

Brominated and organophosphorus flame retardants in South African indoor dust and cat hair

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Highlights

- First report on chloroalkyl, aryl and alkyl OPFRs in the South African indoor environment.
- First results of OPFRs in cat hair as a non-invasive sampler for human exposure, aimed at toddlers.
- OPFRs are the major FRs and contribute for more than 97% to the total FR load.
- TCIPP is the major OPFR in indoor dust and TBOEP the major OPFR in cat hair.
- BEH-TEBP and EH-TBB showed notable contributions to the BFR profile in cat hair.

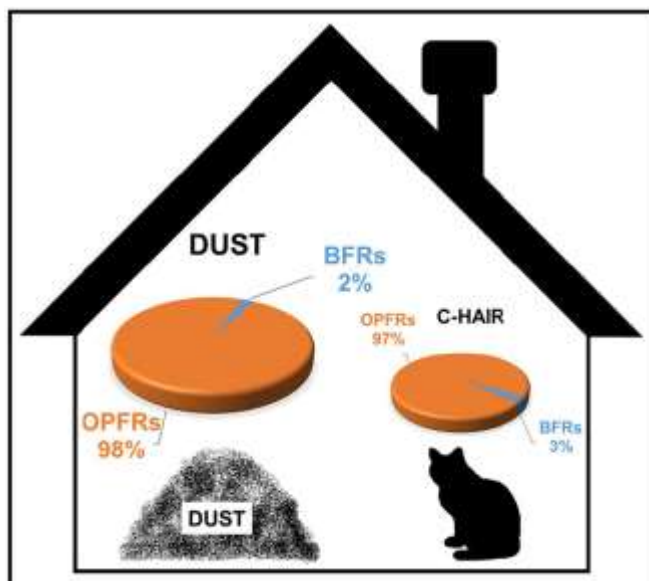
Abstract

Flame retardants (FRs), such as brominated flame retardants (BFRs) and organophosphorus flame retardants (OPFRs), are diverse groups of compounds used in various products related to the indoor environment. In this study concentrations of eight polybrominated diphenyl ethers (PBDEs), two alternative BFRs and ten OPFRs were determined in indoor dust (n=20) and pet cat hair (n=11) from South Africa. The OPFRs were the major FRs, contributing to more than 97% of the total FR concentration. The median Σ_{10} OPFRs concentrations were 44,800 ng/g in freshly collected dust (F-dust), 19,800 ng/g in the dust collected from vacuum cleaner bags (V-dust), and 865 ng/g in cat hair (C-hair). Tris(1-chloro-2-propyl) phosphate (TCIPP) was the dominant OPFR in the dust samples with median concentrations of 7,010 ng/g in F-

dust and 3,590 ng/g in V-dust. Tris(2-butoxyethyl) phosphate (TBOEP) was the dominant OPFR in C-hair, with a median concentration of 387 ng/g. The concentrations of Σ_8 PBDEs were higher in F-dust than in V-dust. BDE209 was the dominant BFR in all three matrices. Bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TBEP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) showed notable contributions to the BFR profile in cat hair. A worst-case dust exposure estimation was performed for all analytes. The estimated TCIPP daily intake through dust ingestion was up to 1,240 ng/kg bw for toddlers. The results indicate that OPFRs are ubiquitous in South African indoor environment. Indoor dust is a major source of human exposure to environmental contaminants. This can for example occur through hand-to-mouth contact of toddlers, and is an important route of exposure to currently used FRs accumulated on dust particles. The presence of FRs, in particular high concentrations of OPFRs, suggests that children and indoor pet cats may have greater exposure to FRs than adults.

Capsule: The quantitative analysis of brominated and organophosphorus flame retardants in indoor dust and cat hair shows higher concentrations of organophosphorus flame retardants; chloroalkyl phosphates were prominent in dust and alkyl phosphates in cat hair

Graphical abstract



1. Introduction

Indoor exposure of humans to flame retardants (FRs) is of concern from a human health perspective. Because of the specific physicochemical properties, FRs such as brominated FRs (BFRs) and organophosphorus FRs (OPFRs) are applied in relatively high concentrations (percentages) to combustible materials, to reduce their flammability and to meet fire safety requirements (Alaee et al., 2003; van der Veen and de Boer, 2012). These materials are used in indoor environments, such as in textiles, building materials, and electrical and electronic equipment (Alaee et al., 2003). For many years polybrominated diphenyl ether (PBDE) formulations were the most widely used BFRs e.g. in polyurethane foam and textile, in acrylonitrile-butadiene-styrene (ABS) resins and in different polymeric materials including high-impact polystyrene (HIPS), ABS, polypropylene, and in cotton and polyester containing textiles (Alaee et al., 2003; Covaci et al., 2011; Shaw et al., 2014). The commercial Penta-BDE and Octa-BDE mixtures have been restricted under the Stockholm Convention (SC) since 2009, and Deca-BDE formulation was added to that Convention in 2017 (<http://chm.pops.int/>). In 2003 Penta BDEs were banned in the European Union (EU) and not much later other PBDEs were either banned (in the EU) or voluntarily phased out (in the USA) (European Commission, 2003).

The restrictions on the production and use of PBDEs has led to an increase in the production and use of OPFRs and alternative-BFRs (alt-BFRs) in products (van der Veen and de Boer, 2012). Whereas PBDE concentrations have been reported for the South African indoor environment, limited information is available for the two alt-BFRs, bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TBEP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) (Brits et al., 2016). BEH-TBEP and EH-TBB have been found in indoor dust, and air at various concentrations (Rantakokko et al., 2019; Al-Omran and Harrad, 2017; Cristale et al., 2018; McGrath et al., 2018; Newton et al., 2015; Stapleton et al., 2009, 2008), and levels were also reported in hair from pet cats and dogs (Ali et al., 2013). In addition to BFRs, OPFRs are considered as effective FRs but are also used as plasticizers and anti-foaming agents in

various materials and consumer products associated with the indoor environment (Marklund et al., 2003; van der Veen and de Boer, 2012). OPFRs are an additive type of FR, i.e. they are mixed into the polymer and can, therefore, migrate from products into the indoor environment by means of volatilization, leaching and abrasion, and/or direct transfer to dust (Marklund et al., 2003; van der Veen and de Boer, 2012). OPFR concentrations have been reported in indoor air, dust and wipe test samples from electronic equipment and window protection film (Cao et al., 2019; Brandsma et al., 2014; Stapleton et al., 2011, 2009; Van Den Eede et al., 2012; Vykoukalová et al., 2017). OPFR levels have also recently been reported in dog hair (González-Gómez et al., 2018). Generally, OPFRs in dust from homes and other indoor environments are dominated by tris(2-butoxyethyl) phosphate (TBOEP), followed by the chlorinated OPFRs (Wei et al., 2015). Recent studies from Europe, China, and South Africa, have shown that chlorinated OPFRs dominate indoor dust profiles (Abafe and Martincigh, 2019; Peng et al., 2017; Wei et al., 2015). Some OPFRs are suspected carcinogens and others exhibit neurotoxic effects, adverse effects on fertility and hormone levels and decreased semen quality in males (Wei et al., 2015). Humans and pets are ubiquitously exposed to various FR's, *via* diet, through direct contact with consumer products, and through household dust, which is used to measure indoor chemical contamination and to assess human exposure risks (Jones-Otazo et al., 2005; Whitehead et al., 2011). Children and indoor pet cats may, therefore, have greater exposures to FRs through dust ingestion than adults (Norrgran Engdahl et al., 2017). Since pet cats have previously been presented as a potential bio-sentinel for indoor pollution exposure, cats might therefore, have relevance as indoor exposure models for children (Dirtu et al., 2013). Cat hair is also directly exposed to the environment and constantly accumulates contaminants from indoor air and dust. Being a non-invasive matrix, hair samples allow for sample stability, information on compound exposure and the high lipid content allows for the analysis of a wide variety of FRs. Evidence suggests that FR exposure through dust ingestion is orders of magnitude higher for toddlers than adults due to potential higher dust ingestion rates (Wei et al., 2015). Accurate and precise measurements of FRs concentrations are critical for risk assessment and decision making.

In previous work, we employed qualitative screening analysis to identify organohalogenated compounds, including BFRs and halogenated OPFRs in the South African indoor environment by using cat hair as matrix (Brits et al., 2017). This study aims to accurately quantify BFRs and OPFRs in indoor dust and cat hair, to estimate the measurement uncertainty associated with each compound, and to preliminary evaluate exposure to toddlers and adults via dust ingestion. Hair samples from six longhair Persian cats and indoor dust were collected. The measurement uncertainty during the method validation procedure was performed, to support the quality of the data and to identify uncertainty sources in the analytical method.

2. Materials and methods

2.1. Chemicals

Standards of tributyl phosphate (TNBP), tris(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris(2-isopropylphenyl) phosphate (TIPPP), tris(methylphenyl) phosphate (mixture of 3 isomers) (TMPP), TBOEP, TCEP, TCIPP, and TDCIPP were purchased from AccuStandard Inc., New Heaven, USA. The PBDE mixture (BDE-MXE), BEH-TEBP, EH-TBB, and the internal standards, $^{13}\text{C}_{12}$ -BDE209, BDE58, TPHP-d15, TNBP-d27, TCEP-d12, TDCIPP-d15, were purchased from Wellington Laboratories Inc., Guelph, ON, Canada. The purity of analytical standards for OPFRs was >98%, except for TBOEP (>94%). Dust standard reference material (SRM 2585) was purchased from The National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). The solvents and chemicals used were all analytical or HPLC grade, unless otherwise stated. Dichloromethane (DCM), methanol acetone, iso-octane, toluene, and n-hexane were purchased from J.T Baker, Deventer, The Netherlands. Whatman® grade 541 filter paper, silica gel, and Florisil® were purchased from Sigma-Aldrich (now Merck), Amsterdam, The Netherlands.

2.2. Sample collection

Dust samples (n=20) were collected in January 2018, from homes in Pretoria, South Africa. F-dust was collected from living rooms where cats spend more than 50% of their time to

investigate contamination in a single room over a short time-span. The participants were asked not to vacuum this area for at least one week prior to sampling to ensure sufficient dust accumulated for collection. The F-dust samples (n=9) were collected as a mixture of floor dust and elevated surface dust using a 2000 W household vacuum cleaner, similar to previous studies (Cristale et al., 2018). Dust particles were retained on a cone-shaped folded filter paper placed between the hose and a pre-cleaned (stainless steel) nozzle. The sampling protocol involves approximate vacuuming time of 2 min for carpeted floors and 4 min for hard surface floors, 2 min for surfaces (tables, TV stands, and shelves) and 1 min for sofas and armchairs. The filter paper was wrapped in aluminium foil, placed in a resealable plastic bag and transported to the laboratory for processing. V-dust samples (n=11) were also collected from the existing vacuum cleaner bags to examine wide indoor contamination over periods of months (average 3 months). The V-dust was collected by emptying the total content of the vacuum cleaner bag or by emptying the contents of canisters from bag-less vacuums on aluminium foil. The aluminium foil was folded, sealed in a plastic re-sealable bag and transported to the laboratory for processing. After sampling, the F-dust was removed from the filters. The dust samples were sieved through a pre-cleaned stainless steel sieve (500 µm) and stored in a pre-cleaned amber vial with Teflon lined lids until chemical analysis. During sample collection Na₂SO₄, spread on aluminium foil was collected as field blank (n=3 for F-dust, and n=3 for V-dust) using the same method employed to collect the dust samples and treated as samples. Cat hair samples (n=11) were collected from Persian cats at a pet grooming service in Pretoria, representing 6 homes. These cats are typically closely associated with indoor environments, thus sharing a common environment with toddlers. Pre-cleaned glass wool was exposed to the air and used to simulate blanks during the hair collection (n=3). All animal owners provided full consent after being informed of the study's objectives. The hair samples were rinsed with distilled water (3 times), dried at room temperature, and wrapped in aluminium foil, placed in resealable plastic bags. The dust and hair samples were stored at room temperature until chemical analysis. To avoid possible compound losses due to hair swelling, as previously reported for forensic hair analysis,

samples were not frozen (Cooper et al., 2012). Details on the samples associated with the homes are provided in the Supplementary Material (Table S1).

2.3. Sample pre-treatment

An accurately weighed aliquot of dust (between 20 and 50 mg) and cat hair (between 200 and 500 mg) was spiked with a mixture of internal standards containing 50 ng $^{13}\text{C}_{12}$ -BDE209, and BDE58 and 80 ng of TPhP-d15, TPrP-d21, TNBP-d27, TCEP-d12, and TDCIPP-d15. The hair samples were cut into small pieces (<5 mm) using pre-cleaned stain-less steel scissors prior to the addition of internal standards. Three blanks and three SRM 2585 samples were analyzed together with each batch of samples. Sample extraction was carried out using accelerated solvent extraction (ASE) with hexane/acetone (3:1, v/v) as previously described by Brandsma et al. (2015). The extracts were concentrated to near dryness, at 30 °C under gentle nitrogen flow. The dust extracts were reconstituted in 0.5 mL hexane to follow fractionation. A major challenge in the analysis of OPFRs in the cat hair samples was the presence of a lipid-based waxy substance (sebum), which resulted in substantial chromatographic interferences. Basic or acidic treatment like saponification could not successfully be applied since OPFRs are prone to degradation under extremely acidic or basic conditions (Kucharska et al., 2014). The cat hair extracts were reconstituted in 2 mL methanol and subjected to a freezing-lipid precipitation step, prior to fractionation, as previously employed for complex lipid-rich samples (Liu et al., 2018). After the addition of methanol, the tube was vortexed for 2 minutes and stored in the freezer for 2 hours at -20 °C. Since most of the wax-like compounds were precipitated as a white condensed precipitate at the bottom of the tube, the cold supernatant was transferred to a pre-cleaned tube. The procedure was repeated with two aliquots of methanol and the combined supernatant was evaporated at 30°C to near dryness and reconstituted in 0.5 mL hexane. This method efficiently removed the chromatographic interferences. The dust and hair extracts were fractionated on silica-florisil columns. Pre-cleaned empty glass columns (inner diameter 10 mm) were fitted with a glass wool plug and filled from the bottom with 0.5 g Silica gel, 0.5 g Florisil and 0.5 g anhydrous

Na₂SO₄. The column was conditioned with 40 mL hexane. The extracts (in hexane) were quantitatively transferred to the column and the first fraction was eluted with 15 mL hexane and 15 mL DCM/hexane (1:1, v/v), the second fraction with 15 mL ethyl acetate. All fractions were evaporated to near dryness at 30 °C under a gentle stream of nitrogen. The first fraction was reconstituted in 500 µL iso-octane for analysis of PBDEs and the two alt-BFRs. The second fraction was reconstituted in 1000 µL iso-octane for the analysis of OPFRs.

2.4. Instrumental analysis

The quantification of PBDEs was performed using two analytical columns, on an Agilent 6890 gas chromatograph (GC) coupled to a 5975 mass spectrometer (MS) in electron capture negative ionisation (ECNI) as previously described by Brandsma et al. (2015). The two alt-BFRs were included in the analysis method for BDE209 and quantified by monitoring *m/z* 356.7 and 358.7 for EH-TBB and *m/z* 463.6 and 461.6 for BEH-TEBP. OPFR analysis was performed using an Agilent 7890B GC coupled to a 7010A triple quadrupole MS in electron impact (EI) mode. The GC method conditions were used as previously described by Brandsma et al. (2014) and quantitation was done in selected reaction monitoring (SRM) mode. The optimised quantitation and qualifier ion transitions, and collision energies are listed in Table S2.

2.5. Quality assurance and quality control

Positive identification of the analytes was made when ion ratios of 2 product ions (for SIM and SRM analysis) were within ±30% (relative) and retention times do not differ by more than 0.1 second from the average of calibration standards. The limits of quantification (LOQ) were calculated as the mean values plus three times standard deviation of analytes in blanks. For compounds not detected in the blanks, the LOQs were estimated by a signal-to-noise ratio of 10. Based on maximum sample intake of 50 mg dust and 500 mg hair the LOQs ranged from 0.9 ng/g to 187 ng/g and 0.09 ng/g to 18.7 ng/g respectively (Table S3). The correlation coefficient (*R*²) for all the analytes was greater than 0.999 (Table S3). If the measurement uncertainty associated with the result overlapped with the LOQ, the concentration was

reported to be below LOQ. The validation of the analytical method was assessed by analysis (n=9) of the dust standard reference material (SRM 2585), and triplicate spiking experiments on both matrices at two concentrations. As shown in Table S4, relative recoveries between 84 and 105% were obtained for the dust samples, with relative standard deviations (RSDs) ranging from 1.9 to 17%. Recoveries for the cat hair samples ranged from 81 to 104%, with RSDs between 0.7 and 20%. Recovery uncertainties were included in the uncertainty budget. As shown in Table S5, results obtained for the SRM 2585 samples agree with the certified values for the PBDE congeners and the reference values for the four OPFRs. There are currently no reference values assigned to for the two alt-BFRs and additional OPFRs included in this study. The results obtained for these compounds (Table S6) compared well with data previously reported for SRM 2585. TCIPP (RSD = 7%), TBOEP (RSD = 11%) and EHDPP (RSD = 11%) were detected in field blanks at average concentrations of 9.2 ng/g, 5.2 ng/g, and 3.2 ng/g, respectively. The blank contamination was present at levels of $\leq 10\%$ of the lowest detected concentrations in the samples and therefore blank corrections were not applied. TNBP was detected at levels between 7 and 21% of the samples (average 4.4 ng/g), and therefore TNBP concentrations were blank corrected. The uncertainty of measurement for the compounds in the two matrices was estimated using validation data.

2.6. Estimation of the measurement uncertainty

The measurement uncertainties for PBDEs, alt-BFRs, and OPFRs in dust and hair were estimated as described by Ellison and Williams (2012). The uncertainty sources were identified as sample weighing, gravimetric preparation of the purity-corrected native and labelled standard stock solutions used to prepare the calibration range, uncertainty in the calibration graph, recovery and repeatability. The uncertainty associated with the recovery was estimated as described by Barwick and Ellison (1999). The calculations used to quantify the uncertainty components and finally calculate combined uncertainty are described in the Supplementary Material. The combined standard measurement uncertainty of the analyte in the matrixes was calculated by Eq. (1).

$$\frac{u_c(A)}{C_A} = \sqrt{\left(\frac{u(C_{Std})}{C_{Std}}\right)^2 + \left(\frac{u(C_{Istd})}{C_{Istd}}\right)^2 + \left(\frac{u(c_0)}{c_0}\right)^2 + \left(\frac{u(R_m)}{R_m}\right)^2 + u(r)^2} \quad (1)$$

where,

$u_c(A)$	Combined standard measurement uncertainty of the analyte
C_A	Concentration of the analyte
$u(C_{Std})$	Combined standard measurement uncertainty of standard solution
C_{Std}	Concentration of standard solution
$u(C_{Istd})$	Combined standard measurement uncertainty of internal standard solution
C_{Istd}	Concentration of internal standard solution
$u(C_0)$	Combined standard measurement uncertainty of calibration curve
c_0	Calculated concentration of the analyte in the sample using calibration curve
$u(R_m)$	Combined standard measurement uncertainty of recovery
R_m	Calculated recovery
$u(r)$	Combined standard measurement uncertainty of repeatability

The expanded uncertainty was obtained from the combined standard measurement uncertainty, calculated with the use of coverage factor $k = 2$, corresponding to a confidence level of 95%. The relative expanded uncertainties (%) for all compounds in the two matrices ranged from 13 to 30% in dust and 11 to 34% for hair (Table S7). The major contributions to the combined uncertainty were due to the uncertainties associated with recovery and repeatability (Fig. S1 and S2).

2.7. Statistical analysis

Basic and descriptive statistics were calculated using Microsoft Excel software. Normality of the data was checked by Shapiro–Wilk test. One-way ANOVA was employed to determine if analyte concentrations were significantly different in dust collected using the two sampling methods.

3. Results and discussion

3.1. Brominated flame retardants

The BFR congener profiles for the different matrices with detection frequencies, mean, median, concentration ranges, and standard deviation are shown in Fig. 1. BDEs 47, 99, 209 and BEH-TEBP were detected in all dust and hair samples. BDE209 was the dominant

congener contributing 85% of the total BFR concentrations in F-dust, 69% in the V-dust samples and 37% in the cat hair samples. The presence of PBDEs in the samples suggests release from legacy sources and products. Concentrations of Σ_8 PBDEs ranged from 97 to 878 ng/g (median 307 ng/g) and 647 to 4,620 ng/g (median 903 ng/g) in the V-dust and F-dust respectively, and were significantly different ($p < 0.05$). The concentration ranges for F-dust were comparable to ranges previously reported (689 to 3,290 ng/g) for freshly collected indoor dust in South Africa (Abafe and Martincigh, 2014). Higher median concentration of the Σ_8 PBDEs (2,000 ng/g) was reported for Australian house dust (McGrath et al., 2018). The median concentration of the Σ_8 PBDEs in cat hair samples was 11.1 ng/g and ranged from 7.7 to 18.1 ng/g. Significantly ($p < 0.05$) higher concentrations of BDE209 were detected in F-dust samples, ranging from 570 to 4590 ng/g (median of 887 ng/g), compared to V-dust which ranged from 77 to 857 ng/g (median of 272 ng/g). Abafe and Martincigh (2014) previously reported BDE209 concentrations ranging from 59.2 to 2,190 ng/g, with a median concentration of 656 ng/g in South African indoor dust. The median BDE209 concentration in the cat hair samples was 9.1 ng/g with concentrations ranging from 4.3 to 14.1 ng/g. When BDE209 is excluded from the PBDE profile (Fig. 1B), comparable congener profiles of the Σ_7 PBDE were observed for the matrices, with BDE99 as the dominant congener. The median Σ_7 PBDE concentrations were 33 ng/g (ranging from 26 to 139 ng/g) and 35 ng/g (ranging from 19 to 290 ng/g) for F-dust and V-dust respectively ($p > 0.05$). The BDE-209 concentrations influenced the correlation observed between PBDE levels found using the two dust collection methods, indicating that BDE209 might have room-specific sources. Estimates of exposure for BDE209 through dust ingestion using household vacuum cleaner dust might therefore underestimate exposure. The Σ_7 PBDE concentrations in cat hair samples ranged from 1.3 to 4.3 ng/g with a median concentration of 2.9 ng/g. Ali et al. (2013) reported median concentration on 2.15 ng/g for Σ_4 PBDE (excluding BDE209) for cat hair collected in Pakistan.

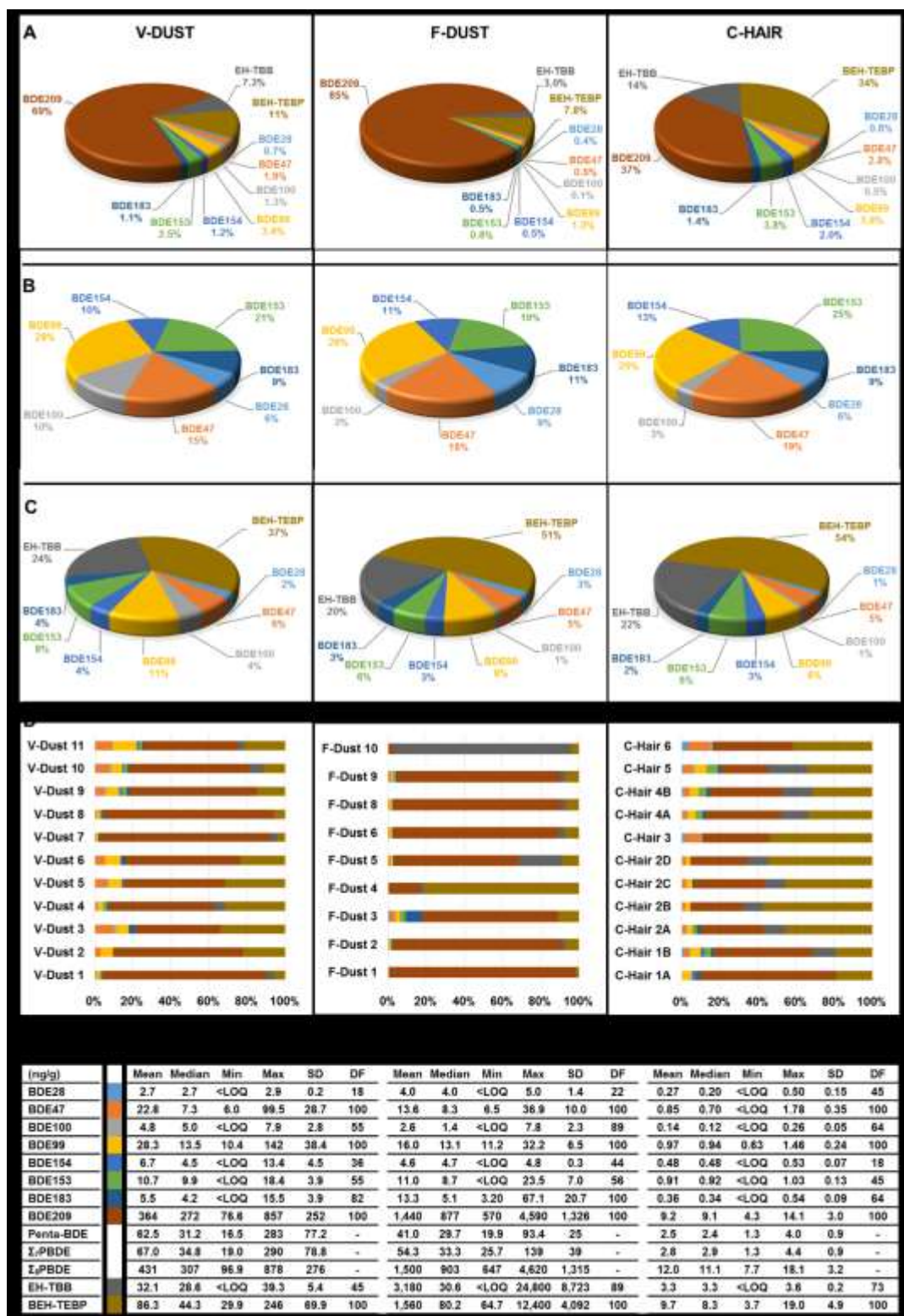


Fig. 1. Comparison of congener profiles of (A) eight PBDEs with EH-TBB and BEH-TEBP in V-dust (n = 11), F-dust (n = 9) and cat hair (n = 11) samples, (B) seven PBDEs (excluding BDE209) and (C) seven PBDEs (excluding BDE209) with EH-TBB and BEH-TEBP. (D) Relative abundances (%) of the eight PBDEs, EH-TBB and BEH-TEBP in the individual V-dust, F-dust and cat hair samples. (E) Summary of the mean, median, concentration range (ng/g), standard deviation (SD) and detection frequency (DF %) for the eight PBDEs, EH-TBB and BEH-TEBP.

EH-TBB and BEH-TEBP, the two alt- BFRs used in FM 550, contributed to 19% of the BFR profile in V-dust, 11% in F-dust and 48% in the cat hair (Fig. 1A). BEH-TEBP was detected in all samples and EH-TBB had a lower detection frequency in the V-dust compared to the F-dust and the hair samples. The median concentrations for BEH-TEBP in the F-dust samples were 80 ng/g, ranging from 65 to 12,400 ng/g and 44 ng/g in V-dust samples, ranging from 30 to 246 ng/g. The median concentration of EH-TBB was 31 ng/g in F-dust and 29 ng/g in V-dust; the concentration ranged from <LOQ to 24,800 ng/g in F-dust and <LOQ to 39 ng/g in V-dust. It should be noted that the F-dust samples 4 and 10 had an exceptionally high concentration of BEH-TEBP and ETHBB respectively, which resulted in the wider concentration ranges. This could be due to the dust sample containing small particles from products which contain these compounds. The analysis of household products could provide more information on the BFR formulations present in these products. McGrath et al. (2018) reported EH-TBB concentration ranges up to 370 ng/g (median of 19 ng/g) for Australian house dust, and BEH-TEBP concentrations up to 130 ng/g, although levels were indicative only. EH-TBB and BEH-TEBP contributed to almost 50% of the total BFR concentration profile in the cat hair, with median concentrations of 3.3 ng/g for ETHBB and 8.3 ng/g for BEH-TEBP. The greater relative abundance of the two alt-BFRs indicates that cats may be in close contact with sources where these contaminants may migrate from the products to the hair. EH-TBB and BEH-TEBP are for example used in PUF and mattresses (Knudsen et al., 2016). The BFR profile, excluding BDE209 (Fig. 1C), show comparable profiles for cat hair and F-dust. The ratio of EH-TBB/BEH-TEBP was similar in all sample matrices (0.4 to 0.7) which is much lower than the ratio previously reported in FM 550 (Stapleton et al., 2014). This suggests that other sources in the home may also be contributing to levels of BEH-TEBP found in dust because degradation of EH-TBB is unlikely. BEH-TEBP is the primary ingredient in a flame retardant mixture known as Uniplex FRP-45, which is used in cable and wires, adhesives, coatings, films and coated fabrics (Silva et al., 2016). Animal studies have shown that EH-TBB and BEH-TEBP absorb to skin and EH-TBB was more permeable (Knudsen et al., 2016). Skin and hair may act as a lipophilic “trap” and given the highly lipophilic nature of EH-TBB and BEH-

TEBP, diffusion into the skin may be significant. For absorption, chemicals would have to partition from the dust to the skin if dust is in contact with skin. Dermal absorption rates for cats and toddlers is of particular importance because of the increased surface area to volume ratio compared to adults.

3.2. Organophosphorus flame retardants

The OPFR profiles for the different matrices with detection frequencies, mean, median, concentration ranges, and standard deviation for the individual OPFRs are shown in Fig. 2. The OPFRs analysed in this study were detected in more than 90% of the samples, except for TNBP and TIPPP. These results are the first to report on the occurrence of chloroalkyl (Cl-OPFR), alkyl (alkyl-OPFRs), and aryl (aryl-OPFRs) OPFRs in the South African indoor environment. As shown in Fig. 2A, TCIPP was the dominant OPFR congener in F-dust, contributing to 42% to the OPFR congener profile. The V-dust shows approximately equal contributions of TCIPP and TBOEP, contributing with 34% and 33%, respectively to the OPFR congener pattern. The cat hair samples present a different profile, with TBOEP (44%) as the dominant congener followed by TCIPP (30%). The median concentrations of Σ_{10} OPFRs were 44,800 ng/g in F-dust (ranging from 7,740 to 183,000 ng/g) compared to 19,800 ng/g in the V-dust (ranging from 6,070 to 156,000 ng/g), and were not significantly different ($p > 0.05$). Similar to previous studies, comparable results were obtained from the two dust sampling methods (Fan et al., 2014). Dust from household vacuum cleaners may be an economical alternative to sophisticated dust sampling for OPFR analysis. The median Σ_{10} OPFRs in cat hair was 865 ng/g and levels ranged from 483 to 1,230 ng/g. To our knowledge, no studies have been published on the analysis of OPFRs in pet cat hair. Recent results on the analysis of organic pollutants in dog hair reported that TPHP, TCIPP, and TBOEP were the most abundant compounds (González-Gómez et al., 2018). Henríquez-Hernández et al. (2017) reported high detection frequencies for TCIPP, TBOEP, TCEP, EHDPP, and TPHP in cat blood. TCIPP was also found to be one of the major OPFRs found in human hair from China (M.-J. He et al., 2018; Li et al., 2016). When comparing the three main OPFR groups, Cl-OPFR, alkyl-OPFRs,

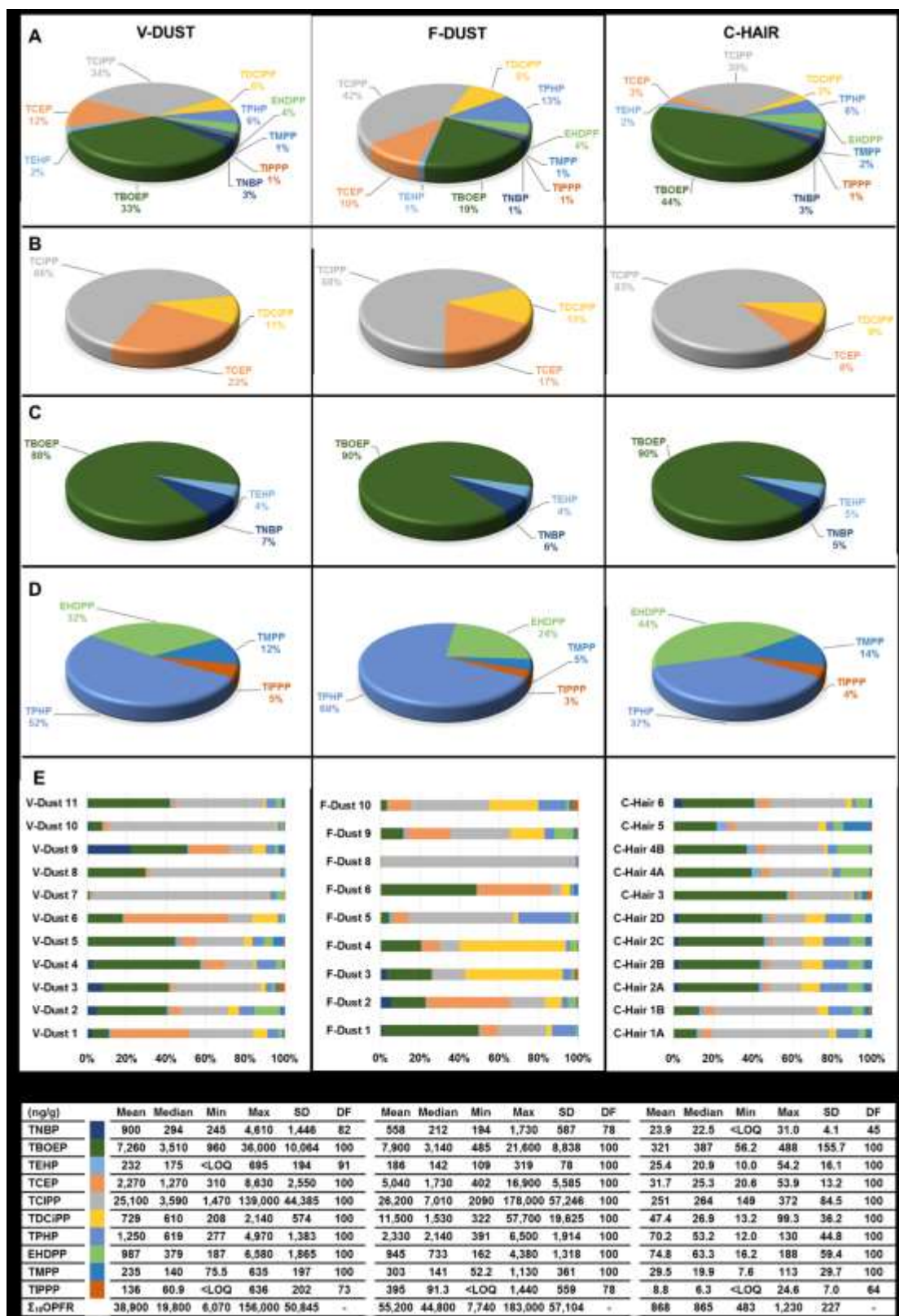


Fig. 2. Comparison of congener profiles of (A) the OPFRs in V-dust (n = 11), F-dust (n = 9) and cat hair (n = 11) samples, (B) the Cl-OPFRs, (C) the alkyl-OPFRs and (D) the aryl-OPFRs. (E) Relative abundances (%) of the OPFRs in the individual V-dust, F-dust and cat hair samples. (F) Summary of the mean, median, concentration range (ng/g), standard deviation (SD) and detection frequency (DF %) for the ten OPFRs.

and aryl-OPFRs, the Cl-OPFRs dominate the profile in dust samples and the alkyl-OPFRs in cat hair. Previous studies have shown that there is a stronger correlation for alkyl-OPFRs between human hair and air than for dust (Kucharska et al., 2015). The dominance of alkyl-OPFRs in the hair might support the finding that indoor dust partly contributes to the pattern observed in the hair.

The Cl-OPFR profiles, comprising TCEP, TCIPP, and TDCIPP, were dominated by TCIPP for the dust and hair matrices (Fig. 2B). The median concentrations of TCIPP, TCEP and TDCIPP in V-dust were 3,590 ng/g, 1,270 ng/g and 610 ng/g and in F-dust 7,010 ng/g, 1,730 ng/g and 1,530 ng/g. The dust matrices show similar patterns for TCIPP, TCEP, and TDCIPP with 66%, 23% and 11% for V-dust and 68%, 17% and 15% in F-dust. A recent study by Shoeib et al. (2019) reported twice as high median Cl-OPFR concentrations (TCIPP = 8,800 ng/g, TCEP = 2600 ng/g and TDCIPP = 2000 ng/g) in dust samples from Vancouver, Canada, collected from vacuum cleaner bags, the pattern (66%, 19% and 15%) was similar to that found in this study. Contradictory to our study, TDCIPP was reported as the dominant Cl-OPFR in indoor dust from South Africa (Abafe and Martincigh, 2019). The median TCIPP concentration in the cat hair samples was 264 ng/g hair and ranged from 149 to 372 ng/g. TCEP and TDCIPP contributed only 17% to the Cl-OPFR profile in the cat hair samples. Cl-OPFRs are mainly used as FRs in flexible and rigid PUFs used in furniture, upholstery, plastic foams, resins, latex, adhesives, and coatings (van der Veen and de Boer, 2012; Wei et al., 2015). In our study, the concentrations of TCEP were lower than TCIPP in both matrices and the ratio TCEP:TCIPP was approximately 1:3 in dust and 1:10 in cat hair, which could most likely be due to increasing use of TCIPP and TDCIPP as a replacement of TCEP (IPCS, 1998).

As shown in Fig. 2C, the alkyl-OPFR congener profile consisting of TNBP, TBOEP, and TEHP was dominated by TBOEP in all matrices (~90%). TBOEP was detected in 100% of the samples and median concentrations in V-dust were 3,510 ng/g and 3,140 ng/g in F-dust. The TBOEP concentrations in our study was approximately 5-fold lower than recently reported values for freshly collected dust from Australia (15,000 ng/g) (C. He et al., 2018), and Brazil

(15,900 ng/g) (Cristale et al., 2018), and vacuum cleaner dust from Canada (23,000 ng/g), and Egypt (13,000 ng/g) (Shoeib et al., 2019). TBOEP was the dominant OPFR in dust, which is in contrast with our study. Regnery and Püttmann (2010) previously showed rapid photochemical degradation of TBOEP when exposed to direct sunlight. However, in the cat hair samples of our study, TBOEP was the dominant OPFR with concentrations ranging from 56.2 to 488 ng/g (median 387 ng/g). A possible explanation for this could be that cats may be in direct contact with a possible source, as TBOEP is used in floor polishing products, as plasticizer in rubber and plastics (van der Veen and de Boer, 2012). The TBOEP concentration in the cat hair was comparable to levels previously reported in hair from children (Kucharska et al., 2015). TNBP and TEHP, which are mainly used as plasticizers but also as FRs (Dodson et al., 2012), had median concentrations of 294 and 175 ng/g in V-dust, 212 and 142 ng/g in F-dust and 22.5 and 20.9 ng/g in cat hair, respectively.

The aryl-OPFR congeners constitute ~10% of the total OPFRs in dust and 22% in the cat hair samples. As shown in Fig. 2D, the aryl-OPFR profile was dominated by TPHP (69% in F-dust and 52% in V-dust) in the dust samples and by EHDPP in the cat hair samples. TPHP is an effective additive FR in many polymers and is used in combination with halogenated and non-halogenated FR mixtures in FM 550 (Stapleton et al., 2009; van der Veen and de Boer, 2012). The median TPHP concentrations were 619 ng/g and 2,140 ng/g in V-dust and F-dust, respectively. The median concentration found in our study was lower than the levels reported for freshly collected dust from the UK (3,300 ng/g) (Brommer and Harrad, 2015) and Brazil (3,900 ng/g) (Cristale et al., 2018). The median EHDDP concentration in cat hair was 53.2 ng/g.

A comparison of median OPFR concentrations from this study with those previously reported for house dust is presented in Fig. S3. The variations in OPFR concentrations between the different studies and countries might be influenced by fire safety regulations, restrictions on the use of specific chemicals as FRs and the import and export of consumer products. The irregular OPFR profiles observed between the dust studies suggest that not only regional

differences in the use of OPFRs or mixtures for these compounds but also (seasonal) temperature changes affect the congener patterns and concentrations (Cao et al., 2014). The climate in South Africa is classified as semi-arid. It has a considerable variation which ranges from Mediterranean in the South West, subtropical in the North East, and semi-arid in the central and North West of the country. Pretoria has a subtropical climate with short cool to cold, dry winters and long humid and hot rainy summers. FRs have different partition characteristics between air, dust, and hair and compounds with higher vapor pressures are more sensitive to temperature changes and photochemical degradation. Temperature could influence the emission of FRs from the products and the partitioning of FRs between air and dust and hair, and the residence of FRs in the indoor environment could also be influenced by ventilation especially in warmer seasons.

3.3 Implications

No information could be sourced on local production of FRs, and we can therefore not provide a full description of the use of FRs, specifically on OPFRs. Recent studies in indoor dust, leachate, and sediment from landfill sites in South Africa also reported high concentrations of Cl-OPFRs, TBOEP was not included in the analysis (Abafe and Martincigh, 2019; Sibiyi et al., 2019). The high concentrations of Cl-OPFRs in indoor dust and landfill sites could indicate that imported consumer products could be an important source for these compounds. The Department of Environmental Affairs is involved in implementing measures to restrict the production and use of listed pesticides in order to fulfill its SC commitments. Based on the information provided in the national implementation plan (accessed through <http://chm.pops.int/>) there are no immediate actions taken for FRs. Although many of the OPFRs are used in textile, foams and insulation materials, a recent study suggested that handheld electronic devices may also be sources of OPFRs (Yang et al., 2019). This also raises questions about these compounds when they are being re-introduced into recycled products. Given the high levels of OPFRs found, substantially higher than the BFR levels, it may be wise for South Africa authorities not only to follow the SC but also pay attention to the

OPFRs when reduction of indoor contamination is considered. The inclusion of samples from townships and informal settlements should provide a more comprehensive demographic representation of the exposure to FRs in South Africa to provide concrete evidence to enforce regulations.

3.4. Human exposure to house dust

The preliminary estimations of the exposure to BFRs and OPFRs through dust ingestion (assuming 100% absorption from the ingested dust) were calculated for adults and toddlers using the median and 95th percentile concentrations (Table 1.). The assumption may introduce exposure estimate uncertainties, and more research is required to fully explain the toxicological effects of such exposure in both adults and toddlers. We calculated the expected daily intake based on mean body weights of 11.4 kg for children between the ages of 1 and 2 years and 80 kg for adults, and average dust ingestion rates (DIR) of 50 mg/day for toddlers and 20 mg/day for adults and high DIR of 100 mg/day and 60 mg/day for the respective groups as recommended in the Environmental Protection Agency (EPA) exposure factor handbook (USEPA, 2011). Due to the relative small sample size, the results should be seen as indicative only, showing average and worst-case scenario exposure estimations from dust ingestion. The exposure estimate of most of the FRs included in this study was lower than their respective reference doses (RfDs). The human exposure (adults and toddlers) through mean dust ingestion ranged from 0.2 to 11.4 ng/kg bw/day for BDE209, from 0.008 to 44 ng/kg bw/day for EH-TBB and 0.02 to 7.2 ng/kg bw/day for BEH-TEBP. The mean dust ingestion scenarios for the OPFRs show exposures ranging from 2.6 to 46 ng/kg bw/day for TCEP, 5.6 to 98 ng/kg bw/day for TBOEP, 7.4 to 131 ng/kg bw/day for TDCIPP and 35 to 618 ng/kg bw/day for TCIPP. The high ingestion exposure estimate for TCIPP (the major FR in the dust) ranged up to 1,240 ng/kg bw/day for toddlers, which were only 8 times lower than the RfD. The high ingestion exposure estimate for TCEP, TDCIPP, and TBOEP were approximately 80-fold lower than their respective RfDs for toddlers. TCIPP, TDCPP, and TBOEP have been suspected to be carcinogenic and neurotoxic effects have been observed for TCEP, TNBP,

Table 1. Exposure estimation of the median and high (95th percentile) dust content (ng/kg bw/day) of flame retardants via South African indoor dust ingestion (mean and high dust intake) for adults and toddlers, and reference doses (RfD) (ng/kg bw/day).

Compound	Toddlers				Adults				RfD
	Mean ingestion 50 mg/day		High ingestion 100 mg/day		Mean ingestion 20 mg/day		High ingestion 60 mg/day		
	Median estimate	High estimate	Median estimate	High estimate	Median estimate	High estimate	Median estimate	High estimate	
	BDE209	2.6	11.4	5.2	23	0.2	0.7	0.5	
Σ₈PBDE	3.0	12	6.0	23	0.2	0.7	0.5	2.0	
EH-TBB	0.1	44	0.3	89	0.008	2.5	0.02	7.6	20,000 ^b
BEH-TEBP	0.3	7.2	0.7	14	0.02	0.4	0.06	1.2	20,000 ^b
ΣBFR	3.8	70	7.6	139	0.2	4.0	0.7	12	
TNBP	1.3	10.8	2.5	22	0.07	0.6	0.2	1.8	10,000 ^a
TCEP	7.2	46	14	91	0.4	2.6	1.2	7.8	7,000 ^a
TCIPP	25	618	50	1,240	1.4	35	4.3	106	10,000 ^a
TDCIPP	3.2	131	6.4	261	0.2	7.4	0.6	22	20,000 ^a
TBOEP	15	98	29	196	0.8	5.6	2.5	17	15,000 ^b
TPHP	4.5	22	9.0	44	0.3	1.3	0.8	3.8	70,000 ^b
EHDPP	1.8	20	3.5	39	0.1	1.1	0.3	3.4	600,000 ^c
TEHP	0.8	2.1	1.5	4.1	0.04	0.1	0.1	0.4	100,000 ^a
TMPP	0.6	2.9	1.2	5.9	0.04	0.2	0.1	0.5	20,000 ^a
TIPPP	0.3	4.8	0.7	9.5	0.02	0.3	0.06	0.8	
Σ₃Alkyl- OPFR	17	101	35	201	1.0	5.7	3.0	17	
Σ₃Cl-OPFR	55	629	110	1,260	3.1	36	9.4	108	
Σ₄Aryl-OPFR	8.6	42	17	84	0.5	2.4	1.5	7.2	
Σ₁₀OPFR	89	689	178	1,380	5.1	39	15	118	

^aData from USEPA (2017)

^bData from Ali et al. (2013)

^cData from C. He et al. (2018)

and TPHP (Wei et al., 2015). The ubiquitous occurrence of these OPFRs in the indoor environment may pose a threat to human health. In addition, several studies also reported adverse effects in lab animals (Van den Eede et al., 2011). To estimate the ingestion exposure for cats, an average body weight of 4.3 kg was used, with similar ingestion rate as toddlers. The ingestion exposure estimate for TCIPP ranged from 1,640 to 3,270 ng/kg bw/day for cats. Although there is undoubtedly a high level of uncertainty associated with the exposure estimate for cats, this provides an indication of the probable exposure range. The estimated exposures via dust ingestion for cats could be up to three times higher than estimated for toddlers, considering that the dust ingestion rate for cats is unknown and could be vastly underestimated. The grooming behaviour of cats might increase their ingestion as well. Cat

hair is exposed to the environment and constantly accumulate contaminants from indoor air and dust. The toxicity of most FRs is not completely understood and exposure to FR mixtures may result in dose-additive effects. The results obtained from the hair samples indicate that cats are directly exposed to mixtures of FRs. In addition to inhalation and dermal contact, the hand-to-mouth activity of toddlers is an important route of exposure to FRs accumulated on dust particles. This activity is most often observed in toddlers, and cat's meticulous grooming behavior.

4. Conclusion

This study presents concentrations of BFRs and OPFRs in indoor dust and cat hair from South Africa. In both matrices the OPFR concentrations were considerably higher than those of the BFRs. Compared to previous studies, low levels for PBDEs were found in indoor dust, with BDE209 as the dominant congener. The two alt-BFRs, BEH-TEBP and EH-TBB showed notable contributions to the BFR profile in cat hair. OPFR profiles in the indoor dust were dominated by the CI-OPFRs, with TCIPP as the major congener. Although the CI-OPFRs were regularly detected in the cat hair samples, the alkyl-OPFRs dominated the profile with higher contributions from TBOEP. For the first time, we show that CI-OPFRs, alkyl-OPFRs, and aryl-OPFRs are ubiquitous in the South African indoor environment. The hand-to-mouth contact of toddlers is an important route of exposure to currently used FRs accumulated on dust particles. The presence of BFRs and OPFRs in indoor dust and cat hair suggests that children may have greater exposure to FRs than adults. To date, there is limited data on OPFRs, especially the CI-OPFRs, in the South African indoor environment and more research is needed to identify sources in order to understand indoor exposures and fate of FRs.

Although the small number of samples analysed in the current study may limit conclusions, the quantitative results can represent an important baseline study for developing larger studies to assess exposure estimates for the volatile FRs, such as TCIPP. The differences in FR congener profiles between dust and cat hair may be of particular importance considering that dust and soil-ingestion rates are commonly used for risk assessments. Cat hair provides

specific information on continuous indoor exposure and might be seen as a non-invasive passive sampler to chronic exposure of FRs in the indoor environment. Although international restrictions are set for the production and use of some BFRs, more attention should be paid to OPFRs when measures to reduce indoor contamination is considered.

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ASSOCIATED CONTENT

Supplementary Material:

Detailed estimation of measurement uncertainty, Tables S1-S9, and Fig. S1-S3

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