri-to hepta- BDE congeners ($\sum_{3-7}$ PBDEs) in indoor $PM_{2.5}$ samples exceeded those in outdoor samples (mean:

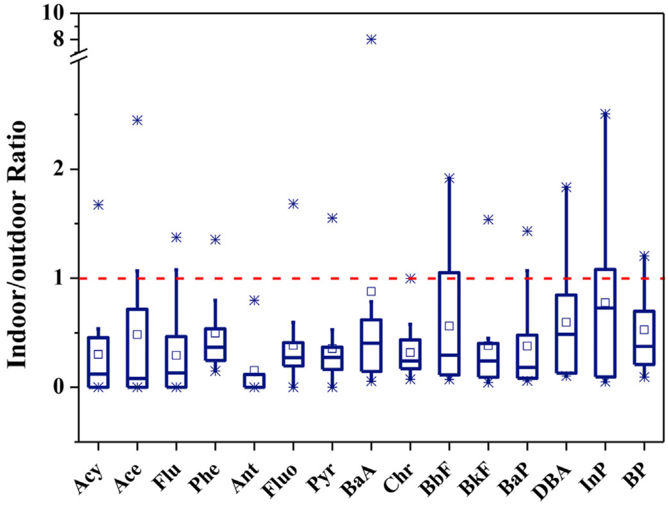

Fig. 2. Indoor/outdoor ratios (I/O) of PAH concentrations in paired atmospheric particles samples. The reference line indicates an I/O ratio of 1. The I/O ratio of Nap was not calculated due to its low detection frequency. The horizontal line inside each box indicates the median, the boxes represent 25th and 75th percentiles, the square represent mean, the whiskers represent the extreme points.

indoor 37.6 pg/m^3 versus outdoor 29.2 pg/m^3, Table 3). For more highly brominated deca-BDEs, the levels observed in outdoor air were considerably greater than those of indoor samples (mean: indoor 180 pg/m^3 versus. Outdoor 239 pg/m^3, Table 3). BDE-209 was the most abundant congener in both indoor and outdoor samples, accounting for 83% and 89% of the total PBDEs in indoor and outdoor air particles, respectively. This is consistent with the high production and usage of commercial deca-BDEs in China. Predominance of BDE-209 has previously been reported in various environmental media including air particles (Ding et al., 2016; Liu et al., 2016) and indoor dust and soil (Yu et al., 2011) from Southern China. The total PBDE concentrations measured in the five studied cities did not differ appreciably except that from SZ, where the relatively lower level (120 pg/m^3) of PBDEs was found. The PBDE concentration ranges observed in this work are consistent with those determined in previous studies on the same geographical area (Liu et al., 2016; Ding et al., 2018; Hu et al., 2019), but higher than those in outdoor air from Shenzhen in 2014 (Peng et al., 2018). The PBDE concentrations in the southern Chinese cities studied here were also higher than those measured in Beijing and Tianjin in northern China (Wang et al., 2019; Zhang et al., 2019c).

The I/O ratio of BDE-209 was lower than 1, but the I/O ratios of tri-to hepta- BDE isomers were greater than or close to 1 (Fig. 3). Similar results were reported by Ding et al. (2016), who identified old household products and electronic appliances as the primary sources of these lower brominated PBDEs. Several studies have previously found that levels of these less brominated PBDEs in indoor air are higher than those in outdoor samples (Wilford et al., 2004; Kurt-Karakus et al., 2017; Khairy and Lohmann, 2018). The I/O ratios of lower tri-to hepta-BDEs varied considerably between samples, suggesting that indoor sources of these compounds differ markedly between individual homes (Fig. 3). On the other hand, deca-BDE is the most widely used PBDE technical product in China, and emissions of this compound due to industrial activities such as e-waste dismantling in Southern China probably contribute substantially to the relatively high levels of BDE-209 observed in the outdoor ambient environment (Liu et al., 2016). Chen et al. (2008) previously reported that the concentration of BDE-209 in outdoor air samples exceeded that in domestic and workplace microenvironments from Guangzhou. Additionally, the concentrations of PBDEs measured in the exterior films of glass window surfaces in Hong Kong and Guangzhou were higher than those in the interior films (Li et al., 2010).

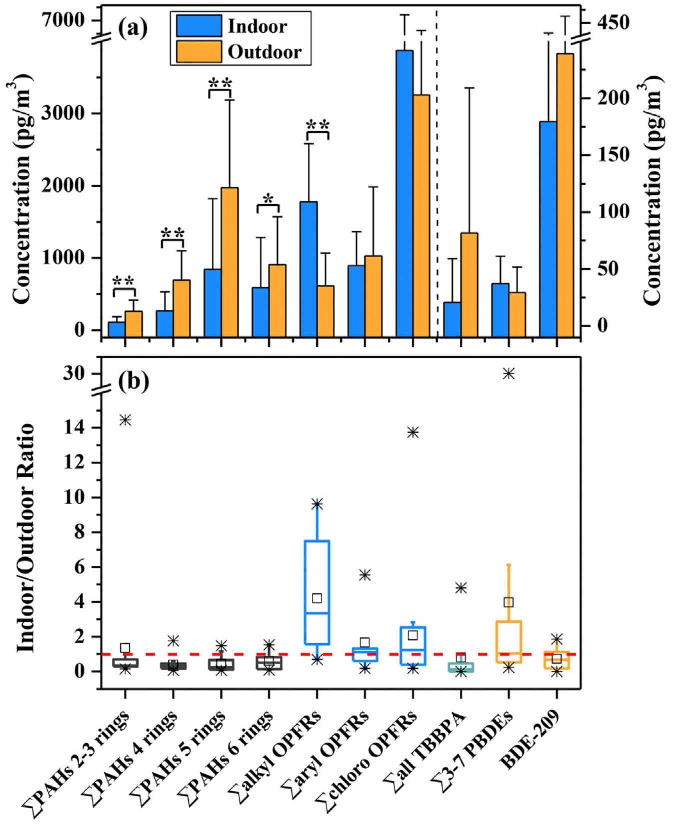

Fig. 3. Comparison of the concentrations and indoor to outdoor ratios of PAHs, OPFRs and BFRs in paired atmospheric fine particles: (a) concentrations; (b) indoor to outdoor ratios. * indicates $p < 0.05$ and ** indicates $p < 0.01$. The horizontal line inside each box indicates the median, the boxes represent 25th and 75th percentiles, the square represent mean, the whiskers represent the extreme points.

TBBPA and its debromination products, 2,2′,6-tribromobisphenol A (TriBBPA) and 2-monobromobisphenol A (MoBBPA), were also detected in atmospheric fine particles, with detection frequencies of 63%, 17%, and 67% for TBBPA, TriBBPA and MoBBPA, respectively. But 2, 2′-DiBBPA (DiBBPA) was non-detectable in all samples. The detection frequencies for all these compounds were higher for outdoor air samples. For example, TBBPA was detected in 80% of outdoor air particle samples but only 47% of indoor air samples, and TriBBPA was exclusively detected in outdoor samples. The sum concentrations of TBBPA and its debrominated congeners in outdoor air particles were also 4 times higher than those of indoor samples, suggesting that outdoor-to-indoor air transfer may be the main source of indoor TBBPA.

The indoor air concentrations of TBBPA observed in this work (mean: 15 pg/m^3) are consistent with these reported in indoor air in Birmingham, UK (gas phase, 15 pg/m^3) (Abdallah et al., 2008), and higher than the background atmospheric concentrations observed in Arctic coastal regions, which range from <0.04 to 0.85 pg/m^3 (Xie et al., 2007). The levels of TBBPA measured in the current work were also significantly lower than those of PBDEs. However, higher relative levels of TBBPA were reported in conditioning filter dust collected from Shenzhen (Ni and Zeng, 2013), as well as dust from printed circuit board workshops (Zhou et al., 2014). In addition, the concentrations of MoBBPA were higher than those of TBBPA in over one third of both indoor and outdoor

$PM_{2.5}$ samples, and the highest level of MoBBPA was observed in an outdoor air sample from Foshan (358 pg/m^3); this value was 36 times higher than the corresponding TBBPA concentration (9.9 pg/m^3). The cause of this particularly high concentration is unknown, but it could be due to some special emissions from an unknown source nearby. Less highly brominated degradation products of TBBPA were also detected in our atmospheric particle samples, which may increase its reactivity towards •OH radicals and O_3 (Ma et al., 2019). This is the first report on the occurrence of TriBBPA and MoBBPA in the atmosphere particles at urban sites, and more studies are needed to clarify their mechanisms of the formation and potential health risks.

3.2. Possible sources identification and implications

As shown in Fig. 3a, the outdoor concentrations of PAHs were significantly higher than those observed indoors. For TBBPA and the more highly brominated BDE-209, outdoor levels tended to be non-significantly higher than indoor levels, suggesting that the presence of these compounds in indoor samples could be due to the transfer of outdoor-to-indoor air particle. Our results are also consistent with the hypothesis that outdoor vehicle exhausts and fossil fuel combustion are the major sources of airborne PAH, while industrial processes such as e-waste recycling are the major sources of highly brominated BDE-209. Although the air concentrations of PAHs and PBDEs in southern China are decreasing slowly, further efforts are needed to reduce emissions of these pollutants because some toxic chemicals such as BDE-209 are still widely used (Liu et al., 2019). On the other hand, the levels of alkyl-OPFRs in indoor air were significantly higher than those of outdoors. Levels of aryl-OPFRs and the lower brominated PBDEs were also higher in indoor air particles than those of outdoor samples, but these differences were non-significant. Additionally, compounds with I/O ratios above 1 generally exhibited highly variable of I/O ratios (Fig. 3b), suggesting that while these compounds originate mainly from indoor sources, the identity of these sources may differ from home to home. The variation in the outdoor air concentrations of these organic pollutants in the five studied cities was generally less pronounced than the indoor variation. The relatively high I/O ratios observed in certain homes should be taken seriously because they may be indicative of currently unrecognized domestic sources. In addition, air exchange rates and lifestyle factors presumably influence the indoor and outdoor air concentrations of these SVOCs (Bohlin et al., 2008). The indoor environment strongly affects human exposure to these chemicals and should be analyzed together with outdoor air when assessing human exposure risks.

Correlations between indoor and outdoor sources of target SVOCs were also investigated. For PAHs with 4 or more rings, positive correlations were observed between indoor and outdoor samples (Table S6). However, only a relatively weak correlation was found between indoor concentrations of low molecular wight (LMW) PAHs with 2–3 rings and HMW PAHs found mainly outdoors. This might be related to the partitioning of PAHs between gas and particle phases: LMW PAHs are mainly distributed in gas phase while HMW PAHs are mainly associated with particles. Outdoor-indoor air exchange may also explain the migration of outdoor pollutants into buildings. Additionally, concentrations of PAHs with 4 or more rings in outdoor samples correlated positively with those of indoor samples. This suggests that indoor sources might contribute appreciably to overall atmospheric PAH levels. The total concentrations of chlorinated OPFRs ($\sum_{\text{chloro}}$ OPFRs) of indoor air were significantly correlated with those of HMW PAHs, whereas in outdoor air samples, levels of aryl OPFRs ($\sum_{\text{aryl}}$ OPFRs) correlated significantly with $\sum_{\text{chloro}}$ OPFRs (Table S6). No significant correlations between OPFR levels in indoor air samples and those in outdoor samples were detected. As noted above, emissions from individual homes appeared to be a major source of OPFRs and contributed to the relatively high variability in the I/O ratios of these SVOCs. The lack of correlations between indoor and outdoor OPFR concentrations support the conclusion that the release of OPFRs differs significantly between individual homes. With respect to less brominated PBDEs in indoor air, significant correlations were found between $\sum_{3\text{-}7}$ PBDEs and BDE-209, and between PBDEs and PAHs with 4–6 rings. However, PBDE concentrations in outdoor $PM_{2.5}$ samples were only weakly correlated (or not correlated at all) with PAH concentrations. In addition, there were no detectable correlations between TBBPA concentrations and those of other target chemicals. This suggests that different sources may govern the occurrence and distribution of these compounds. More studies using large-scale sampling are needed to identify potential sources of these emerging organics and determine their fates in atmospheric environments.

3.3. Estimation of daily intakes and risk assessments

The calculated daily human exposure to PAHs, OPFRs, PBDEs and TBBPA in the studied cities fell within ranges of 4.3–102, 51.5–230, 0–14.2 and 0–2.9 ng per person, respectively. The inhalation exposure to these target SVOCs in southern China varied greatly from site to site. Nevertheless, the daily inhalation exposure was comparable to that reported from other regions (Zeng et al., 2020; Liu et al., 2016; Ding et al., 2018; Hu et al., 2019).

Total hazard index (THI) values for inhalation exposure to the studied SVOCs were calculated using the risk addition method, and the results are presented in Fig. 4. The mean THI values of the studied SVOCs ranged from 8.0×10^{-5} to 2.4×10^{-4}, and the exposure from indoor air accounted for 74%–90% of the total risk. The highest risk was obtained for individuals in ZQ, followed by GZ, DG and FS, while the lowest risk was obtained in SZ. PBDEs contributed a greater share of risk (range from 59% to 60%, except only 26% in SZ) than the other compounds considered herein, while the risk from TBBPA was negligible due to its relatively low concentrations and high RfD value. The differences in exposure risk for individuals of different regions are mainly caused by the variability PBDEs. Overall, our results indicated that inhalation exposure to these four typical kind SVOCs posed no non-carcinogenic risks to human health.

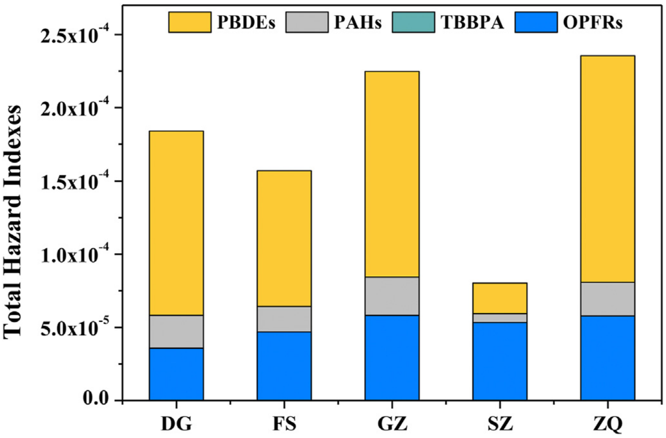

Fig. 4. INon-carcinogenic risk of inhalation exposure to typical SVOCs from indoor and outdoor air particles.

4. Conclusion

Levels of four classes of SVOCs, PAHs, OPFRs, PBDEs, and TBBPA, were investigated in paired indoor and outdoor $PM_{2.5}$ samples from five cities in the PRD region. The target analytes were widely detected, and the results found that OPFRs exhibited the highest concentrations, followed in decreasing order by PAHs, PBDEs, and TBBPA. The concentrations of PAHs, TBBPA, and the highly brominated species BDE-209 in outdoor particles tended to be higher than those in indoor particles. Levels of aryl-OPFRs and less brominated PBDEs in indoor samples were similar to those of outdoors, while the concentrations of alkyl- and chlorinated OPFRs were higher in indoor samples than that of outdoor samples. The release of alkyl- and chlorinated OPFRs from indoor household products, together with outdoor sources (e.g. vehicle exhausts for PAHs and emissions from industrial activities of BDE-209), will together determine the indoor and outdoor concentrations of these SVOCs. Because relatively high concentrations of alkyl and chlorinated OPFRs were observed in indoor particles, systematic investigations of indoor and outdoor air particles are needed to accurately assess human exposure risk in indoor and outdoor environments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.116123.

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