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DOI:
10.1016/j.chemosphere.2017.11.147

Document Version
Peer reviewed version

Citation for published version (Harvard):
Al-Omran, LS & Harrad, S 2018, 'Within-room and within-home spatial and temporal variability in concentrations of legacy and “novel” brominated flame retardants in indoor dust', *Chemosphere*, vol. 193, pp. 1105-1112. https://doi.org/10.1016/j.chemosphere.2017.11.147

WITHIN-ROOM AND WITHIN-HOME SPATIAL AND TEMPORAL VARIABILITY IN CONCENTRATIONS OF LEGACY AND "NOVEL" BROMINATED FLAME RETARDANTS IN INDOOR DUST

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ABSTRACT

To test the hypothesis that assessments of human exposure to PBDEs and NBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) via dust ingestion should take into account spatial and temporal variability in dust contamination; 238 dust samples were collected from nine different rooms within three homes in Birmingham UK. In each room, three different dust samples were taken at monthly intervals for nine months, one sample from elevated surfaces and two samples from two different floor areas. Substantial within-room and within-home spatial variability in BFR concentrations was apparent between two floor areas and between different rooms due to the varying distances of sampled surfaces from potential BFR sources. With the exception of DBDPE, BFR concentrations in elevated surface dust exceeded significantly ($p < 0.05$) those in floor dust from the same rooms. Considerable within-room and within-home temporal variability in BFR concentrations was also apparent over a nine month sampling period. This is likely attributable to changes in room contents. The relative standard deviation of BFR concentrations observed in such temporal variation sample series exceeded those obtained from replicate analyses of SRM2585. Based on observed spatial and temporal variability, exposure estimates based on analysis of a single dust sample taken from one specific floor area at one specific point in time may not be entirely representative of human exposure in that room. Noticeable variability in BFR concentrations was also observed between colder and warmer seasons. In 13 out of 17 floor areas, concentrations of $\Sigma_8$tri-deca-BDEs were higher in colder seasons, while those of Σ_5NBFRs were higher in warmer seasons. Significant negative correlation was observed in three rooms between concentrations of BDE-99, $\Sigma_6$tri-hepta-BDEs and BEH-TEBP and dust loading (g/m^2), suggesting "dilution" occurs at higher dust loadings.

KEYWORDS: PBDEs; NBFRs; Indoor dust; Spatial and temporal variability; Human exposure.

1. INTRODUCTION

The toxicity of some brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) and "novel" brominated flame retardants (NBFRs) has led to concern about human exposure (USEPA, 2006; 2008a; 2008b; 2008c; NICNAS, 2007; Noyes et al., 2010; Chevrier et al., 2010; EFSA, 2012; European Commission, 2012; Johnson et al., 2013; Li et al., 2014; Mankidy et al., 2014; Mariani, et al., 2015). Moreover, several studies show significant positive correlation between concentrations of BFRs in indoor dust and human tissues such as human milk (Wu et al., 2007, Toms et al., 2009; Coakley et al., 2013), human hair (Kang et al., 2011; Tang et al., 2013) and serum samples (Johnson et al., 2010; Stapleton et al., 2012); suggesting that indoor dust ingestion is a major pathway of exposure to such chemicals, particularly for young children due to their hand-to-mouth behaviour (Stapleton et al., 2005; Wang et al., 2010; Hoffman et al., 2015)

Assessments of human exposure to chemical pollutants via indoor dust ingestion require knowledge about locations where people spend their time and thus come into contact with such pollutants. However, few studies have investigated within-room (dust samples taken at the same time from different locations within the same room) and within-home (dust samples taken at the same time from different rooms within the same home) spatial variability. From five separate floor areas within the same room in five dwellings, Harrad et al., (2008a) found substantial within-room spatial variability in BFR concentrations. The relative standard deviations (RSD) for Σtri-hexa-BDE ranged between 28% and 80%. Another study of HBCDs revealed little spatial variability in some rooms (RSD = 7% - 8%), while others displayed large variability (RSD = 19% - 100%) (Harrad et al., 2009). More recently, Muenhor and Harrad, (2012) also examined within-room spatial variability in PBDE contamination of dust from separate rooms, finding that the PBDE concentrations in an area close to putative PBDEs sources (TV, laptop, and sofa) exceeded significantly those in an area 2 m away from the same sources. This is considered to reflect the relationship between contamination and potential emission sources. In terms of within-room vertical variability in dust contamination, our previous studies (Al-Omran and Harrad 2016a; 2016b) revealed concentrations of several BFRs to be significantly higher ($p < 0.05$) in dust collected from elevated surfaces (ESD) like chairs and tables than in floor dust (FD) from the same rooms. This is likely due to differences

in the particle size distribution in ESD and FD. Higher proportions of finer particle sizes were found in ESD with higher concentrations of BFRs detected in the finer particle sizes. Another study (Cequier et al., 2014) reported that median concentrations of BFRs in elevated surface dust exceeded those in floor dust. Within-home spatial variability has also been reported in a small number of studies. Concentrations of Penta- and Deca-BDE congeners were, on average, significantly higher in the living room than those in the bedroom (Allen et al., 2008), while average concentrations of ΣPBDE in the bedroom (430±180 ng/g) exceeded substantially those in another bedroom (170±340 ng/g) from the same home (Muenhor and Harrad, 2012). However, recent studies (Venier et al., 2016; Kuang et al., 2016) found no statistically significant differences in BFR concentrations in dust from the living room and bedroom.

To date, only four studies (Allen et al., 2008; Harrad et al., 2008a; 2009; Muenhor and Harrad, 2012) have investigated within-room and within-home temporal variations in concentrations of BFRs; collectively suggesting that most temporal variability is attributable to changes in room contents of putative BFR sources. Over a 9-10 month monitoring period, a substantial month-to-month rise in BDE-209 contamination of dust was found following fitting of a new fabric padded bed and polyester fabric blinds (Harrad et al., 2008a). In a similar vein, Muenhor and Harrad (2012) reported substantial within room temporal variability in ΣPBDE concentrations in monthly samples collected over an 8 month sampling period as a consequence of the introduction and removal of putative sources such as a TV and a bed. The RSD values for ΣPBDEs were between 15% and 200% (Muenhor and Harrad, 2012). Another study (Allen et al., 2008) reported no significant difference between Penta- and Deca-BDE concentrations in house dust in 20 homes collected 8 months apart, attributing this to minimal changes in room furnishings between the sampling periods.

Noticeable seasonal variability in BFR concentrations has also been observed between colder and warmer months or between different seasons. Out of fourteen floor areas, while in seven sampled areas, average concentrations of ΣPBDEs in the colder months was higher than in warmer months, the reverse was observed in the other seven areas (Muenhor and Harrad 2012). According to Muenhor and Harrad (2012), the lack of clear seasonal variation is attributable to the greater volatile emissions of BFRs in warmer months being offset by higher ventilation during the same period. Elsewhere, Yu et al., (2012) noted that PBDE concentrations were summer > winter > spring > autumn; while over a 10 months monitoring

period, Cao et al., (2014) reported maximum: minimum concentration ratios were between 2 and 10, underlining the importance of the time of dust collection for exposure assessments.

Despite a lack of data on how dust ingestion rates vary with dust loading, it is plausible that higher dust loadings will lead to increased dust ingestion rates. While this would suggest higher exposures in dustier rooms, it is also plausible that higher dust loadings will dilute BFR concentrations in dust, and it is not clear how these two competing factors will impact on exposure. To date, while three studies (Harrad et al., 2008a; 2009; Muenhor and Harrad 2012) have examined the evidence for such "dilution" of BFR concentrations in the dust at higher dust loadings; their findings are inconclusive. It has been hypothesised that, under certain conditions, "dilution" of BFR concentrations will occur at greater dust loadings. These conditions are: (a) BFR emissions remain constant through the monitoring period, and (b) the source of the dust and BFRs are independent – i.e. the main source of the BFR to dust is not direct abrasion of fibres or particles from a source material (Harrad et al., 2008a; 2009).

Against this background; the location of the sample, time of sampling, and surface loading are potentially important factors affecting the levels of pollutants in indoor dust. This study therefore aims to test the hypothesis that assessments of human exposure to PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and their potential replacement NBFRs{(pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenylethane (DBDPE)}via dust ingestion, are affected by spatial, temporal and seasonal (warmer and colder months) variability in dust contamination. We furthermore investigate the relationship between BFR concentrations (ng/g) and BFR dust loading (g/m^2). To the best of our knowledge, this study is the first to examine spatial and temporal variability in concentrations of PBEB, EH-TBB, BEH-TEBP and BTBPE in indoor dust.

2. MATERIALS AND METHODS

2.1. Sampling and sample preparation

From three homes (H1, H2, and H3) in Birmingham, UK, 238 indoor dust samples were collected at monthly intervals from three different rooms (R1 = living room, R2 = adult bedroom, and R3 = study or child's bedroom in H3). From each room, two dust samples were obtained from two different floor areas F1 and F2, following the sampling protocol described

elsewhere (Harrad et al., 2008a), with an additional dust sample collected from the elevated surfaces (ES), such as sofas, tables, shelves, and large articles present on tables and shelves (Al-Omran and Harrad 2016a, 2016b). Dust was not collected from under furniture or from highly elevated surfaces with which human contact is rare, such as the tops of wardrobes. For calculation of dust loadings, the mass of floor dust collected per unit surface area sampled was recorded. Sampling was conducted for nine months between May 2013 and March 2014, with no samples collected in July and August 2013. Information on the potential influences on BFR contamination such as: the number and type of putative sources like electronic devices, foam-filled furniture and floor material, ventilation system, and house cleaning method was recorded. Because of the low dust loading on elevated surfaces, 2-3 dust samples from elevated surfaces were combined into one sample for analysis, yielding a total of 193 samples. Figures S1, S2, and S3 illustrate the room contents of Home 1, Home 2 and Home 3 respectively, showing both floor dust sample areas (F1 and F2) and elevated surface dust sample locations (ES).

2.2. Analytical methods

PBDEs and NBFRs in dust samples were analysed following the same extraction and clean-up methods as reported in our previous study (Al-Omran and Harrad, 2017). Briefly, accurately weighted aliquots of dust (~ 0.1 g) were spiked with a mixture of internal standards (20 ng of BDE-77, BDE-128, ^{13}CBTBPE, ^{13}CBEH-TEBP, and 40 ng of ^{13}CBDE-209) and extracted with *n*-hexane: acetone (3:1 v/v) using an ultrasonic extraction method. Concentrated crude sample extracts were purified involving two steps. In the first step, the extract was fractionated into two fractions (Fraction 1 and Fraction 2) using a 2 g Florisil SPE cartridge. Fraction 1 (containing PBDEs, DBDPE and PBEB) was eluted with *n*- hexane and fraction 2 (containing the rest of the targeted NBFRs) was eluted with ethyl acetate. A second purification steps were conducted on acid silica (44% w/w) for fraction 1 and aminopropyl functionalised silica for fraction 2. The both fractions were eluted with *n*-hexane/DCM (1:1, v/v) and combined then evaporated to incipient dryness, before resolubilisation in 100 µL of iso-octane containing PCB-129 at 250 pg/µL ready for GC/MS analysis. Target PBDEs and NBFRs were quantified using a gas chromatograph (GC) (Trace 1310 Gas Chromatograph) coupled to a mass spectrometer (MS) (ISQ Quadrupole MS); both (Thermo Fisher Scientific, USA). The GC was equipped with a programmable temperature vaporiser (PTV) injector and fitted with a capillary fused silica column (RESTEK, USA, 15 m x 0.25 mm inner diameter,

0.25 μm film thickness). The MS was operated in the electron capture negative ion (ECNI) mode.

2.3 Quality assurance/Quality control

To avoid any degradation that may occur via exposure to light, glassware and the turbo vap instrument were covered with aluminium foil. To assess any possible contamination during sample preparation and analysis method, one laboratory blank was processed in parallel with every set of 6 dust samples and one quality control sample (NIST SRM 2585, organics in indoor dust) was processed with every 20 real dust samples. Limits of detection (LOD) were estimated based on a signal to noise ratio 3:1 and limits of quantification (LOQ) were estimated based on signal to noise ratio 10:1. Field blanks (n = 9) were also conducted to assess any contamination contributed as a result of sampling, transport and storage of samples, in addition to any introduced as a result of extraction and clean-up. The average of internal standard recoveries in dust samples ranged from 78-90%.

2.4. Statistical analysis

Statistical analysis of our data was performed using Microsoft Excel 2013 and IBM SPSS statistics software (V. 20). Within-room spatial variability in concentrations of PBDEs and NBFRs was evaluated using a paired t-test applied to samples: a) taken from two different floor areas; and b) taken from elevated surfaces and floors. Within- home spatial variability was tested on samples taken from three different rooms in the same home via a repeated measures ANOVA test. For the purposes of statistical evaluation, all concentrations below LOQ were assigned a value of 0.5 LOQ. A p value < 0.05 was taken to indicate statistical significance. A Pearson correlation was used to test the relationship between concentrations of BFRs (ng/g) and dust loading (g/m^2).

3. RESULTS AND DISCUSSION

3.1. Concentrations of PBDEs and NBFRs in indoor dust samples

In the three investigated homes, the detection frequencies of BDE-209 and BEH-TEBP were 100%, followed by DBDPE with 100%, 97% and 94% in Home 1, Home 2 and Home 3 respectively. Only those BFRs ($\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs) displaying detection frequencies ≥ 90% were taken into account for statistical summary. $\Sigma_7$tri-hepta-BDEs refers to the summation of seven congeners (BDE-28, BDE-47,

BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183), Σ_5NBFRs represent the sum of PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE with ΣBFRs equalling the sum of $\Sigma_7$tri-hepta-BDEs, BDE-209 and Σ_5NBFRs. Among all target BFRs, BDE-209 was predominant, making average percentage contributions to ΣBFRs of 92.3%, 90.9%, and 62.8% in H1, H2 and H3 respectively. The high relative abundance of BDE-209 is not surprising, as Deca-BDE was used extensively in the UK (Harrad et al., 2008a: 2008b). The next most abundant was Σ_5NBFRs making average percentage contributions of 6.6%, 7.8% and 36.7% in H1, H2 and H3 respectively. $\Sigma_7$tri-hepta-BDEs made the lowest average percentage contributions of our target BFRs; specifically 1.1%, 1.3% and 0.5% of ΣBFRs in H1, H2 and H3 respectively. Table 1 lists average concentrations and relative standard deviation values (RSD) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in dust samples from two floor areas (F1 and F2) and elevated surface dust (ES) from the three rooms (R1, R2 and R3) of three homes (H1, H2 and H3) during a nine-month sampling period. Figure S4 displays distribution profiles of our target compounds.

3.2 Within-room spatial variation of PBDEs and NBFRs in floor dust from two different areas.

In dust samples taken from different floor areas within the same room in nine rooms, no significant difference in BDE-209 concentrations was observed, while $\Sigma_7$tri-hepta-BDEs (in three rooms), BEH-TEBP (in one room) DBDPE and Σ_5NBFRs (in two rooms) were significantly ($p = < 0.05$) different between different floor areas. Where observed, such spatial variability in BFR concentrations is likely driven by varying distances from potential emission sources, which are influenced by room dimensions, For instance, in the bedroom of Home 1, concentrations of BEH-TEBP, DBDPE and consequently Σ_5NBFRs in samples from F1 exceeded significantly those from F2, with p values of 0.012, 0.053 and 0.006 respectively. As shown in Figure S1 (H1R2), F1 is the rug area closest to the iron, foam chair, and the curtain, while F2 is the bare floor area located closest to the door and further away (≈ 3 m) from these potential emission sources. Figure 1 illustrates average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in floor areas F1 and F2 in the three rooms (R1, R2 and R3) of Home 1, Home 2 and Home 3, along with standard deviation (y error bar). Table S5 shows p values obtained from t-test comparison of concentrations of our target compounds in floor dust samples within the same room. These data indicate that dust from a single area

within a given room will likely not provide a representative measure of contamination in the room overall.

3.3 Within-room spatial variation of PBDEs and NBFRs between floor and elevated surface dust

Taking all 9 investigated rooms together, concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and Σ_5NBFRs in elevated surface dust exceeded significantly ($p = < 0.001$) those in floor dust. The one exception to this is that concentrations of DBDPE in floor dust exceeded significantly ($p = 0.015$) those in elevated surfaces. On an individual room basis, concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE (in 7, 4, 5 and 4 of 9 rooms respectively) in dust samples from elevated surfaces exceeded significantly ($p < 0.05$) those from the floor in the same room. Figure 2 illustrates average concentrations of the target BFRs in floor dust and elevated surface dust in the three different rooms (R1, R2 and R3) of Home 1, Home 2 and Home 3. Table S6 shows *p* values obtained from t-test comparison of concentrations of our target compounds between elevated surface dust and floor dust samples. These results indicate that both floor and elevated surface dust should be considered for human exposure assessment, particularly for adults who likely are in contact with elevated surfaces more than the floor.

3.4 Within-home spatial variation in concentrations of PBDEs and NBFRs

Among the nine rooms investigated, limited within-home variability in BFR concentrations between different rooms was observed, that is likely attributable to differences in the putative sources present in the rooms studied. In Home 1, only concentrations of BDE-209 in the bedroom (H1R2) exceeded significantly those in the living room (H1R1) with a *p* value of 0.010, while for other BFRs, no significant differences were found between different rooms. In Home 2, concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, and DBDPE displayed significant differences between different rooms. Concentrations of $\Sigma_7$tri-hepta-BDEs in the study (H2R3) exceeded significantly ($p = 0.050$) those in the living room (H2R1). In contrast, BDE-209 concentrations in the living room exceeded significantly ($p = 0.033$) those in the study, while BEH-TEBP and DBDPE concentrations in the study exceeded significantly those in the bedroom with *p* values of 0.041, 0.001 respectively. Meanwhile, in Home 3, significant differences were found between concentrations of BEH-TEBP in the two bedrooms and living room. BEH-TEBP concentrations in H3 fall in the order of: child's

bedroom > adult's bedroom > living room. The high levels in the bedrooms might be due to the new mattresses that may have been treated with BEH-TEBP. However, there is no obvious reason for the high concentrations of BEH-TEBP in the child's bedroom compared with adult's bedroom. Figure 3 illustrates within-home spatial variability in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and BEH-TEBP and DBDPE in the three investigated homes.

3.5 Temporal and seasonal variability in concentrations of BFRs in indoor dust.

The relative standard deviation of concentrations of individual BFRs in the 18 floor area samples taken in each room ranged between 4% and 159%, and in the corresponding 9 elevated surface dust samples ranged between 9% and 117%. In both instances, these RSD values exceeded those obtained from replicate analysis of SRM2585, which ranged from 9% to 14%. This observed temporal variation in BFR concentrations is likely attributable to concomitant changes in room contents with respect to putative sources of target BFRs. $\Sigma_7$tri-hepta-BDEs concentrations were associated with the presence/absence of electronic devices and old foam furniture, while those in BDE-209 were associated with carpets and fabric materials. BEH-TEBP variability was associated with new bedroom furnishings, while DBDPE temporal variability was not associated with any specific source. However, changes in room contents did not explain the gradual decline in concentrations of BEH-TEBP in the bedrooms of H3 over the first seven months of sampling. This might instead reflect gradual attainment of equilibrium between the gas phase and particulate phase of this BFR in indoor air. Figures S7, S8 and S9 illustrate the intra-room temporal variation in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE, and Σ_5NBFRs in dust from different floor areas (F1 and F2) from different rooms (R1, R2 and R3) during the nine monitored months in Home 1, Home 2 and Home 3 respectively. In addition, noticeable variation in maximum: minimum BFR levels were found depending on a given area, particularly for $\Sigma_7$tri-hepta-BDEs and DBDPE. The ratio of maximum: minimum concentrations of $\Sigma_7$tri-hepta-BDEs were 30, 24 and 21 in areas H1R2F1, H1R2F2 and H1R3F1 respectively, and for DBDPE were 28, 71, 61, 43 and 42 in areas H2R1F2, H3R1F1, H3R2F1, H3R3F1, and H3R3F2, respectively. Table S10 lists maximum: minimum concentration ratios of these compounds in floor areas.

Noticeable seasonal variability in BFR concentrations was also observed between colder and warmer seasons. In 13 out of 17 floor areas, average concentrations of $\Sigma_8$tri-deca-BDEs were

higher in colder seasons than warmer, while in the same number of floor locations, Σ_5NBFRs were higher in warmer seasons, with the exception of DBDPE. In general, average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and BEH-TEBP in elevated surface dust samples were higher in warmer seasons than in colder, while in floor dust, average concentrations of BDE-209 were comparable in both colder and warmer seasons. With the exception of $\Sigma_8$tri-deca-BDEs in two floor areas and Σ_5NBFRs in four floor areas, no significant differences in concentrations of these two groups were apparent between warmer and colder seasons. Higher concentrations in colder seasons were only observed for BDE-209 and DBDPE, which might be due to the low vapour pressure of these compounds which facilitate partitioning to indoor dust, which will be more favoured at lower temperatures.

3.6 The relationship between the BFR dust concentration and dust loading

To test the relationship between BFR dust concentration (ng/g) and dust loading (g/m^2), we used our data addressing temporal variability in BFR concentrations in dust from Home 1, Home 2, and Home 3. The Pearson correlation showed a significant negative correlation between the logarithms of BFR concentrations and dust loadings for Home 2 and Home 3 for BDE-99 (R = 0.675, p = 0.046) and $\Sigma_7$tri-hepta-BDEs (R = 0.760, p = 0.018) in H2R2F2 and for BEH-TEBP (R = 0.749, p = 0.020) in H3R2F2. In other words, in three out of seventeen individual floor areas, concentrations of lower brominated compounds (i.e. BDE-99 and $\Sigma_6$tri-hepta-BDEs) and BEH-TEBP decreased as dust loading increased. This implies that "dilution" has occurred in these rooms due to the high dust loading and indicates that the source of these compounds and of indoor dust are independent. However, in one sampled area, a positive correlation between DBDPE concentration and dust loading suggested the source(s) of both dust and DBDPE in that area to be the same, implying that DBDPE enters indoor dust via abrasion of fibres or particles from a putative source.

3.7 The impact of spatial and temporal variability on human exposure assessments

To evaluate the extent to which human exposure to our target contaminants via dust ingestion are affected by spatial variability, we compared the mean ± SD concentration in dust samples collected from: 1) different floor areas in the same room, 2) elevated surfaces and floor in the same room and 3) different rooms in the same home. As observed in Figure 1, substantial differences are apparent in concentrations of BFRs between the two floor areas (F1 and F2), particularly for $\Sigma_7$tri-hepta-BDEs and DBDPE. For example, in H2R2, concentrations of

$\Sigma_7$tri-hepta-BDEs in floor area F2 (average ± SD = 62 ± 17 ng/g) exceed substantially those in floor area F1 (average ± SD = 27 ± 17 ng/g). In this room, F1:F2 = 61:4 for one sampling event, implying that exposure assessment in that room could vary by a factor of 15 depending on the sampling area. In addition, substantial within-room spatial variability in BFR concentrations was observed between elevated surface dust and floor dust in the nine rooms studied (Figure 2). To illustrate, in H3R1, BEH-TEBP concentrations in elevated surface dust (average ± SD = 4187 ± 2004 ng/g) exceeded substantially those in floor dust (average ± SD = 1196 ± 301 ng/g), with ESD:FD ~5 during 1 sampling event. Moreover, BFR concentrations in separate rooms in the same house can differ quite markedly (Figure 3). For example, concentrations of BEH-TEBP in H3R3 (average ± SD = 3992 ± 1906 ng/g) exceeded those in H3R1 (average ± SD = 1811 ± 1498 ng/g). Due to this substantial within-room and within-home spatial variability, exposure estimates based on dust taken from one specific floor area, floor surface only or one room alone are subject to uncertainty.

To assess the extent to which temporal and seasonal variability may affect human exposure assessment, we compared the RSD values for selected BFRs and examined the extremes of exposure assessment using maximum: minimum concentration ratios for a given room. Our findings highlighted uncertainties in exposure assessments for BFRs based on a single dust sample taken from a given area at a given point in time. In Home 1, the highest RSD values of $\Sigma_7$tri-hepta-BDEs were 92%, 86% and 123%, observed in H1R2F1, H1R2F2 and H1R3F1 respectively. This implies that human exposure to $\Sigma_7$tri-hepta-BDEs via contact with dust in these areas would vary to the same extent. In addition, in these same floor areas, $\Sigma_7$tri-hepta-BDE maximum: minimum ratios were 30, 24, and 21 respectively, implying that exposure assessments could be underestimated or overestimated by factors of 30, 24, and 21 if by chance one sample was taken from these areas in the month recording the lowest concentration as opposed to the month when the highest concentration was recorded. The highest RSD value for BEH-TEBP (73%) was found in H1R1ES with the highest maximum: minimum ratio of 9.2 in H2R1F2. Moreover, considerable temporal variation in concentrations of DBDPE were found in the three homes studied, particularly in Home 3. The RSD values of DBDPE in H3R2F2 and H3R3F2 were the highest among all BFRs, with values of 138% and 159% respectively.

The considerable temporal and seasonal variability observed in this study of just 9 rooms indicates the uncertainty associated with basing exposure assessments via dust ingestion for BFRs based on a single grab sample taken from a given area at a given point in time.

4. CONCLUSIONS AND RECOMMENDATIONS

Substantial vertical spatial variations in BFR contamination indicate that both floor dust and elevated surface dust should be considered for human exposure assessments, particularly for adults who likely are in contact with elevated surfaces more than the floor. In addition, the appreciable horizontal variations in BFR concentrations in floor dust, indicate that floor dust samples should be taken from the most-frequented parts of the room in order to best reflect human exposure. Our findings reveal substantial variability in the concentrations of some BFRs during the sampling period. Temporal variations in BFR concentrations appear affected by the addition or removal of a potential emission source. Our findings highlight the uncertainty associated with assessments of exposure to BFRs based on a single dust sample taken from a given area at a given point in time.

ACKNOWLEDGEMENTS

The authors express their thanks to all the dust donors from Birmingham, UK. Layla Salih Al-Omran acknowledges gratefully the Iraqi government for a PhD Scholarship, the Iraqi Establishment of Martyrs for financial support and the Ministry of Higher Education and Scientific Research for administrative support.

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Table 1: Average concentrations (ng/g) and relative standard deviation (RSD) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the three rooms (R1, R2 and R3) over nine monitored months of three homes (H1, H2 and H3)

Sampling area	$\Sigma_7$tri-hepta-BDEs		BDE-209		BEH-TEBP		DBDPE		Σ_5NBFRs	
	Average	RSD	Average	RSD	Average	RSD	Average	RSD	Average	RSD
H1R1F1	21	44	2061	29	93	23	40	64	151	22
H1R1F2	18	35	1901	45	85	16	42	60	142	27
H1R1ES	70	28	3679	22	323	73	131	36	540	50
H1R2F1	23	92	3342	51	127	13	71	80	216	35
H1R2F2	34	86	2786	24	106	19	41	50	159	27
H1R2ES	128	31	6506	25	168	27	90	117	268	49
H1R3F1	22	123	2334	30	110	35	70	80	207	40
H1R3F2	17	50	2777	12	66	29	29	62	113	13
H1R3ES	79	48	6572	42	225	13	78	61	365	17
H2R1F1	31	36	3414	27	120	21	130	72	263	42
H2R1F2	30	31	3123	28	105	40	102	78	217	53
H2R1ES	111	26	7269	40	445	65	56	62	523	60
H2R2F1	27	64	2687	17	113	27	92	56	231	32
H2R2F2	62	28	2947	24	111	55	117	57	247	48
H2R2ES	83	35	6675	41	135	32	27	96	186	36
H2R3F1	48	29	2672	19	120	15	134	50	265	27
H2R3F2	36	34	2924	21	122	12	274	38	411	25
H2R3ES	126	31	4309	16	428	46	49	103	502	42
H3R1F1	33	38	5639	94	1371	40	163	104	1553	35
H3R1F2	30	61	4403	39	926	49	37	80	976	46
H3R1ES	64	55	3568	11	4187	48	11	91	4274	47
H3R2F1	18	71	4252	6	2486	35	95	138	2622	32
H3R2F2	36	54	4129	9	2362	50	69	78	2462	47
H3R2ES	83	87	8451	25	5397	34	45	40	5635	32
H3R3F1	37	43	4498	4	3046	33	109	112	3199	29
H3R3F2	25	36	4401	5	3044	32	116	159	3201	28
H3R3ES	57	23	7138	30	7049	9	48	82	7559	5

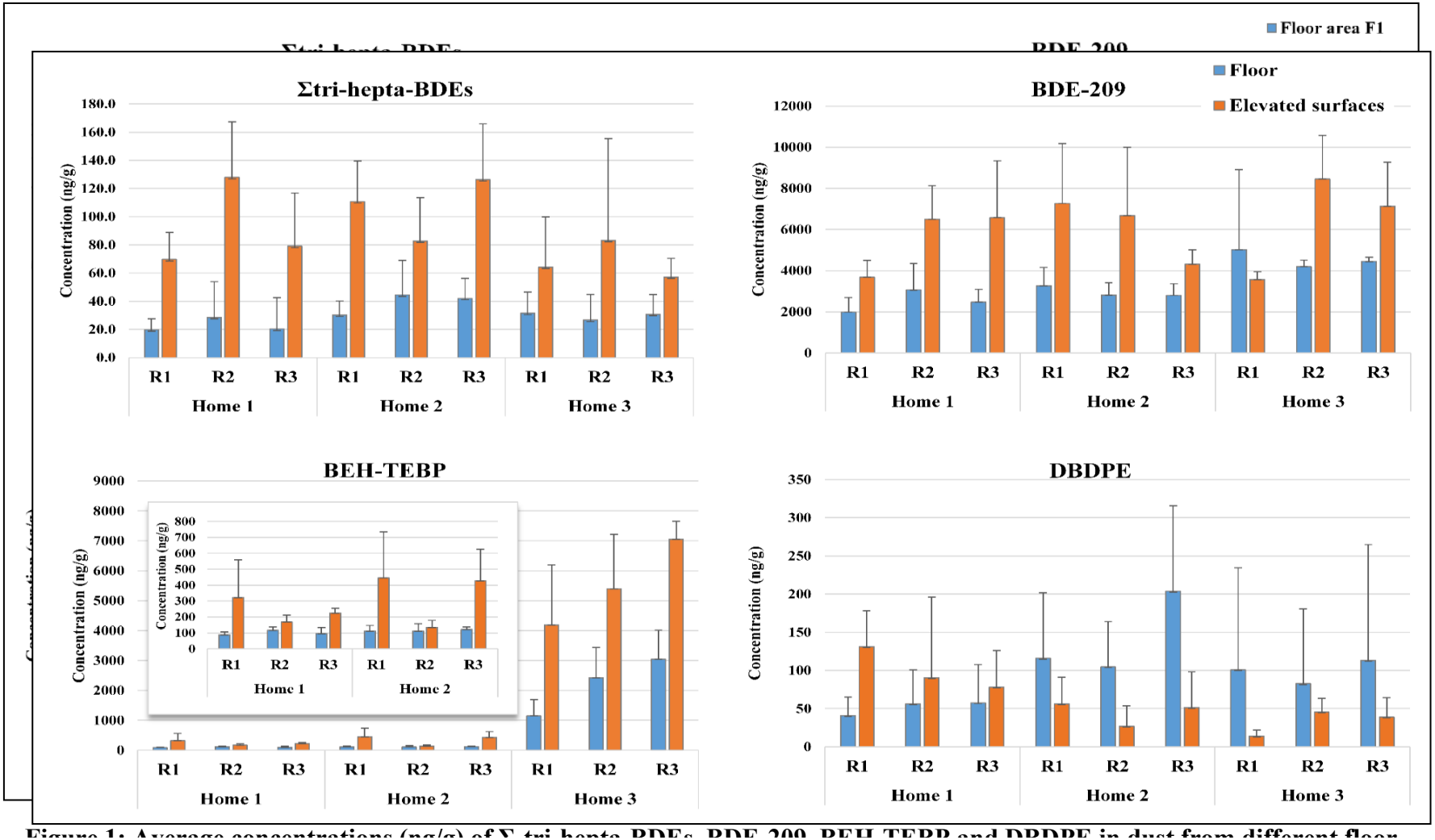

Figure 2: Average concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in floor dust and elevated surface dust from different rooms (R1 = Living room, R2= Bedroom, and R3 = Study, except in Home 3= Bedroom) in Home 1, Home 2 and Home 3

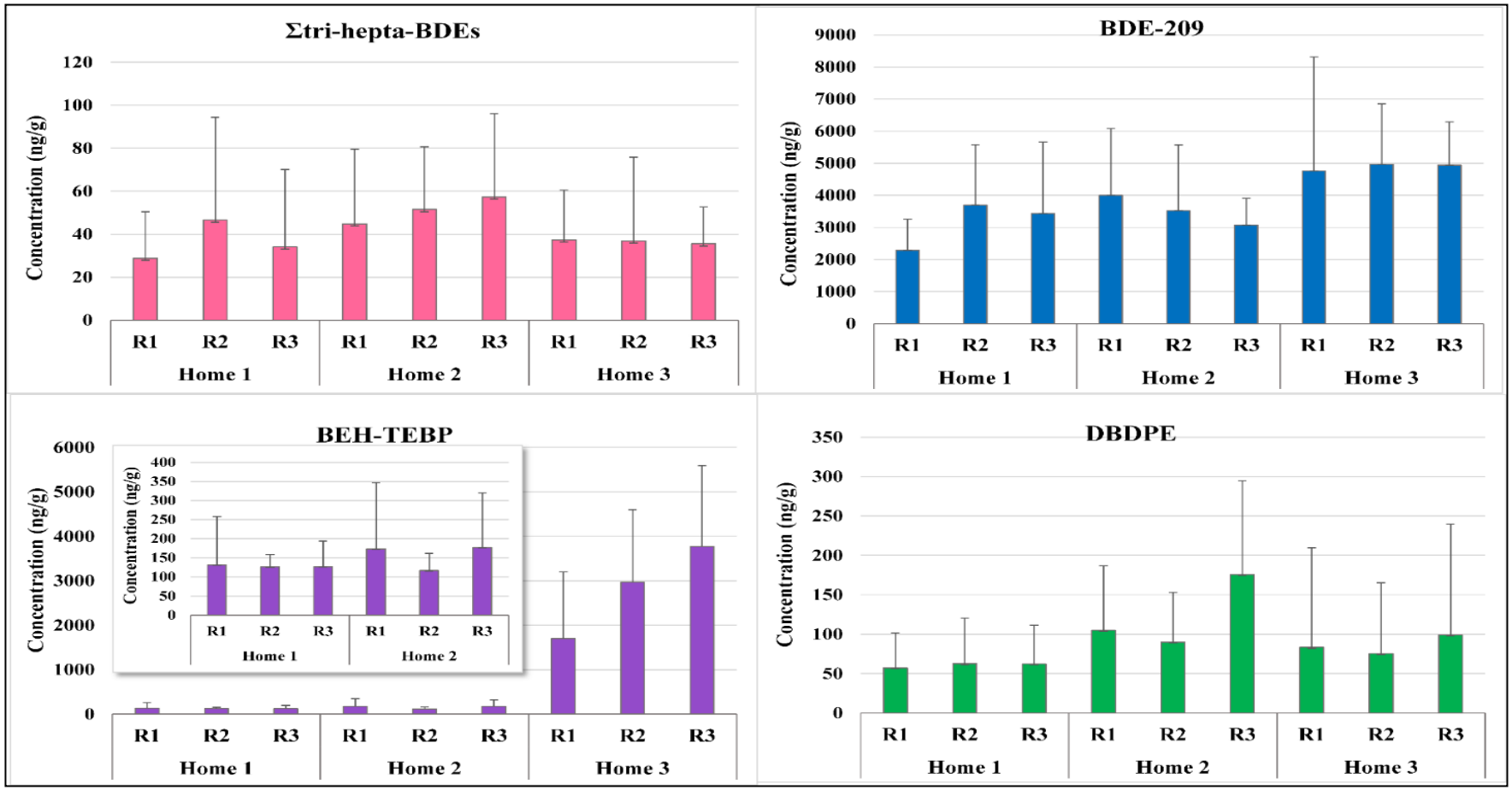

Figure 3: Average concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in dust from different rooms (R1 = Living room, R2= Bedroom, and R3 = Study, Home 3 = Bedroom) within the same home in Home 1, Home 2 and Home 3

WITHIN-ROOM AND WITHIN-HOME SPATIAL AND TEMPORAL VARIABILITY IN CONCENTRATIONS OF LEGACY AND "NOVEL" BROMINATED FLAME RETARDANTS IN INDOOR DUST

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Electronic supporting information contains:

- Figure S1: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H1R1), bedroom (H1R2) and study room (H1R3) of Home 1
- Figure S2: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H2R1), bedroom (H2R2) and study room (H2R3) of Home 2
- Figure S3: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H3R1), adult bedroom (H3R2) and a child's bedroom (H3R3) of Home 3
- Figure S4: Average concentrations (ng/g) and distribution profiles of tri-hepta-BDEs and NBRs in Home 1, Home 2 and Home 3
- Table S5: *p* values obtained from the T-test comparison of concentrations of BFRs between the two floor areas (F1 and F2) within the same room.
- Table S6: *p* values obtained from the T-test comparison of concentrations of BFRs between the elevated surface dust and floor dust within the same room.
- Figure S7: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = bedroom and R3 = study) of Home 1

- Figure S8: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = bedroom and R3 = study) of Home 2
- Figure S9: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = adult bedroom and R3 = child's bedroom) of Home 3
- Table S10: Maximum: minimum ratio in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in floor dust samples (F1 and F2) from three rooms (R1, R2 and R3) in Home1, Home2 and Home3 (H1, H2 and H3)

Figure S1: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H1R1), bedroom (H1R2) and study room (H1R3) of Home 1

Figure S2: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H2R1), bedroom (H2R2) and study room (H2R3) of Home 2

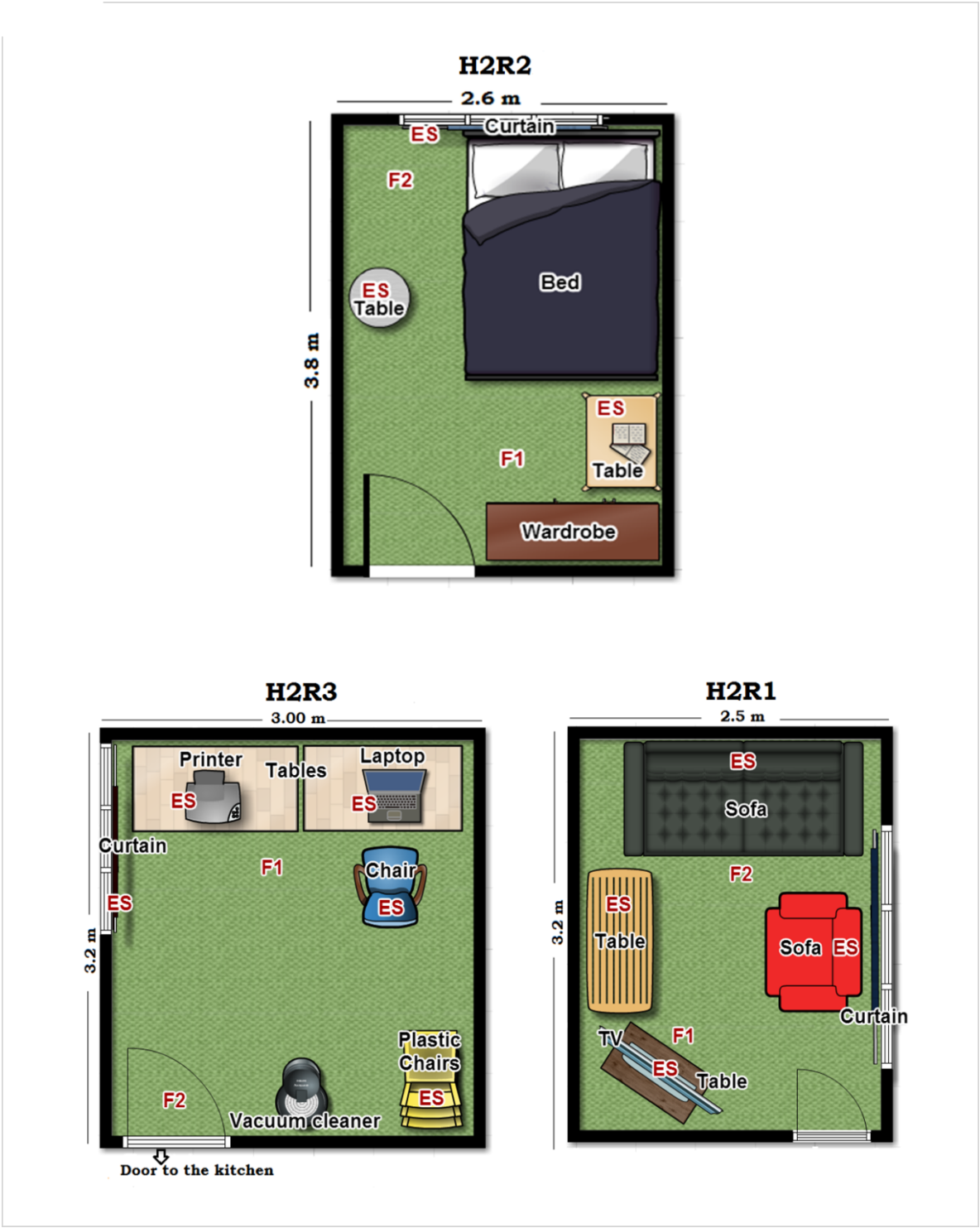

Figure S3: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H3R1), adult bedroom (H3R2) and a child's bedroom (H3R3) of Home 3

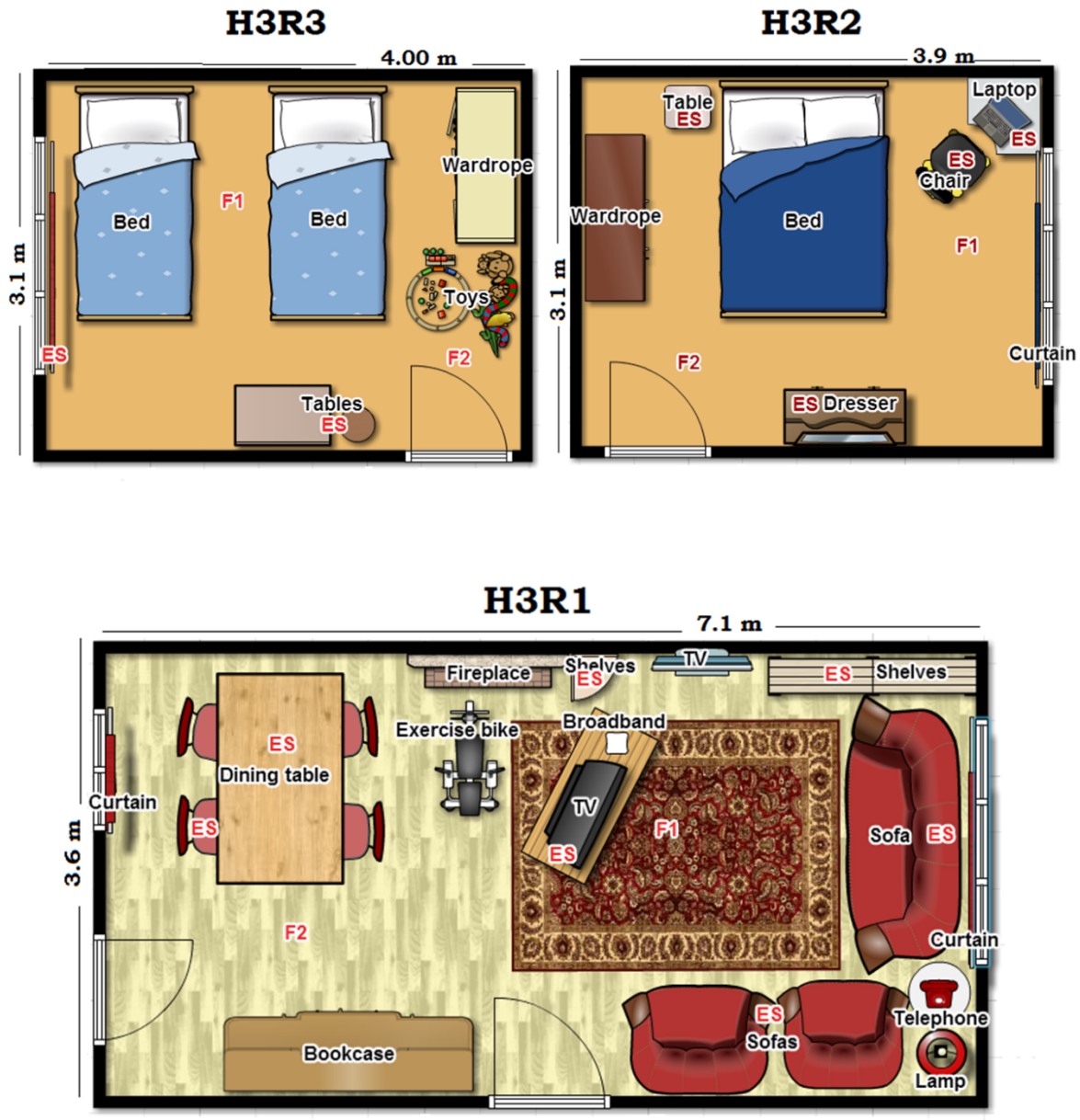

Figure S4: Average concentrations (ng/g) and distribution profiles of tri-hepta-BDEs and NBRs in Home 1, Home 2 and Home 3

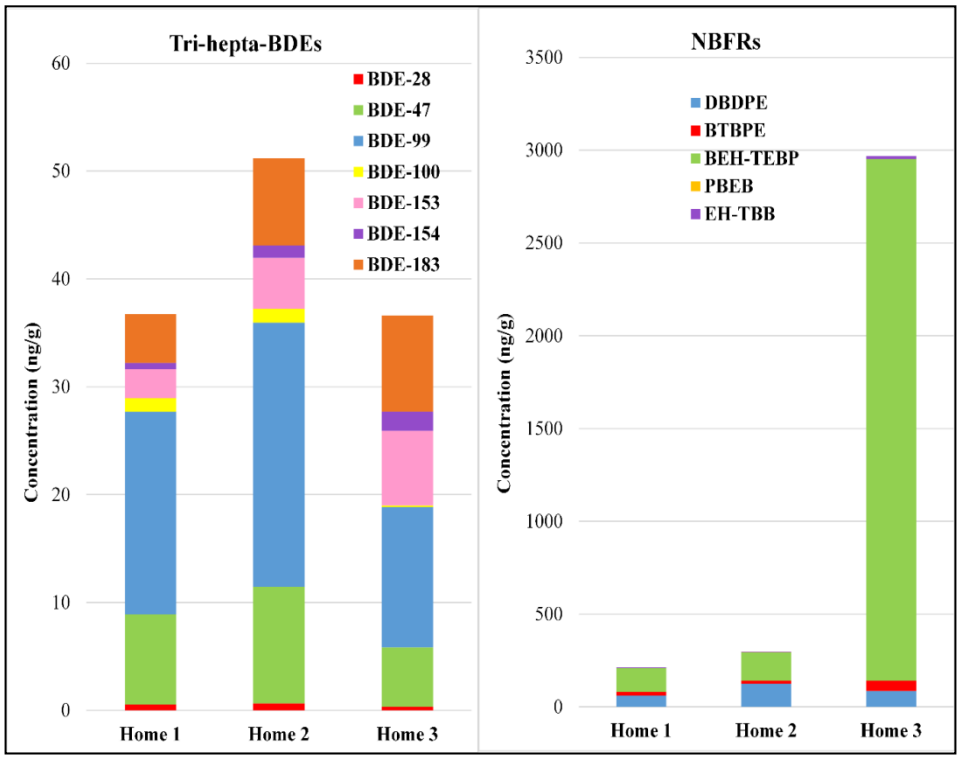

Table S5: *p* values obtained from the T-test comparison of concentrations of BFRs between the two floor areas (F1 and F2) within the same room.

Sampling room	$\Sigma_7$tri-hepta	BDE-209	BEH-TEBP	DBDPE	NBFRs
H1R1	0.277	0.508	0.323	0.81	0.55
H1R2	0.269	0.232	0.012	0.054	0.006
H1R3	0.359	0.576	0.411	0.613	0.285
H2R1	0.575	0.247	0.219	0.438	0.335
H2R2	0.0003	0.233	0.939	0.217	0.557
H2R3	0.006	0.109	0.561	0.001	> 0.001
H3R1	0.71	0.341	0.102	0.055	0.024
H3R2	0.052	0.347	0.66	0.405	0.572
H3R3	0.071	0.244	0.994	0.785	0.992

Table S6: *p* values obtained from the T-test comparison of concentrations of BFRs between the elevated surface dust and floor dust within the same room.

Sampling room	$\Sigma_7$tri-hepta	BDE-209	BEH-TEBP	DBDPE	NBFRs
H1R1	0.022	0.045	0.138	0.026	0.062
H1R2	0.031	0.042	0.071	0.573	0.3
H1R3	0.046	0.058	0.029	0.398	0.003
H2R1	0.007	0.089	0.096	0.108	0.11
H2R2	0.056	0.107	0.68	0.012	0.199
H2R3	0.041	0.013	0.048	0.002	0.205
H3R1	0.15	0.354	0.047	0.016	0.056
H3R2	0.201	0.03	0.04	0.393	0.037
H3R3	0.042	0.092	0.008	0.34	0.003

Figure S7: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = bedroom and R3 = study) of Home 1

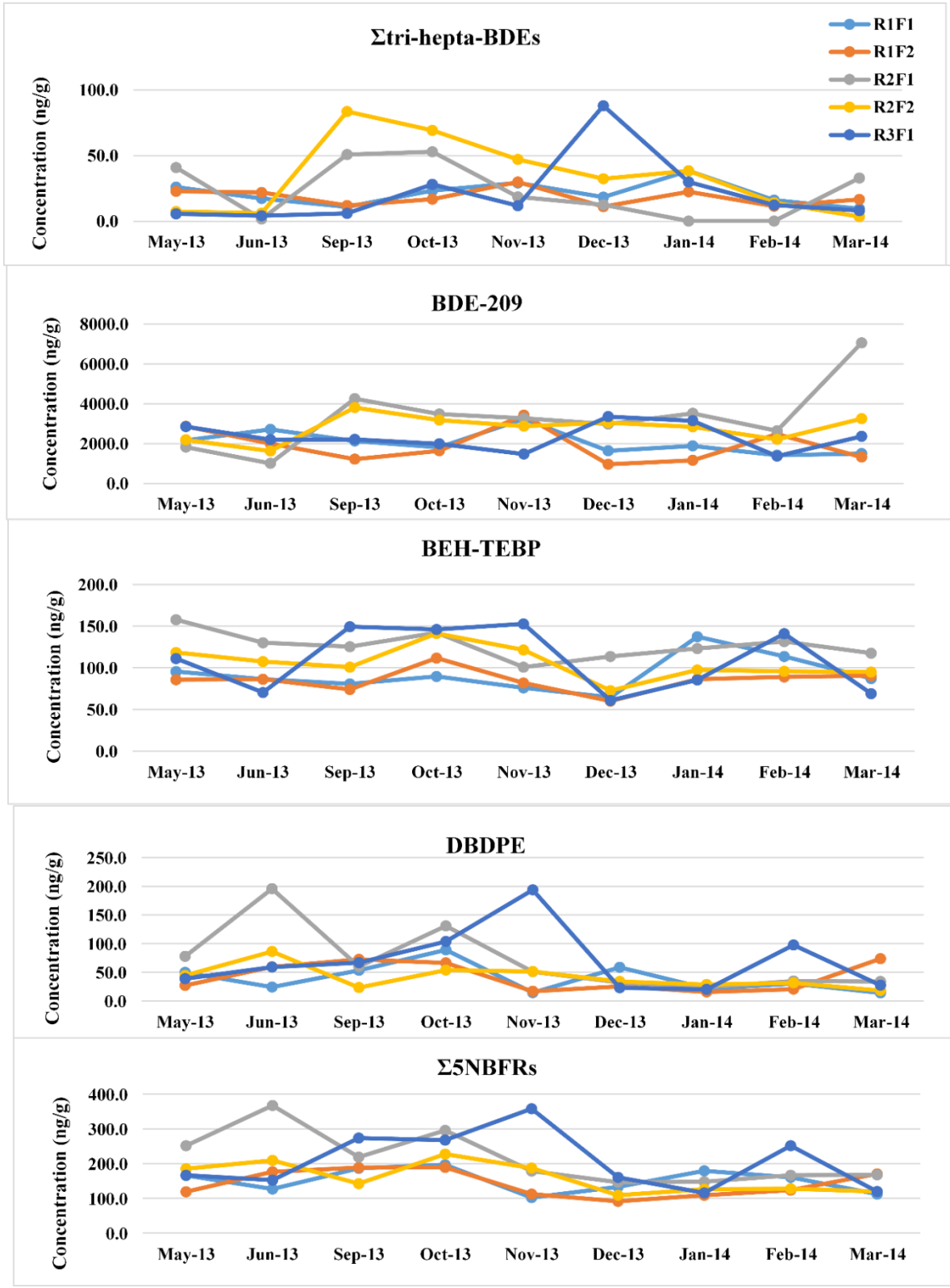

Figure S8: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = bedroom and R3 = study) of Home 2

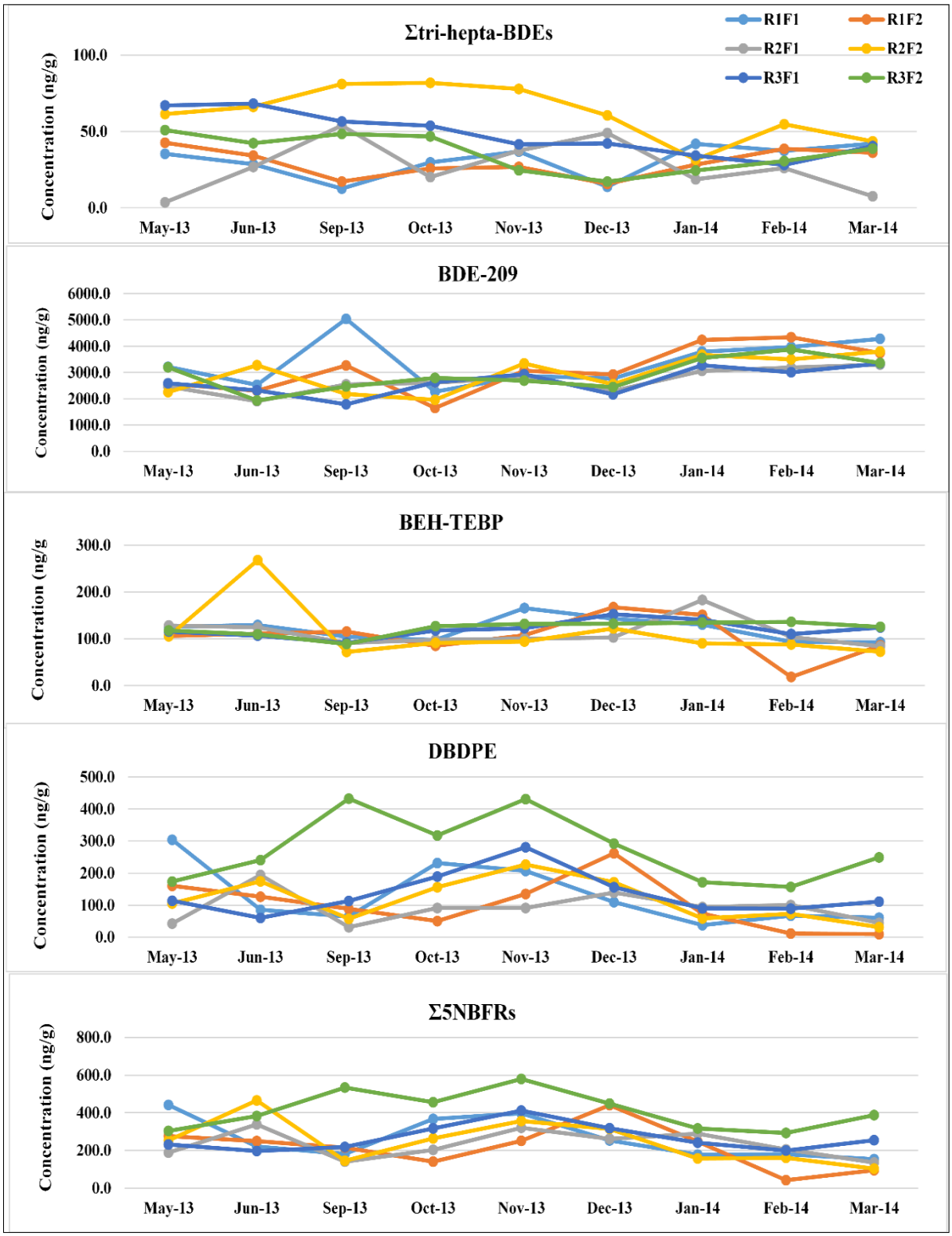

Figure S9: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = adult bedroom and R3 = child's bedroom) of Home 3

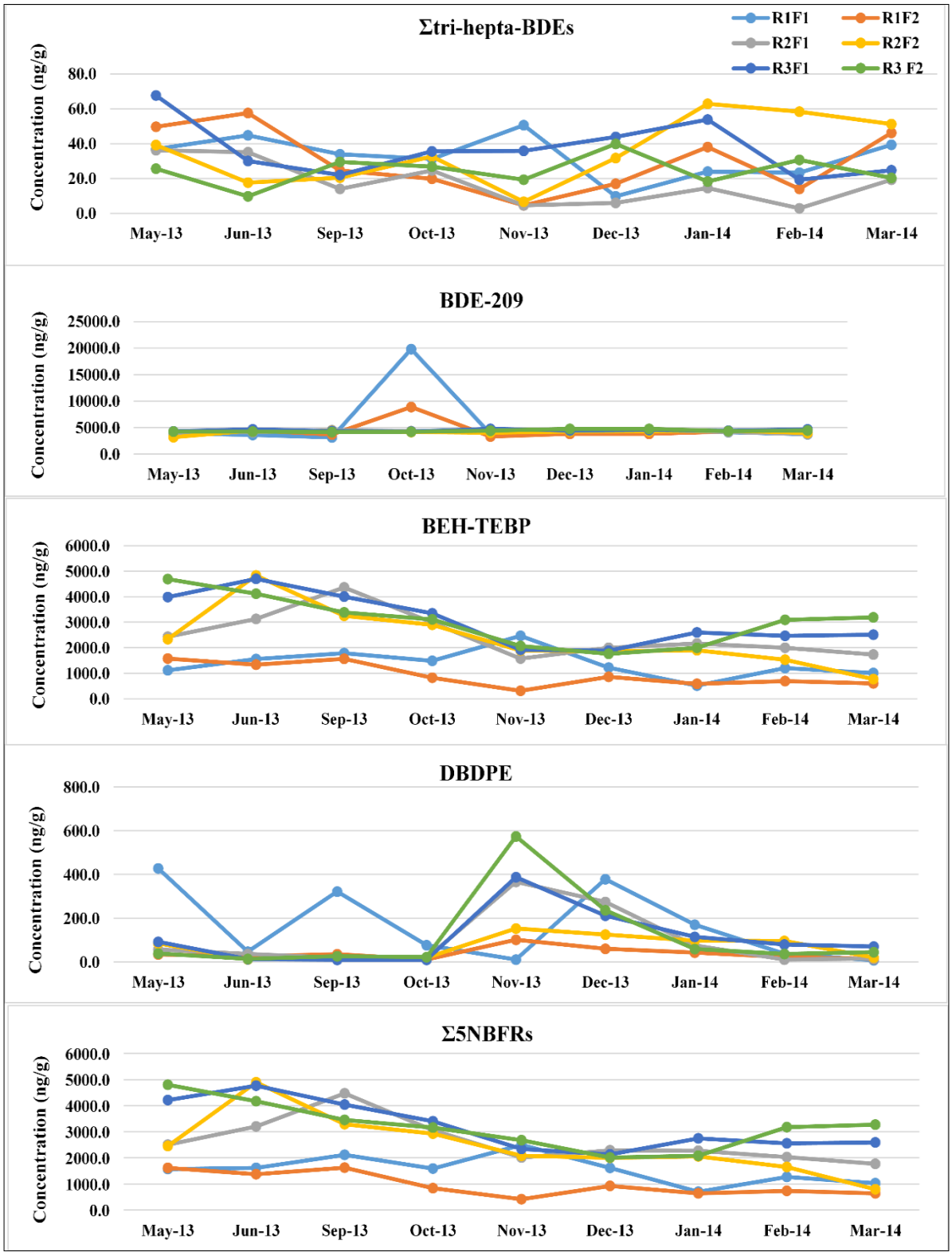

Table S10: Maximum: minimum ratio in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and Σ_5NBFRs in floor dust samples (F1 and F2) from three rooms (R1, R2 and R3) in Home1, Home2 and Home3 (H1, H2 and H3)

Sampling area	$\Sigma_7$tri-hepta-BDEs	BDE-209	BEH-TEBP	DBDPE	Σ_5NBFRs
H1R1F1	4.0	2.3	2.1	6.4	1.9
H1R1F2	2.7	3.5	1.9	4.7	2.1
H1R2F1	29.5	7.0	1.6	8.1	2.5
H1R2F2	23.8	2.3	1.9	4.7	2.1
H1R3F1	21.1	2.4	2.5	9.7	3.1
H1R3F2	2.9	1.3	1.8	3.5	1.4
H2R1F1	3.4	2.2	1.8	8.0	2.9
H2R1F2	2.7	2.6	9.2	28.0	10.4
H2R2F1	15.1	1.7	2.2	6.2	2.5
H2R2F2	2.6	1.9	3.7	7.3	4.5
H2R3F1	2.4	1.9	1.7	4.7	2.1
H2R3F2	3.0	2.0	1.5	2.8	2.0
H3R1F1	5.2	6.3	4.8	71.4	3.6
H3R1F2	12.6	2.7	5.1	16.8	3.9
H3R2F1	12.0	1.2	2.8	60.9	2.5
H3R2F2	9.3	1.4	6.3	13.4	6.2
H3R3F1	3.5	1.1	2.5	43.2	2.2
H3R3F2	4.1	1.1	2.7	42.3	2.4