2018

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Citation/Publisher Attribution

Khairy, M. A., & Lohmann, R. (2019). Organophosphate flame retardants in the indoor and outdoor dust and gas-phase of Alexandria, Egypt. *Chemosphere*, 220(2019), 275-285. doi: 10.1016/j.chemosphere.2018.12.140

Available at: <http://dx.doi.org/10.1016/j.chemosphere.2018.12.140>

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**Organophosphate Flame Retardants in the Indoor and Outdoor Dust and Gas-Phase of
Alexandria, Egypt**

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Highlights

- Indoor levels of OPFRs were significantly higher than outdoors.
- PBDEs>OPFRs> NFRs and OPFRs>PBDEs>NFRS In the gaseous and dust samples respectively.
- TDCIPP, TCIPP, TBOEP and TPHP dominated OPFRs in all samples with more indoor variability.
- Significant log-linear $K_{\text{dust-air}}-K_{\text{OA}}$ relationships indicated equilibrium partitioning.
- Dermal and ingestion pathways are important exposure routes.

Abstract

Little is known about the presence of organophosphate flame retardants (OPFRs) as a substitute for polybrominated diphenyl ethers in developing countries. This study investigated - for the first time - concentrations, sources and exposure levels of OPFRs in the indoor and outdoor environments of Alexandria, Egypt, in dust and gas-phase samples. Passive samplers were deployed (n = 78) to determine gaseous concentrations, and various dust samples were collected from apartments (n = 25), working places (n = 14), cars (n = 18), and outdoors (OD, n = 30). Indoor concentrations (air: 7.0 – 64 pg/m³; dust: 150 – 1,850 ng/g) were significantly higher than outdoor (2.0 – 16 pg/m³ and 83 – 475 ng/g) concentrations. Tris-1,3-dichloropropyl phosphate (TDCIPP), tris(1-chloro-2-propyl) phosphate (TCIPP), tri (2-butoxyethyl) phosphate (TBOEP) and triphenyl phosphate (TPHP) dominated in all samples with more indoor variabilities. Profiles of OPFRs in OD and floor dust (collected from carpets and floors) were similar but differed from elevated fine dust (collected 1 m above the floor from all available surfaces), possibly due to the influence of carryover of OD by shoes. Despite the high uncertainty in dust – air partitioning coefficients, significant log-linear relationships were observed with octanol – air-partitioning coefficients in all microenvironments, indicating an equilibrium partitioning between dust and vapor. Exposure assessment indicated the importance of the dermal exposure route for adults and ingestion route for children.

Keywords: OPFRs, dust, gas-phase, indoor, outdoor, equilibrium partitioning, exposure

1. Introduction

Halogenated organophosphate flame retardants (OPFRs) are now widely used in consumer products (textiles, car upholstery, furniture, building materials, plastics and electronic equipment) as a replacement for polybrominated diphenyl ethers (PBDEs) to reduce flammability (Larsson et al., 2018; Van den Eede et al., 2011). Non-halogenated ones are also used as plasticizers and floor polishes (Stapleton et al., 2009; van der Veen and de Boer, 2012). Because they are used as additive flame retardants, OPFRs can undergo volatilization and/or dissolution and spread in the environment (Kurt-Karakus et al., 2017). Accordingly, OPFRs have been detected in all environmental compartments (Abdallah and Covaci, 2014; Cao et al., 2012, 2014; Dodson et al., 2012; Salamova et al., 2014). They were also reported in biota (Sundkvist et al., 2010), human blood and milk (Shah et al., 2006; Sundkvist et al., 2010) indicating their bioaccumulation potential. Some OPFRs are known to have mutagenic and carcinogenic effects, alter human thyroid hormone levels (TDCIPP, TCIPP and TPHP; Behl et al., 2016; Hendriks and Westerink, 2015; Noyes et al., 2015; Preston et al., 2017; Zhang et al., 2016), cause endocrine disruptive effects (TPHP; Kojima et al., 2013), act as neurotoxins (TDCIPP; Yuan et al., 2016), and could cause asthma and allergic rhinitis (TNBP; Araki et al., 2013). In the EU, some chlorinated OPFRs are classified as either category 2 (tris-1,3-dichloropropyl phosphate) (Abdallah and Covaci, 2014) or category 3 (tris-2-chloroethyl phosphate) (Abdallah and Covaci, 2014) carcinogens.

Low density polyethylene sheets (LDPE) have been used for monitoring of atmospheric HOCs (Bartkow et al., 2005, 2004; Kennedy et al., 2007; Khairy and Lohmann, 2018, 2017, 2014, 2013, 2012). Compared to other passive samplers, LDPE is the simplest (in its chemical makeup), cheapest and easy to deploy (Lohmann, 2012). Extracts from LDPE seldomly need any of the complicated cleanup techniques. LDPE can be operated in the uptake (kinetic) or equilibrium

(thermodynamic) sampling mode by varying the thickness of the PE and the exposure time (days, weeks and months), and was previously calibrated/validated for measuring vapor phase concentrations of HOCs (Khairy and Lohmann, 2014).

Although OPFRs have been detected in the dust from various indoor microenvironments of North America (Cao et al., 2014; Dodson et al., 2012; Schreder and La Guardia, 2014; Shoeib et al., 2012; Stubbings et al., 2018), Asia (Ali et al., 2013; Cao et al., 2012; Kanazawa et al., 2010) and Europe (Brommer et al., 2012; Cao et al., 2014; Fromme et al., 2014; Kademoglou et al., 2017; Kanazawa et al., 2010), few studies were performed in Africa (Abdallah and Covaci, 2014; Shoeib et al., 2019). Additionally, studies investigating the levels of OPFRs in the indoor air (Cequier et al., 2014) and outdoor dust and air are very rare (Cequier et al., 2014; Möller et al., 2011; Salamova et al., 2014). Previous indoor studies collected floor dust (FD), and one study investigated and compared the levels of chlorinated OPFRs in FD and elevated fine dust (EFD), which is collected ~ 1 meter above the ground (Allgood et al., 2017). In previous studies, some variations were observed in the levels and patterns of PBDEs and other flame retardants between FD and EFD (Al-Omran and Harrad, 2016; Allgood et al., 2017; Björklund et al., 2012; Cequier et al., 2014; Khairy and Lohmann, 2018).

In a recent study (Khairy and Lohmann, 2018), we investigated the presence of PBDEs and alternative flame retardants (NFRs) in Alexandria, Egypt and found significantly higher concentrations ($p < 0.05$) of PBDEs and NFRs in the gaseous and EFD samples of the indoor microenvironments compared to the outdoor environment. In the current study, we report on concentrations of OPFRs for that sample set. For the vapor-phase samples, low density polyethylene passive samplers (LDPE) were used, which has proven to be an easy, cost-effective monitoring tool for hydrophobic organic compounds (HOC) in the ambient air (Bartkow et al.,

2004; Booij et al., 2002; Khairy and Lohmann, 2014; McDonough et al., 2016) but rarely used indoors (Khairy and Lohmann, 2018). LDPE sheets were deployed at different outdoor locations (n = 30) and various indoor microenvironments (n = 30), including cars (n = 18). EFD samples were collected from the same locations as LDPE. At the same time, FD was collected from selected homes (n = 9). Our main objectives were to: i) investigate and compare concentrations, profiles and potential sources of OPFRs in the indoor and outdoor environments, ii) determine variations in the concentrations and profiles of OPFRs in EFD and FD, and iii) compare the concentrations and gas-particle distribution of OPFRs with the legacy flame retardants (PBDEs and NFRs) and iv) estimate human exposure to OPFRs via inhalation, ingestion and dermal contact for toddlers, children and adults. To our knowledge, this is the first comprehensive study to measure OPFRs in the indoor and outdoor environments, and to utilize LDPE as an indoor passive sampler for OPFRs.

2. Materials and Methods

Detailed description of the study area, sampling, extraction and cleanup, instrumental analysis, selected physicochemical properties, calculation of atmospheric concentrations from LDPE and the estimation of the daily intakes of OPFRs are provided in Appendix A (supplementary information), in Khairy and Lohmann, 2018 and are briefly summarized below.

Indoor and outdoor samples were collected from Alexandria, Egypt (Fig. A1) during the late autumn – winter of 2014 (November – December) when indoor ventilation (indoor-outdoor air exchange) effects are minimum. EFD (settled dust from elevated surfaces such as tables, shelves and bookcases; Al-Omran and Harrad, 2016) was collected 1 m above the floor from the living (working) areas in apartments (n = 16) and working places (n = 14) using an Electrolux JetMaxx Bag Canister Vacuum cleaner (Model EL4042A) in cellulose thimbles fitted between the crevice

tool and the vacuum tube. FD was collected from selected homes ($n = 9$) by slowly passing the crevice tool of the vacuum cleaner on carpets and bare floor of the living area. The dust was allowed to pass to the dust collection bag (Kajiwara and Takigami, 2016). Samples were wrapped in a pre-combusted aluminum foil, sealed in plastic zip bag, and stored at -20°C until analysis. For cars, dust ($n = 18$) was collected from all the available surfaces except the floor. Participants were asked to follow specific guidelines for the samples to be valid (see Appendix A and Table A1 for more details).

Outdoor dust samples ($n = 30$) from the same locations as the indoor samples, were collected from smooth surfaces using small plastic brushes and a small aluminum shovel. Samples were kept in small amber glass jars and stored in a freezer at -20°C until analysis.

LDPE [10×30 cm strip of ~ 2 g each ($51\ \mu\text{m}$ thickness) for the outdoor samples, and 10×20 cm strip of ~ 1 g each ($25\ \mu\text{m}$ thickness) for the indoor samples] were pre-cleaned and spiked with performance reference compounds (PRCs) (Booij et al., 2002). Outdoor samples ($n = 30 \times$ duplicates) were deployed for 2 months near the indoor sampling locations in two inverted bowls as a shelter for protection against sunlight and precipitation. In the indoor microenvironments, one LDPE sheet was deployed for 2 months at each of the sampled rooms ($n = 2 - 3$) of the living area starting two weeks before the dust sampling campaign. Samplers were hung in protected places away from direct exposure to the light and direct contact with participants. The total number of deployed LDPE were 66 ($33 \times$ duplicates) at apartments, 36 at the cars, and 60 at working places (total = 162 samples). In the extraction/analysis step, all LDPE sheets deployed within a unit (apartment or working place) were pooled and extracted as one sample ($n = 16, 14$ and $18 \times$ duplicate for apartments, working places and cars respectively).

Dust samples (indoor and outdoor) were sieved through a 3-inch, 100 mesh (150 μ m) stainless steel sieve (Dodson et al., 2012), and ~ 0.50 g dry weight were extracted in an ultrasound after spiking with labelled OPFR surrogates. Samples were then purified and fractionated (F1 and F2) over silica gel. F2 containing the OPFRs was concentrated to a final volume of ~ 25 μ L (in methylene chloride) after the addition of the injection standard (p-terphenyl-d₁₄). LDPE samplers were spiked with surrogate standards (same as above) and extracted twice for 24 h each. After extraction, no further cleanup was required and the extracts were concentrated as shown above for the dust samples.

Samples were analyzed for 12 OPFRs [tris-2-chloroethyl phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP), tris-1,3-dichloropropyl phosphate (TDCIPP), tris(2,3-dibromopropyl) phosphate (TDBPP), tri-n-butyl phosphate (TNBP), tri (2-butoxyethyl) phosphate (TBOEP), 2-ethylhexyldiphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPHP), tri-o-totyl phosphate (o-TMPP), tri-m-totyl phosphate (m-TMPP) and tri-P-totyl phosphate (p-TMPP)] on an Agilent 6890N gas chromatograph coupled to a Waters Quattro Micro mass spectrometer (GCMS/ MS) in electron ionization mode (EI, 70 eV) using multiple reaction monitoring (MRM).

Field blanks, matrix spikes, and duplicate samples (30% of the total dust samples and all the LDPE samples) were included with each sample batch. Field blanks (10 for dust and 10 for LDPE) were analyzed with the samples (Table A2), and samples were corrected for the blanks. When an analyte was not detected, the noise was quantitated for the limit of detection (LOD) calculations. LODs were determined in the different matrices as the upper limit of the 95% confidence interval for the field blanks (Table A3). We used ½ the LOD for concentrations that were below the detection limit. Recoveries of the surrogate standards generally ranged from 68 – 90 % and 66 – 94 % for

the outdoor and indoor LDPE respectively, 60 – 85 % for the outdoor dust, 61 – 90 % for the indoor fine dust and 62 – 94 % for the floor dust. Matrix spikes recoveries (n = 6 for LDPEs and 7 for dust) ranged from 74 ± 3.0 % (TNBP) to 101 ± 1.0 % (m-TMPP) for the LDPE and from 73 ± 3.0 % (TNBP) to 104 ± 1.0 % (TPHP) for the dust (Table A4) with a relative standard deviation < 20%. Results of the replicate analysis of LDPE and the dust samples indicated that the reproducibility of the analysis ranged from 18 % – 25 %.

For **exposure assessment**, the daily exposure doses from inhalation, ingestion and dermal exposure pathways were calculated according to the USEPA guidelines (Means, 1989) as detailed in Khairy and Lohmann, 2018 and as shown in Appendix A.

Analysis of variance (ANOVA) and the student t-test were performed with SigmaPlot 11. All numbers were log-transformed before the statistical test for normality. Factor analysis (FA) and bivariate correlation were performed with IBM SPSS (V 23, USA). In the factor analysis model, principle component analysis (PCA) was used as the extraction method with Kaiser Normalization and varimax rotation. Only factors with eigen values > 1 were used for identification of the possible sources. Before applying FA, all numbers were log transformed for normality. Each sample was entered as a separate variable, and each sample included concentrations of PBDEs and NFRs from our previous work (Khairy and Lohmann, 2018) and OPFRs from the current study. Independent-samples t-test and Repeated Measures of ANOVA were used to determine the difference in OPFR levels between the different samples and the indoor microenvironments. Correlation analyses were used to investigate the possible sources of OPFRs.

3. Results and Discussion

3.1. Indoor Concentrations

3.1.1. Vapor Phase Samples

Concentrations of Σ OPFRs in the gas phase ranged from 6.0 - 39 pg/m³ (apartments), 7.0 - 64 pg/m³ (working places) and 10 - 45 pg/m³ in cars (Table A5). Cars showed the highest median concentration (20 pg/m³) followed by working places (18 pg/m³) and apartments (15 pg/m³). TPHP was detected in 100 % of the samples with comparable median concentrations in cars (2.5 pg/m³) and working places (2.3 pg/m³), and a lower median concentration in apartments (0.79 pg/m³). TDCIPP was detected in all the samples from apartments (median: 3.0 pg/m³) and cars (1.1 pg/m³), TBOEP in all the samples from working places (median: 1.2 pg/m³), and TCIPP in all the car samples (median: 7.2 pg/m³; Table A5). TCEP, TBOEP and EHDPP were below the LOD in all the samples from apartments and working places, whereas only EHDPP was below LOD in cars. TCEP and TBOEP were detected in 61 % (median: 1.8 pg/m³) and 89 % (median: 1.3 pg/m³) respectively of the car samples.

For each indoor microenvironment, there was a different profile of OPFR observed (Fig. A2). Apartments were generally dominated by the chlorinated organophosphate flame retardants (mostly TCIPP and TDCIPP, less so of TNBP and TPHP, see Fig. A2a). This variability in the contributions was also observed in working places (58 % with TCIPP, 21 % with TNBP and 14 % with TDCIPP; Fig. A2b) and cars (67 % of the samples with TCIPP and 28 % with TDCIPP; Fig. A2c). In cars, TDCIPP was more abundant in German-made cars compared to TCIPP in Japanese and Korean cars. The varying contributions of OPFRs imply that volatility alone cannot explain these observed OPFR profiles in the different microenvironments and that probably the type of OPFR used in furniture, car upholstery, plastics, among others, is the main reason for this observed variability.

3.1.2. Dust Samples

Σ OPFRs ranged from 153 to 1,117 ng/g, 189 – 1,138 ng/g, and 272 – 1,849 ng/g in the EFD of the apartments, working places and cars respectively. Concentrations of OPFRs in the cars (median: 692 ng/g) were significantly higher (one-way repeated measures of ANOVA; $p < 0.001$) than concentrations observed at working places (median: 359 ng/g) and the apartments (Table A6) which was similar to what was previously found in Cairo, Egypt (Abdallah and Covaci, 2014) and Germany (Brommer et al., 2012).

Concentrations of Σ OPFRs in the FD samples of the apartments ranged from 122 ng/g to 514 ng with a median concentration of 243 ng/g (Table A6). No statistically significant difference was observed between detected samples in the FD and the EFD (162 – 1,117 ng/g; median: 260 ng/g).

Some variability was observed when the different microenvironments were compared with respect to the detected analytes (Fig. 1b). TDCIPP was detected in all the EFD samples (Table A6). TPHP was also detected in 100 % of the apartment, working places, FD and in 94 % of the car samples ($n = 18$). TBOEP and TCIPP were detected in all the EFD samples from working places and cars respectively. (Table A6). TNBP was below LOD at apartments and working places but detected in 56 % of the car samples. TDBPP, TEHP, EHDPP and o-, m- and p-TMPP were the least abundant and have low detection frequencies in all the samples. Our results were in good agreement with other studies (either EFD or FD) in Cairo, Egypt (Abdallah and Covaci, 2014), Norway (Cequier et al., 2014), Japan (Kanazawa et al., 2010) and USA (Dodson et al., 2012; Stapleton et al., 2009).

TDCPP dominated in 75 % and 38 % of the indoor samples of the apartments and working places respectively (Fig. A3a, b) followed by TPHP (13 % and 19 % respectively) and TCIPP (6.0 % and

13 %) and TBOEP (6.0 % and 13 %). In cars (Fig. A3c), TCIPP dominated OPFR profiles in 61 % of the samples (mainly Japanese and Korean cars) followed by TDCIPP (in the German cars; 28 %), TBOEP (13 %) and TPHP (only in one sample). TDCIPP was the dominant analyte in dust samples collected from cars in Germany (Brommer et al., 2012). TCIPP and TPHP were also found to be the dominant analytes in cars from Kuwait (Ali et al., 2013) and Pakistan (Ali et al., 2013) respectively.

Unlike the EFD, FD samples of the apartments were dominated by TBOEP (59 ng/g) comprising 11 – 36 % of the total concentrations followed by TPHP (36 ng/g; 11 - 22 %) and TDCIPP (35 ng/g; 5.0 - 25 %), which was in good agreement with other studies worldwide (Brommer et al., 2012; Cequier et al., 2014; Dodson et al., 2012; Kanazawa et al., 2010; Shoeib et al., 2019). TBOEP is used in floor polishing (waxing) (Dodson et al., 2012) and thus its predominance in the FD samples is not surprising. However, the difference in the observed profiles between the EFD and the FD of the same sampling locations (Fig. A3a, d) may possibly indicate different sources (see below). In the apartments sampled for EFD and FD (n = 9), median concentrations of TCEP (14 ng/g), TCIPP (29 ng/g) and TDCIPP (70 ng/g) in the EFD samples were higher than in the FD samples (<LOD, 18 ng/g and 35 ng/g respectively) but statistically insignificant. Similar finding was observed for TDCIPP and TCIPP in EFD and FD samples collected from a university campus in California, USA (Allgood et al., 2017). In contrast, median concentrations of TBOEP (58 ng/g) and TPHP (47 ng/g) in the FD samples of the current study were higher than concentrations reported for the EFD samples (26 and 30 ng/g respectively).

3.2. Outdoor Concentrations:

3.2.1. Vapor Phase Samples

Outdoor vapor phase concentrations of Σ OPFRs ranged from 2.4 to 9.0 pg/m^3 and 2.3 to 16 pg/m^3 at the residential-industrial and residential sites respectively (Table A5) with no statistical significance difference in the detected concentrations (t-test, $p > 0.05$). TNBP showed the highest median concentration at the residential - industrial (1.9 pg/m^3) and residential sites (2.0 pg/m^3) and was detected in 67 % and 73 % respectively of the samples ($n = 15$ each) probably due its higher volatility compared to the other OPFRs (Reemtsma et al., 2008). TCIPP was the second highest at the residential site (1.9 pg/m^3) but it was only detected in 47 % of the samples (Table A5). All the other OPFRs displayed lower median concentrations ($< 0.70 \text{ pg}/\text{m}^3$). TDBPP, TEHP, o-TMPP, m-TMPP and p-TMPP were below LOD in all the samples. Except for TCIPP, which showed significantly higher concentrations (t-test, $p < 0.05$) at the residential sites (2.0 pg/m^3 compared to 0.90 at the residential-industrial sites), no statistical significance difference was observed between the residential and residential- industrial sites for all the other detected OPFRs (Fig. 1b).

TNBP and TCIPP dominated in the outdoor samples (Fig. A2d, e) comprising 3.0 – 92 % and 10 – 53 %, respectively, of the total concentrations of OPFRs.

3.2.2. Dust Samples

Concentrations of Σ OPFRs generally ranged from 83 – 480 ng/g with comparable concentrations at the residential and residential – industrial regions (Table A6). Median concentrations of TCEP, TDBPP, TEHP, EHDPP, o-TMPP and p-TMPP were below LOD at all the sites, whereas median concentrations of TNBP were below LOD only at the residential sites (Table A6). Some variability was observed in the contributions of the investigated OPFRs in the outdoor samples (Fig. A3e, f). At the residential sites, TPHP showed the highest median concentration (32 ng/g) comprising 3.0

- 49 % of the total concentrations followed by TDCIPP (median: 28 ng/g; % contribution: 3.0 - 59 %), TCIPP (20 ng/g; 3.0 - 30 %) and TBOEP (18 ng/g; 1.0 – 28 %). At the residential – industrial sites, the following descending order was observed: TBOEP (30 ng/g; 16 - 51 %) > TPHP (22 ng/g; 12 - 69 % each) > TNBP (16 ng/g; 11 – 33 %) > TDCIPP (15 ng/g; 11 - 33 %).

3.3. Comparison with Other Studies Worldwide

As shown in Fig. 2 and Table A7, detected vapor phase concentrations in all the indoor microenvironments were much lower than those reported for Norwegian houses (Cequier et al., 2014) (Fig. 2a), the North Sea (Möller et al., 2011) and the Great Lakes (Salamova et al., 2014) (Table A7). Similarly, detected dust concentrations of OPFRs in the current study were generally lower than worldwide concentrations observed in the indoor microenvironments (Ali et al., 2013, 2012; Brommer et al., 2012; Cequier et al., 2014; Dodson et al., 2012; Kademoglou et al., 2017; Kanazawa et al., 2010; Van den Eede et al., 2011) (Fig. 2), but comparable to previously reported concentrations for the FD samples in Cairo (sampled during 2012 – 2013), Egypt in one study (Abdallah and Covaci, 2014) and much lower than reported concentrations of OPFRs in FD samples collected from Cairo (sampled during 2013 – 2014) in another study (Shoeib et al., 2019). It is important to mention that differences in sampling year, sample type (EFD vs FD) and the general characteristics of the microenvironments (year of construction, number of foamed furniture and number of electronics) are all major variables that could greatly influence the validity of such comparison.

3.4. Comparison between levels and profiles of OPFRs in the different microenvironments

3.4.1. Vapor phase

Chlorinated organophosphate flame retardants dominated all the samples from the investigated indoor microenvironments, and comprised 46 – 69 % of the total vapor phase concentrations. TCIPP concentrations were significantly higher (One-Way repeated measures of ANOVA, $p < 0.01$) in cars (median 7.2 pg/m^3) compared to working places (median: 2.9 pg/m^3) and apartments (median: 4.0 pg/m^3). In contrast, TDCIPP showed significantly lower concentrations ($p < 0.008$) in cars (median: 1.1 pg/m^3) compared to apartments and working places (median: 3.0 and 2.6 pg/m^3 respectively; Fig. 1a), and TBOEP and TPHP concentrations were significantly higher ($p < 0.01$) at cars and working places compared to apartments (Fig. 1a). No statistically significant differences were observed for concentrations of TCEP, TNBP and EHDPP in the different indoor microenvironments.

3.4.2. Elevated fine dust

Detected EFD concentrations of OPFRs at the apartments were lower than concentrations reported for the working places and cars (Fig. 1c). TBOEP and TPHP concentrations at working places were significantly higher (Repeated measures of ANOVA, $p: 0.024, 0.01$) than detected concentrations at the apartments. Similarly, TCEP was detected at working places (median: 17 ng/g), but below LOD at the apartments. TBOEB and TPHP were the dominant OPFRs in the FD collected from working places in Belgium (Van den Eede et al., 2011) and Germany (Brommer et al., 2012). We assume that the higher contribution of the chlorinated OPFRs is attributed to their wide use as flame retardants in PUFs and as plasticizers (Larsson et al., 2018; Stapleton et al., 2009). It has been suggested that chlorinated alkyl OPFRs are now used as a replacement for the penta-BDE formulation in polyurethane foam (PUFs) (Dodson et al., 2012). As was previously observed in California (Dodson et al., 2012), TDCIPP and TCIPP were not correlated with detected

concentrations of TCEP ($r = 0.23, 0.33, p = 0.067 - 0.089$) as both can be used as a replacement for the TCEP. Additionally TDCIPP is known to be an expensive flame retardant and is used only when an efficient flame retardant is needed (Dodson et al., 2012) which explains its wide use in apartment foam goods. Our findings for the indoor microenvironments were similar to results from Cairo, Egypt (dominance of TDCIPP and TPHP) and in US household dust (Stapleton et al., 2009) but different from Norway (Cequier et al., 2014), California, USA (Dodson et al., 2012), Japan (Kanazawa et al., 2010) and FD samples from houses in Cairo, Egypt (Shoeib et al., 2019), where TBOEP (164 – 87,200 ng/g) showed the highest median concentration in either the FD or EFD.

In cars, dust samples were dominated by TCIPP (median: 184 ng/g), TBOEP (median: 154 ng/g), TPHP and TDCIPP (90 ng/g each), which is in good agreement with dust samples collected from cars in Cairo, Egypt (Abdallah and Covaci, 2014) and Kuwait (Ali et al., 2013). In cars, concentrations of TCIPP and TBOEP were significantly higher (Repeated measures of ANOVA, $p < 0.008$) than apartments and working places. Similarly, TPHP concentrations in cars were significantly higher ($p = 0.01$) than apartments. Chlorinated OPFRs are used as plasticizers in car interior and as flame retardants in upholstery foam (Van den Eede et al., 2011; van der Veen and de Boer, 2012), which may explain their higher detected concentrations in cars. TBOEP is also used in rubber and in plastics (Van den Eede et al., 2011; van der Veen and de Boer, 2012), and TPHP as a flame retardant, plasticizer, synthetic rubber and thermoplastics (Abdallah and Covaci, 2014).

3.5. OPFRs vs PBDEs and NFRs

Detected OPFR concentrations were compared with concentrations of PBDEs and NFRs measured in the same samples (Khairy and Lohmann, 2018). Vapor phase concentrations of PBDEs (Fig.

3a) were significantly higher (one-way repeated measures of ANOVA; $p < 0.001$) than concentrations of NFRs and OPFRs. On the other hand, concentrations of OPFRs in the dust samples (Fig. 3b) were the highest (one-way repeated measures of ANOVA; $p < 0.001$), followed by PBDEs and NFRs which showed the lowest concentrations. This is probably a reflection of the increased dependence on OPFRs in consumer goods in recent years. Detected concentrations of NFRs in the samples imply that they have not been widely used in the imported consumer products in Egypt. Interestingly, gaseous concentrations of PBDEs were higher than OPFRs. This could be attributed to the higher detected gaseous concentrations of the lower brominated PBDEs (BDE- 2, 8, 15, 28) (Chaoyang Yue and Loretta Y. Li, 2013) in addition to BDE-47 and 99, which have higher vapor pressure [more volatility; $\log P_L$ (Pa) = -0.67 to -2.9] (Brommer et al., 2014) than the dominant OPFRs [$\log P_L$ (Pa) = -1.3 to -4.3], and the longer usage history of PBDEs.

3.6. Indoor vs Outdoor OPFRs

All the gaseous and EFD concentrations in the indoor samples (excluding cars) were significantly higher (t-test, $p < 0.006$) than their corresponding outdoor samples. Additionally, variability in the observed profiles (Fig. A2, A3) in the indoor and outdoor environments suggests that detected concentrations in the indoor microenvironments are mainly from the indoor emission sources and that the indoor microenvironments are acting as a source of OPFRs to the outdoor environment (Indoor/outdoor > 1 for all analytes).

Some variations in the detected OPFRs were observed between the EFD and FD samples (dominance of the chlorinated FRs in the EFD compared to TBOEP and TPHP in FD) as outlined in Fig. A4. Similar to FD, median concentrations of TPHP and TBOEP in the outdoor dust were

higher than TDCIPP. This implies that OPFRs in EFD and FD samples for the same locations were probably produced and/or influenced by different sources.

For further investigation, factor analysis (FA) was performed separately for the vapor phase and dust samples. In this analysis, OPFR data from the current study and NFR and PBDE data from our previous study were included. Samples were entered as the variables. The main purpose was to check the variabilities/similarities between the different microenvironments, the different dust samples investigated (EFD vs FD vs OD) and within each microenvironment. Results are shown in Tables A8 and A9. For the vapor phase, four factors were extracted identifying 91 % of the variance. Factor 1 was responsible for 31 % of the total variance and was heavily loaded on the outdoor samples and moderately loaded on the majority of the samples of the indoor microenvironments (Table A8) thus representing the outdoor environment. Factor 2 identified 29 % of the variance and was heavily loaded on the indoor samples from working places and cars, few outdoor samples, and moderately loaded on the majority of the outdoor samples. Factor 3 identified 21 % of the total variance and was heavily loaded on the indoor samples. Factor 4 identified 10 % of the total variance and was heavily loaded on one indoor sample from apartments and low to moderately loaded on the rest of the samples. The output of the FA for the gaseous samples separated the outdoor samples from the indoor samples, which were loaded on several factors. This is a reflection of the between (indoor vs outdoor and between the different indoor microenvironments) and within (investigated samples within a given indoor microenvironment) variabilities in the profiles of flame retardants.

Similar outputs (due to variations in the profiles of flame retardants) were observed for the dust samples (Table A9), where EFD samples from the different indoor microenvironments were loaded on two factors (Factors 1 and 3) and were separated from the outdoor dust samples (Factor

2), which were loaded together with the FD samples. The loading of FD and outdoor dust on the same factor is a reflection to the similarities in their profiles of OPFRs (Fig. A4), PBDEs and NFRs (Khairy and Lohmann, 2018). Since all the samples were sieved (excluding the influence of particle size differences in samples), we suggest that FD samples are probably affected by carryover of dust by the shoes from the outdoor places. Based on our pre-sampling conditions (as requested from volunteers as shown in the supplementary information), we assume that this carryover process is of minimum influence on EFD samples.

3.7. Sources and Relations between OPFRs in the Samples

In the air and EFD samples (Tables A10, A11), significant correlations were observed between the individual OPFRs (TCIPP, TCEP, TDCIPP, TPHP and TBOEP; $r = 0.45 - 0.62$, $p < 0.05$) indicating possible common sources. TCIPP, TDCIPP and TBOEP were significantly correlated with the number of foamed furniture in the air ($r = 0.39 - 0.54$, $p < 0.05$) and EFD samples ($r = 0.38 - 0.45$, $p < 0.05$), possibly due to the use of these OPFRs in foam-containing furniture (Van den Eede et al., 2011; van der Veen and de Boer, 2012). TBOEP significantly correlated with the type of floor in air and EFD, where concentrations increased in places with wood floors probably due to its wide use as a floor polish (Dodson et al., 2012).

In cars, TCIPP in the vapor phase and dust samples ($r = 0.50, 0.67$; $p = 0.036, 0.002$) showed significant positive correlation with the model year ($r = 0.52 - 0.67$, $p < 0.05$). TBOEP and TDCIPP were significantly higher in the German cars ($r = 0.67 - 0.85$, $p < 0.05$) in both air and dust samples (Tables A13, A14). However, these findings should be carefully considered due to the small number of investigated samples ($n = 6$ each).

Based on the correlation analysis, other variabilities within the sampled indoor locations, origin and age of the imported consumer goods greatly influenced the observed patterns and concentrations of OPFRs in the indoor samples despite the observed significant correlations for the chlorinated flame-retardants and TBOEP in the indoor microenvironments, which identified their sources. Accordingly, a clear image about the possible sources of all the investigated OPFRs could not be obtained in the current study as was previously observed for various organic flame retardants in the indoor microenvironments of Norway (Cequier et al., 2014).

3.8. Relationship between OPFRs in Air and Dust

Equilibrium partitioning of OPFRs in air and dust of the same indoor and outdoor sampling sites was investigated in the current study. Significant positive correlations between gaseous and dust OPFRs (TCIPP, TDCIPP, TBOEP, TPHP, Σ OPFRs) were observed in the indoor microenvironments ($r = 0.50 - 0.75$; $p < 0.006$) and cars ($r = 0.51 - 0.90$, $p < 0.01$), but only for TDCIPP and Σ OPFRs in the outdoor environment ($r = 0.40 - 0.55$, $p < 0.03$). Similar findings were observed for indoor OPFRs in Norway (Cequier et al., 2014), for PBDEs in Toronto, Canada (Zhang et al., 2011) and for PBDEs and NFRs at Alexandria, Egypt (Khairy and Lohmann, 2018) despite differences in sampling techniques (conventional air sampling in Norway vs PUF passive samplers in Canada vs LDPE in Alexandria, Egypt). Log dust – air partitioning coefficients ($K_{\text{EFD-air}}$, m^3/g) were calculated by dividing the detected concentrations in the dust samples by those obtained from the LDPE. When these were plotted against log octanol – air partitioning coefficients ($\log K_{\text{OA}}$), significant log-linear relationships were observed for the indoor (apartments + working places, Fig. 4a), cars (Fig. 4b) and the outdoor environment (Fig. 4c) indicating an equilibrium partitioning between air and the organic phase of the dust particles (Weschler and Nazaroff, 2010). A similar finding was observed for FD samples. Equilibrium

partitioning between air and dust for a wide range of flame retardants was also previously observed in Norway (Cequier et al., 2014). In contrast, significant log linear $K_{\text{dust-air}} - K_{\text{OA}}$ relationships were only for PBDEs with $\log K_{\text{OA}} < 11$ and no relation for higher brominated ones in Toronto, Canada (Zhang et al., 2011). In the current study, we observed strong log-linear correlations for all flame retardants (Fig. 4). We assume that the difference in the passive samplers used is the reason for this variation. In the study performed in Toronto, PUF samplers were used, which are known to collect the vapor phase in addition to particles (Strandberg et al., 2018; Zhang et al., 2011) thus overestimating vapor phase concentrations. In contrast, LDPE passive samplers have the advantage of sampling gaseous phase with no influence from particles, thus assumed to give more accurate estimation of the vapor phase concentrations.

Interestingly, $K_{\text{EFD-air}}$ values varied widely for the different flame retardants with the same K_{OA} values. In general, $K_{\text{EFD-air}}$ values for OPFRs, were always higher (Fig. 4) than values calculated for NFRs and PBDEs that showed comparable values. $K_{\text{EFD-air}}$ of TCEP (4.1) was double that of BDE-2 (2.3) despite their close K_{OA} values (7.6 and 7.2 respectively). For flame retardants with K_{OA} values ~ 10.5 , $K_{\text{EFD-air}}$ values of TDCIPP (4.5) and TPHP (4.5) were higher than calculated values for hexabromobenzene (2.1) and BDE-47 (2.8). Three reasons could be responsible for this observed trend: i) chemical differences (apolar bromines in PBDEs and NFRs vs monopolar phosphate group in OPFRs); (ii) uncertainties in the physicochemical parameters (K_{OA}) and $K_{\text{PE-a}}$ and (iii) uncertainties in measured gaseous concentrations since underestimated gaseous concentrations result in higher $K_{\text{EFD-air}}$ as was observed for OPFRs. In the current study, gaseous concentrations of all flame retardants were determined using LDPE. Accumulated amounts of flame retardants in the plastic sheets (C_{PE}) were converted to gaseous concentrations using LDPE-air partitioning coefficients ($K_{\text{PE-A}}$, L/kg). $K_{\text{PE-A}}$ s for all the analytes were calculated from the

subcooled liquid vapor pressures (P_L , Pa) of the target analytes as shown elsewhere (Khairy and Lohmann, 2014). However, several P_L values exist in literature with great variability. To study, the influence of uncertainties in P_L , we used different available P_L values from literature to calculate K_{PE-A} values, estimate gaseous concentrations and use these estimated concentrations to calculate $K_{EFD-air}$ for the analytes. For PBDEs, we used the K_{PE-A} values from our field calibration study (Khairy and Lohmann, 2014) and incorporated the estimated uncertainty for each congener. P_L values for NFRs and OPFRs were obtained from SPARC calculator (Ruan et al., 2009), EPI suite and Absolv (Ruan et al., 2009), in addition to literature (Bergman et al., 2012 and Dirtu et al., 2013 for NFRs and Brommer et al., 2014 for OPFRs). As shown in Fig. 4, calculated $K_{EFD-air}$ values for all the analytes were within the uncertainty range (dashed red lines) estimated from the uncertainties in P_L values. However, the highest $K_{EFD-air}$ uncertainties were observed for OPFRs (39 – 200 %, average: 135 %) which were significantly higher (One Way Repeated Measures ANOVA, $p < 0.001$) than $K_{EFD-air}$ uncertainties for NFRs (0.24 – 66 %) and PBDEs (20 – 75 %). Future work should confirm that OPFRs partitioning to LDPE is as expected based on apolar compounds.

3.9. Human Exposure Assessment

In the current study, the exposure to OPFRs via ingestion of EFD, inhalation (gaseous concentrations) and dermal contact (with EFD) was investigated. The detailed description of the models used and constants used are given in the supplementary information. For each exposure route, daily exposure dose was calculated for adult males and females (both working and non-working), children (> 6 years old) and toddlers. The exposure times (ET) at home, work, cars, school and outdoor were obtained from the answers of the participants in the questionnaires. All the other parameters such as body weight, inhalation rates, ingestion rates, dermal adherence rate,

surface area and absorbed dose were obtained from the EPA guidelines for human health risk assessment (Means, 1989). **Calculated** daily dose for each target analyte from each exposure route is given in Table A15. Total daily doses (sum of doses from inhalation + ingestion +dermal contact) ranged from 0.050 – 1.2, 0.060 – 1.3, 0.050 – 1.2, 0.28 – 7.1 and 0.52 – 12 ng/kg bw/d for adult **working** females, **non-working females**, adult males, children and toddlers respectively. All daily doses of TCEP, TCIPP, TDCIPP, TNBP, TBOEP and TPHP from the ingestion pathway (both worse- and best-case scenarios) were much lower than their corresponding oral reference doses. For all the exposure routes, TDCIPP showed the highest estimated daily doses for all the sex and age groups (Fig. 5). For adults, dermal contact was the main source of exposure, where it was responsible on average for 74 % of the total calculated daily doses. Dust ingestion was responsible on average for 25 % of the total daily doses. In children and toddlers, dust ingestion was the major exposure pathway, where it represented on average 58 % and 67 % respectively of the total daily doses followed by the dermal contact (41 % and 33 %). Inhalation showed only minor contribution as most of the analytes were below LOD in the vapor phase.

4.0. Conclusion

This study presented for the first-time data on the concentrations, profiles, sources and health exposure assessment of OPFRs considering gaseous and dust phases in the indoor and outdoor environments. The inclusion of all these different samples helped us to i) highlight the similarities in the observed profiles of OPFRs in the FD and outdoor dust samples and their differences from the EFD samples, ii) suggest that EFD should be considered as a better representative of the indoor microenvironments in similar places characterized by high concentrations of ambient particulate matter, iii) highlight the importance of dermal contact as a major human exposure route for adults, and thus should be considered together with the ingestion exposure route. However, toxicological

data expressing the effect of the exposure to OPFRs via dermal contact and inhalation are missing and thus are greatly needed in future studies for better understanding of the possible overall adverse health effects associated with the exposure to OPFRs from all atmospheric exposure routes. In contrast to previous work, we observed strong log-linear partitioning for OPFRs between gas-phase and dust samples, though offset from other brominated flame retardants. The reason for the higher abundance of OPFRs in the dust relative to PDBEs and NFRs is not clear, but might indicate that current physico-chemical properties of OPFRs are not well constrained.

Appendix A. Supplementary data

Supplementary data to this article can be found online.

5.0. References

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