Brominated and organophosphate flame retardants in indoor dust of Jeddah, Kingdom of Saudi Arabia : implications for human exposure

Brominated and Organophosphate Flame Retardants in Indoor Dust of Jeddah, Kingdom of Saudi Arabia: Implications for Human Exposure

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Abstract

In present study, we have evaluated the occurrence of various flame retardants (FRs) including polybrominated diphenyl ethers (PBDEs), emerging brominated/ chlorinated flame retardants (Br/Cl FRs), and organophosphate FRs (PFRs) in cars, air conditioner (AC) filters and floor dust of different households from Jeddah, Kingdom of Saudi Arabia (KSA). To the best of our knowledge, this is first study in literature reporting emerging Br/Cl FRs and PFRs in AC filter dust and also first to report on flame retardants in dust from KSA, which makes these findings very important. Among FRs: chlorinated alkyl phosphate (TDCPP, TCEP, and TCPP), penta-BDEs, BDE-209, and DBDPE were found to be the major chemicals in all kind of dust samples. PFRs were the major analytes in all four microenvironments, followed by PBDEs and by emerging Br/Cl FRs. ΣPFRs occurred at median concentrations of 15,400 ng/g in AC filter dust, 10,500 ng/g in car dust and 3750 ng/g in house dust, respectively. For all classes of analytes, relatively lower levels were observed in house dust than those of car and AC filter dust, and our data is comparable to other studies in Gulf countries. The profiles of analytes in car dust were different from those in the AC filter and house dust, which reflected their wider application as both FR and plasticizer in variety household communities and other commercial products. Different exposure scenarios using 5th percentile, median, mean, and 95th percentile levels were estimated for adult, taxi drivers and toddlers. For toddlers, assuming high dust intake, mean and 95th percentile concentrations, the values computed for penta-BDEs were higher than RfD values, while for ΣNFBRs and ΣPFRs, the exposure was many-fold lower than the corresponding RfD.

Key Words: Brominated Flame Retardants, Organophosphate Flame Retardants, Indoor dust, Kingdom of Saudi Arabia, Human exposure

1. Introduction

Industrialized societies have developed a broad spectrum of synthetic chemicals for various applications such as Flame Retardants (FRs), plasticizers, lubricants, refrigerants, fuels, solvents, pesticides and preservatives (Ali et al., 2012 a,b). These chemicals, such as FRs can enter the natural environment during their production, use and through accidental leakage etc. (Ali et al., 2013 a,b; Covaci et al., 2011; Wang et al., 2014). With wide range of applications these synthetic organic chemicals can be found in virtually every compartment of our environment, including soil, groundwater, surface water, plants, animals, indoor environment (air and dust) and in our bodies (Ali et al., 2013 a,b; Covaci et al., 2011; Wang et al., 2014).

Brominated flame retardants (BFRs) and organophosphate flame retardants (PFRs) are diverse group of chemicals that are used in consumer products as FRs to prevent and minimize fire hazards and/or as plasticizers (Dirtu et al., 2012; Wang et al., 2014). They have found a wide range of applications in consumer products and building materials including printed circuit boards, thermal insulation boards, housing for electronic and electrical equipment, fabrics and furniture foams, wall coverings, floor finishing products, antifoaming agents and hydraulic fluids (Abdallah et al., 2014; Covaci et al, 2011; Meeker et al., 2013). Most of these chemicals are used as additives rather than chemically bonded to the product matrix, thus easily release into the environment where their persistence leads to exposure of humans through various pathways such as dermal contact, ingestion, and inhalation, and dermal of aerosols and dust, among other sources (Johnson et al., 2010; Stapleton et al., 2012). The exposure to these contaminants is of great concern due to the potential health risks such as endocrine disruption, neuro-developmental, hepatic and behavioral abnormality and many of them have possible carcinogenic properties (Ali et al., 2013a; Meeker et al., 2013). Such evidences have contributed to list polybrominated biphenyl ethers (PBDEs) formulations (Penta- and Octa-BDE) under the Stockholm Convention list of persistent organic pollutants (POPs), while use of Deca-BDE has also been subjected to restrictions (European Court of Justice, 2008; Zehra et al., 2015). However, despite the increasing regulations human exposure to PBDEs is likely to continue for some time due to their persistence in the environment and ubiquity in the consumer materials (Ali et al., 2013 a,b; Dirtu et al., 2012). Regulations have paved the way for alternative FRs as replacements for the regulated/ banned formulations (Covaci et al., 2011). In recent years, several studies have investigated the occurrence of alternative FRs as well as PBDEs at high concentration in dust from different countries (Ali et al., 2013 a,b; Dirtu et al., 2012; Stapleton et al., 2012). These alternative FRs were described less persistent and less likely to bio-

accumulate than their predecessors, but recent studies have documented their occurrence in different environmental samples including air, dust, humans and household pets (Ali et al., 2013b; Covaci et al., 2011; Wang et al., 2014).

Indoor dust has been associated with human exposure to various organic contaminants and risk posed to human health by indoor contaminants particularly to the most vulnerable groups, such as toddlers and pregnant women is of great concern (Abdallah et al., 2014; Ali et al., 2013a; Meeker et al., 2013). People spend more time inside the home/office, while indoor they are continuously exposed to chemicals and indoor dust samples could be a source for these chemicals (WHO, 1999). However, no information is available about the occurrence and dynamics of these FRs in the indoor environment of Kingdom of Saudi Arabia (KSA). Therefore, reporting these chemicals in indoor media from the country is a highly essential. The aims of the present study were: (i) to evaluate the levels and profiles of classes of organic FRs in indoor dust from two microenvironments of Jeddah, (ii) to establish potential sources of targeted contaminants in the studied areas, (iii) to evaluate the evidence that alternative FRs are replacing PBDEs, (iv) to estimate exposure to these chemicals for toddlers and adults *via* dust ingestion.

The following FRs were analyzed in the study:

(i) PBDEs: (28, 47, 99, 100, 153, 154, 183, 209).

(ii) Emerging brominated/chlorinated flame retardants (Emerging Br/Cl FRs): (i) 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), (ii) 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), (iii) Bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), (iv) Decabromodiphenylethane (DBDPE), (v) Dechlorane plus (DPs).

(iii) PFRs: (i) Tris–(2-chloroethyl)-phosphate (TCEP), (ii) Tris–(1,3-dichloro-isopropyl)-phosphate (TDCPP), (iii) Tris–(1-chloro-2-propyl)-phosphate (TCPP), (iv) Triphenyl phosphate (TPhP), (v) Tris(2-ethylhexyl) phosphate (TEHP), (vi) Tri-n-butyl phosphate (TnBP), (vii) Tris(2-butoxyethyl) phosphate (TBEP), (viii) 2-ethylhexyl-diphenyl phosphate (EHDPP).

2. Experiment methodology

2.1. Materials

Standards for PBDEs and emerging Br/Cl FRs were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany) and Wellington Laboratories (Canada), respectively. Standards of T*n*BP, TPhP, TCEP, TEHP, EHDPP, TBEP and TDCPP (mixture of 2 isomers) were purchased from

Chiron AS (Trondheim, Norway), while TCPP (mixture of 3 isomers) were obtained from Pfaltz & Bauer (Waterbury, CT, USA). Purity of analytical standards for PFRs was > 98%, except for TBEP (> 94%). Internal standards (ISs) BDE 77 and BDE 128 (AccuStandard Inc., USA), $^{13}C_{12}$-BDE 209, ^{13}C-TBPH, ^{13}C-anti-DP, ^{13}C-syn-DP, (Wellington Laboratories), TAP (TCI Europe, Zwijndrecht, Belgium), labeled TPP-d_{15}, TDCPP-d_{15}, TBEP-d_6, TCEP-d_{12} (Sigma) were used to quantify these chemicals.

All solvents used during the analysis were of pesticide-grade. Acetone (Ace), dichloromethane (DCM), ethyl acetate, *iso*-octane and toluene were purchased from Merck (Darmstadt, Germany), while *n*-Hexane (Hex) was purchased from Acros Organics (Geel, Belgium). Concentrated sulfuric acid (98%) (H_2SO_4) and silica gel were purchased from Merck. Empty polypropylene filtration tubes (3 mL) SPE cartridges and 500 mg/3 mL Supelclean™ ENVI™ — Florisil® cartridges were purchased from Supelco (Bellefonte, PA, USA). Silica gel was washed with Hex and activated overnight at 140 °C. Prior to each experiment, silica was heated for 2 h at 140 °C for activation. Acid impregnated silica (44%, *w*/*w*) was prepared by adding drop wise 22 mL concentrated sulfuric acid (98%) to 50 g silica under continuous stirring. All glassware was soaked for 12 h in an alkali solution (diluted RBS 35, pH 11–12) to degrade any remaining chemicals. After washing, the glassware was rinsed with water and dried at 400 °C for 5 h. Prior to use, the all glassware was rinsed thoroughly with Hex.

2.2. Sampling and sample preparation

Indoor dust samples (N = 45) were collected from Jeddah, KSA (household floor N = 15, household AC N = 15, and cars N = 15). For floor dust, vacuum cleaner bags were collected from volunteer houses. AC filters were cleaned with brush to collect dust samples. To avoid cross contamination, brushes from the respective houses were used after pre-cleaning. For car dust, inside of the car (dash board, seats, trunk) except floor was vacuumed and, before each sample, the vacuum cleaner was cleaned thoroughly to avoid any cross contamination. To achieve homogenized samples, 250 µm mesh was used to sieve all samples. Details about sampled sites were collected on a well prepared questionnaire.

The sample extraction and purification method is described in detail elsewhere (Van den Eede et al., 2012). Briefly, an accurately weighed aliquot of dust (typically 50 mg) was spiked with internal standards and extracted by ultrasonication and vortexed with Hex: Ace (3:1, *v*/*v*). Florisil was used to obtain two fractions; a 1st fraction was eluted with 8 mL Hex and a 2nd fraction with 10 mL ethyl acetate. All PBDEs and emerging Br/Cl FRs, except TBPH, were present in the 1st fraction, while TBPH and

PFRs were present in the 2nd fraction. After concentration under nitrogen, the 1st fraction was further cleaned on acid silica (44%) and analytes were eluted with 10 mL Hex:DCM (1:1, *v*/*v*). After evaporation to dryness, each fraction was resolubilized in 100 µL of *iso*-octane prior to GC–MS analysis.

2.3. Instrumentation

Details about the instrumentation are found elsewhere (Van den Eede et al., 2012). In summary, the analysis of emerging Br/Cl FRs and PBDEs was performed by 6890 Agilent (Palo Alto, CA, USA) gas chromatography (GC) coupled to a 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI). A DB-5 column (15 m × 0.25 mm × 0.10 µm) was used for separation and the MS was deployed in selected ion monitoring (SIM) mode. The ion source, quadrupole and interface temperatures were set at 200, 150 and 300 °C, respectively. The analysis of PFRs was performed by GC–MS in electron ionization (EI) mode. A HT-8 column (25 m × 0.22 mm × 0.25 µm) was used and the MS was operated in SIM mode with two characteristic ions acquired for each compound. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively.

2.4. Quality assurance

As a part of the quality assurance protocol, field blanks (N = 3 for car samples), laboratory blanks (N = 8) and an indoor dust standard reference materials (SRM) from National Institute of Standards & Technology - SRM 2585 (N = 4) were analyzed in parallel with the dust samples to account for eventual external contamination during sampling, sample preparation and to evaluate method accuracy. Levels of analytes were blank-corrected and to avoid possible photodegradation, extraction and clean up steps were performed using amber glass under fume hood without light. The values of PBDEs, emerging Br/Cl FRs, and PFRs in SRM 2585 were in agreement (RSD < 15%) with reported values (Ali et al., 2011; Van den Eede et al., 2011; Wise et al., 2006).

2.5. Statistical analysis

Descriptive analysis was performed using Microsoft Excel 2007. Non-detects were replaced by ½ LOQ, keeping in mind the small dataset in this study, non-parametric tests were applied. The significance level for the result was set $P < 0.05$. To study correlations between the levels of analytes between floor and AC dust, Spearman rank order correlation coefficient was performed using the online

tool http://vassarstats.net/corr_rank.html. PCA was also employed for source identification and their patterns of occurrence in the studied dust samples from KSA using MVSP 3.2.2.

3. Results and discussion

To the best of our knowledge, few studies have reported occurrence of PBDEs in AC filter dust, but this is a very first study reporting emerging Br/Cl FRs and PFRs in AC filter dust. Targeted PBDEs, emerging Br/Cl FRs and PFRs were detected in all analyzed dust samples from different microenvironments (i.e., AC-filter, household, and car dust) with a detection frequency up to 100% for most contaminants. A statistical summary of the concentrations of studied FRs in the analyzed dust from is provided in Table 1 and Figure 1.

3.1. Fingerprinting of FRs in dust of different microenvironments

3.1.1. PFRs

In current study, PFRs were the most important chemicals in analyzed dust samples from different micro-environments of KSA (Figure 1). ∑PFRs were found in significantly higher levels than those of other chemical classes (i.e., PBDEs and emerging Br/Cl FRs), and ranged between 500 and 109,000 ng/g. The higher levels of ∑PFRs in house floor dust compared to ∑PBDEs and ∑Emerging Br/Cl FRs are similar to those reported in the literature (Ali et al., 2013a; Dirtu et al., 2012; Kanazawa et al., 2010; Van den Eede et al., 2011; Stapleton et al., 2009). This shows wider application of PFRs in polymers used in household items and their higher use as a replacement to the by now regulated PBDEs. Similar to our current results, higher levels of ΣPFRs were documented in dust from cars compared to household dust are documented in recent literature (Ali et al., 2013a; Abdallah and Covaci, 2014; Brommer et al., 2012). This is possibly due to the use of polypropylene polymers and acrylonitrile butadiene styrene in the instrument panels, textiles, PUFs in the interior upholstery and numerous electronics in a confined area of vehicle, most of these polymers being flame-retarded with PFRs (Abdallah and Covaci, 2014; Ali et al., 2012b; Ali et al., 2013a). To the best of our knowledge, this is a very first study reporting PFRs in AC filter dust, which makes these findings very important for their implication of human exposure in this region, since air conditioning is a vital part of daily life. Among selected microenvironments, AC filter dust showed highest median values (15,400 ng/g) of ∑PFRs, followed by car dust (10,500 ng/g) and house floor dust (3,750 ng/g).

Similarly, the PFR profiling for different microenvironment has also shown distinct composition (Figure 2), which is possibly due to use of different consumer products, which might contain specific formulations (Abdallah and Covaci, 2014). Chlorinated-PFRs were found in all analyzed samples (Table 1), the predominant contribution of chlorinated PFRs (TDCPP, TCPP, and TCEP) were found mainly in AC and car dust, with highest median levels of these chemicals in AC dust (7800, 2000, 820 ng/g, respectively) and car dust (2700, 1650, 1200 ng/g, respectively), while in house floor dust TCPP (1650 ng/g) was the major PFR (Figure 2). The reason for consistent and higher occurrence of chlorinated PFRs could be attributed to their extensive use into a number of flexible and rigid polyurethane foams (PUFs), and as a result release from wide variety of consumer products containing PUFs. Another argument suggested in literature is that chlorinated-PFRs shows high resistance and are known to be relatively stable toward biodegradation.

The distribution pattern of PFRs in various occupational settings of different countries exhibited similar distribution patterns with an overwhelming dominance of chlorinated PFRs (Figure 5). For example, remarkably high levels of TCPP (73,000 ng/g), TDCPP (67,000 ng/g), and TCEP (94,000 ng/g) were detected in the floor dust from Swedish office (Marklund et al., 2003). Chlorinated-PFRs in car dusts from Germany (TDCPP (mean = 130,000 ng/g) and Kuwait (TCPP (30,000 ng/g) were high implying their higher utilization in vehicle seating upholstery (Figure 3) (Ali et al., 2013a; Brommer et al., 2012). Similarly, Kanazawa et al. (2010), has also reported very high levels (ng/g, median) of TDCPP (15,000), TCPP (9,000), and TCEP (50,000) in multi-surface and floor dust of modern household settings. In contrary, although levels were still comparable, Romanian and Spanish household floor dust (Figure 5) reported different PFRs compositional patterns i.e., TBEP < TCPP < TPP ≈ TCP < TiBP (Dirtu et al., 2012). Such country specific heterogeneity of the PFR profiles in the indoor micro environment might be explained by priority of their usage as FRs and/or as plasticizers, by the time of usage (recent/past application), as well as by the sampling location (country specific) and sampling method (room type/research methodology) (Dirtu et al., 2012; Ali et al., 2014).

Non-halogenated PFRs were also measured at high levels in the collected dust samples of the studied microenvironments. TPhP and EHDPP were detected in all analyzed dust samples, while other i.e., TEHP, TnBP and TBEP were detected in 40-80% of the samples (Table1). The profile for household floor dust was TPhP > EHDPP > TEHP > TnBP, while for AC and car dust, TEHP levels were higher than EHDPP. The levels and profiles of non-halogenated FRs are in agreement with the reported levels (Figure 5) from Kuwait and Pakistan dust (Ali et al., 2012a, 2013a, 2014), and from

Egypt (Abdallah and Covaci, 2014). However, in contrary to our levels, much higher levels of non-halogenated phosphates are reported from Sweden (Marklund et al., 2003), Japan (Kanazawa et al., 2010), China (Wang et al., 2014) and USA (Stapleton et al., 2009). TPhP and EHDPP are well known for their board range of commercial applications e.g., both as plasticizers in PVC, unsaturated polyester resins and FR commercial mixtures, such as AC073 (Supresta) and/or FM550. Given the wider application of both TPhP and EHDPP as both FR and plasticizers in a variety of household communities and other commercial products, their occurrence in all micro-environments is justified and also reported elsewhere (Abdallah and Covaci, 2014). TBEP, used in floor wax or as a plasticizer in vinyl plastics and rubber products, was measured at significantly higher levels in household dust compared to car and AC dust, and reflects its wider application for household commodities and personal products (Marklund et al., 2003; Ali et al., 2014). TBEP, was also found predominantly in the house dust from Belgium (Van den Eede et al., 2011), Japan (Kanazawa et al., 2010), Sweden (Marklund et al., 2003), Spain (García et al., 2007), Romania (Dirtu et al., 2012), but the levels were several times higher than those of current levels in KSA (Figure 5). Furthermore, TEHP and TnBP were also detected in most of the samples and their levels were comparable to those of reported by Abdallah et al., (2014).

3.1.2. PBDEs

Although the use and production of PBDEs (Penta-, Octa-, and partly Deca-BDE mixtures) are banned by the Stockholm's convention (2009) and UNEP, (2009) due to their several adverse environmental concerns, but these chemicals are still reported at very higher levels into various environmental media including dust (Dirtu et al., 2012). In the current study, the levels of ∑PBDEs (ng/g) ranged 50-5,300 (median = 350) in house floor dust, 100-23,500 (median = 350) in AC filter dust, 70-35,550 (median =310) in car dust. As shown in Figure 2, BDE 209 and Penta-BDE congeners (BDE-47 and -99) were the principal contributors to the PBDE profile. BDE-209 was found in all samples at highest levels (ng/g) i.e., household floor dust (25-1,670 (median = 275)), AC filter dust (60-800 (median = 170)), and car dust (15-35,500 (median = 200)). Similarly, BDE-47 and BDE-99 were also measured in >95% collected analyzed dust samples (Table 1). PBDE composition differed between the type of dust, e.g., car dust was dominated by BDE-209, while household floor and AC filter dust showed reasonable contributions from the Penta-BDE congeners.

Our results are in agreement to those presented from European (Dirtu et al., 2012) and Gulf countries (Gevao et al., 2012; Ali et al., 2013a) (Figure 5). However, the obtained levels were lower than

255 those from reported from China (Zhang et al., 2009), USA, UK (Harrad et al, 2008) and Canada (Shoeib
256 et al., 2012). According to Ramu et al., (2007), most of the environmental samples in Asian countries
257 including China and South Korea, are dominated by Deca-BDE and exhibited higher levels of PBDEs in
258 many cases. Moreover, phasing out of PBDEs in Asian countries is still not followed strictly and mega
259 production of electronics and other commercial products in these countries resulted into huge
260 contamination of the surrounding environment (Ramu et al., 2010). For example, previous studies
261 highlighted that the sediments from Korean coast (Ramu et al., 2010), and biota of South China Sea
262 (Chen et al., 2013) showed very high levels of PBDEs (predominance of BDE-209) due to extensive
263 industrial activities in the country. Similar results have also been discussed by Dirtu et al (2012) for
264 European countries, and described their sources due to widespread past usage in different commercial
265 formulations. However, despite the increasing regulations, exposure to PBDEs is likely to continue for
266 some time due to their persistence in the environment and ubiquity in the older consumer materials
267 (Dirtu et al., 2012).
268
269 **3.1.3. Emerging Br/Cl FRs**
270 Restrictions and bans on the use of PBDE formulations has resulted in a market for emerging
271 Br/Cl FRs to meet the flammability standards. These alternatives are perceived as less persistent and less
272 likely to bio-accumulate than their predecessors, but recent studies have documented their occurrence in
273 different environmental media, including air, dust, humans and household pets (Ali et al., 2013a; Covaci
274 et al., 2011; Wang et al., 2014). Our results are also in agreement with other studies and the levels of
275 emerging Br/Cl FRs were in similar range to the levels of PBDEs. ∑Emerging Br/Cl FRs (ng/g) ranged
276 120-1,850 (median = 950) in house floor dust, 275-6,400 (median = 750) in AC filter dust, 70-11,100
277 (median = 450) in car dust. In our samples (Figure 2), DBDPE was the dominant emerging BFR and
278 exhibited higher median concentration (3,275 ng/g) in car dust, following by household floor dust (800
279 ng/g) and AC filter dust (650 ng/g). DBDPE median levels were lower than in Chinese household dust
280 (Wang et al., 2010), though they were higher and/or comparable to those of other studies (Ali et al.,
281 2011; 2012; 2013; Dirtu et al., 2012). According to Zhang et al., (2009), DBDPE is one of the major
282 BFR products currently used in China as a replacement for deca-BDE. Since China is one the major
283 producer of Emerging Br/Cl FRs, the higher levels in its environment compared to other developing and
284 European countries are not surprising (Figure 4).

TBB and TBPH, principal components of FM-550, a replacement for Penta-BDE, were detected in most of the samples (>95 %) and were the second important emerging Br/Cl FRs (Figure 2). Their concentrations ranged between 10-32 ng/g without any significant difference among different microenvironments. BTBPE (<LOD-5, ng/g) and DP (<LOD-3, ng/g) were also detected in >75 % of the samples and had a minor contributors towards the total HFRs loads in both floor and AC filter dust. In comparison to literature data (Figure 4), the median concentrations of TBB, TBPH and BTBPE in this study were comparable to the levels reported in house dust from Australia (Toms et al., 2009), Belgium (Ali et al., 2011), Kuwait (Ali et al., 2013a) and Romania (Dirtu et al., 2012), but were lower than those from China (Wang et al., 2009; Zhang et al., 2009), USA, UK (Harrad et al, 2008) and Canada (Shoeib et al., 2012). In contrary to these studies, Indian house dust contained higher BTBPE (48 μg/kg) and as major emerging BFR (Devanathan et al., 2011).

3.2. Source apportionments of analyzed chemicals

We computed Spearman rank-order correlation and principal components analysis (PCA) in order to explore the possibility of common sources and to fingerprint the use of PBDEs and their replacement/emerging FRs, whether the manufactures are complying with the regulation imposed by UNEP (2009). Computed Spearman rank-order correlation coefficient among the sample collected from AC and household floor dust showed significantly positive correlation for TCEP, TBB and PBDE congeners (p<0.05), suggesting common sources of emission for these compounds. No such correlation (p>0.05) was observed for other analytes, suggesting more diverse emission sources and/or different environmental fates for these compounds in indoor microenvironments. Also, different microenvironments exhibited the specific profiles of analytes classes. For example, major components of Penta-BDE (BDE-47, and -99) showed their loading towards the most of AC filter dust and few household dust (Figure 3) and showed weak association with the components of FM-550 i.e., TBB, TPhP, and TBPH and reflected negligible of their replacement in AC filter dust and few household dust. Octa-BDE components (BDE-183, -153, -154) also dominated in the household and AC filter dust and their comparison with BTBPE (replacement of Octa-BDE), clearly indicated that the negligible contribution of the latter to AC-filter and few household dust.

Considering these profiles, it can be suggested that AC-filter dust compositions resembles with the BDE commercial formulation of DE-71 and Bromokal 70-5DE (Zehra et al., 2015). A possible explanation for these trends is that, despite imposing the strict regulations, the exposure to PBDEs is

likely to continue for some time due to their persistence in the environment and ubiquity in the older consumer materials (Dirtu et al., 2012). Car dust and household floor dust showed an association between BDE-209 and its replacement DBDPE, and suggested a common emission source. This scenario also suggested that the phasing out of PBDEs is still in process worldwide.

All analyzed PFRs (noticeably chlorinated alkyl phosphates) were shown its loading in car dust and AC dust, and few household sample group, which originated from common sources e.g., use of commercial formulations of AC073 from Supresta and/or FM-550. Nevertheless, few of exceptions were also observed from various microenvironments, which showed the burden of all analyzed chemical including PBDEs, emerging Br/Cl FRs and PFRs, and can be justified by their wider application as both FR and plasticizer in variety household communities and other commercial products and also reported elsewhere (Abdallah et al., 2014; Ali et al., 2013a). Such group-specific heterogeneity of the PFR profiles in the indoor micro environments might be explained by their usage as FRs and/or as plasticizers, by the time of usage (recent/past application), as well as by the sampling location and sampling method (room type/research methodology) (Dirtu et al., 2012; Ali et al., 2014). In the current study, it can be suggested that in recent years KSA imported new car models from other countries and this has resulted into emission of emerging Br/Cl FRs and PFRs. However, the AC-filter dust and house hold dust chemical profiles reflected the exposure to these commodities of both aged and recent imports. The differences in the levels and profiles of FRs in indoor dust from various countries could also be attributed to the specific country fire safety regulations, which are generally more stringent in North America and UK. Another hypothesis might be the different timing for the replacement of PBDEs in various countries. There is no local production of these chemicals and no strict regulations are placed for the use of FRs in KSA. Most of the furniture, electronics and vehicles are imported from Europe, USA, Japan and China, the occurrence of FRs is assumed to arise *via* the presence in imported stuff. The heterogeneous profile (Figure 1) in analyzed dusts might indicate the imported products from different countries.

3.3. Exposure assessment via dust ingestion

Humans are exposed to indoor pollutants via diet, dermal intake, inhalation, diet, and dust ingestion. The daily intake (DI) of contaminants from dust ingestion was estimated from the algorithm (Guo and Kannan, 2011):

$$DI = C_{dust} f_1 f_2 / M_1$$

where C_{dust} is the concentration of contaminants in dust (ng/g), f_1 is the fraction of time spent indoors, f_2 is the dust ingestion rate (mg/day), and M_1 is the body weight (kg).

In order to make a preliminary evaluation of the exposure *via* dust ingestion to selected FRs, we combined the data of floor and AC filter dust. In absence of bioavailability data for selected FRs, for consistency we assumed 100% absorption of contaminants from ingested dust and average dust intake of 20 and 50 mg/day, and high dust ingestion figures of 50 and 200 mg/day for adults and toddlers, respectively. We assumed an average body weight (bw) of 70 kg for adults and 12 kg for toddlers. Due to the extreme temperatures that are experienced in KSA, people spend less than an hour a day outdoors. Therefore, the time spent outdoors does not significantly affect the calculations. The considered values are based on our previous published work (Ali et al., 2011; 2012a,b; 2013a) which reported from different countries. Keeping in mind the dry environment of KSA and the more dusty particles in the environment, these calculations could underestimate the exposure.

Different exposure scenarios were calculated using 5^{th} percentile (low end exposure), median, and 95^{th} percentile (high end exposure) concentrations. For both groups, the estimated exposure levels (Table 2) for most FRs were several orders of magnitude lower than their reference dose (RfD). However, high end exposures of Penta-BDE congeners for toddlers were even higher than the corresponding RfD. These findings are in agreement with the recent studies where ingestion of indoor dust is suggested as significant exposure pathway to FRs (Meeker et al., 2013; Coakley et al., 2013; Zheng et al., 2011). Together with other exposure pathways i.e., indoor and outdoor air or food is a matter of concern for the chronic exposure to these FRs. However, due to the relatively small number of samples analyzed in the study, it should be stressed that the range of exposure estimates is only an indication of the likely range for toddlers and adults within the population. The substantial inter–individual variation in exposure depends on the time spent in indoor and the quantity of the dust ingested.

4. Conclusions

The study documented the preliminary levels and profiles for different classes of FRs in dust samples from various microenvironments of KSA. To the best of our knowledge, this is the first study on the occurrence of these contaminants in indoor environment of KSA. This study demonstrated the use of PBDEs, emerging BR/Cl FRs, and PFRs and in wide range of consumer products which lead to

significant contamination of the indoor environments of KSA. The profile and levels of different classes of FRs varies among and within micro-environments which suggest evidenced the existence of different chemical formulations. The results of the present study evidenced the existence of different chemical formulations in the indoor environment of KSA. Nonetheless, with limitations in sample size and sampling procedures, the results cannot be assumed to be representative of all indoor environments of KSA therefore further work is required to validate these results. Yet with all limitations, our results add to the increasing evidence of ubiquitous indoor contamination with various organic FRs and showed toddlers are highly exposed to them via dust ingestion. The extreme weather conditions in KSA may lead to considerable contamination of indoor environments with semi-volatile compounds and increase human health risk as people spend the majority of the time indoors. This warrants a clear need for thorough investigations of these chemicals in various indoor environments and their impact on the human health.

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488 **Table 1.** Descriptive data (mean, standard deviation, median, minimum and maximum) of studied FRs measured in household
489 floor, AC filter and car dust samples, all results are given in (ng/g dust).
490

Analytes	House (N=15)			AC filter (N=15)			Car (N=15)		
	Detection (%)	Mean±SD	Median (Mini-Max)	Detection (%)	Mean±SD	Median (Mini-Max)	Detection (%)	Mean±SD	Median (Mini-Max)
TEHP	73	100±80	70 (LOQ-270)	100	170±125	130 (30-500)	80	195±205	150 (LOQ-850)
TnBP	73	55±50	35 (LOQ-165)	44	18±10	10 (LOQ-35)	100	540±1670	60 (20-6550)
TCEP	100	560±515	410 (125-1650)	100	2650±4500	820 (120-16500)	100	7020±13850	1200 (30-52300)
TBEP	60	580±880	205 (LOQ-2750)	38	280±420	50 (LOQ-1300)	47	1650±4000	50 (LOQ-12500)
TPhP	100	310±270	230 (65-1200)	100	880±720	600 (120-2500)	100	786±1100	470 (40-4150)
EHDPP	100	220±125	220 (55-520)	100	450±380	350 (80-1600)	100	1050±2300	180 (60-9000)
TDCPP	100	1770±2500	500 (150-8700)	100	14300±18000	7800 (1000-61234)	100	8850±13500	2700 (100-45600)
TCPP	100	1600±1150	1650 (200-3700)	100	3300±3600	2000 (200-11500)	100	16250±28700	1650 (100-92000)
∑PFRs	100	5200±4000	3750 (1000-13800)	100	22000±18300	15400 (3800-74200)	100	36300±37700	10500 (500-109000)
BDE 28	0	1±0	1 (LOQ-1)	31	3±4	1 (LOQ-15)	0	LOQ	LOQ
BDE 47	100	125±370	27 (3-1450)	100	1150±2450	50 (4-9050)	87	21±50	10 (LOQ-200)
BDE 100	87	35±100	5 (LOQ-450)	94	420±850	10 (LOQ-2800)	53	7±17	2 (LOQ-700
BDE 99	100	220±670	35 (5-2650)	100	2000±3600	45 (5-10550)	93	40±100	9 (LOQ-400)
BDE 154	53	20±50	3 (LOQ-210)	44	150±250	1.5 (LOQ-850)	20	3±6	1.5 (LOQ-25)
BDE 153	60	25±80	4 (LOQ-310)	56	200±425	4 (LOQ-1600)	33	6±9	1.5 (LOQ-30)
BDE 183	73	4±2	4 (LOQ-8)	38	7±9	2 (LOQ-35)	7	3±5	2 (LOQ-20)
BDE 209	100	450±440	275 (25-1670)	100	250±200	170 (60-800)	100	5900±11650	200 (15-35500)
∑PBDEs	100	880±1300	350 (50-5300)	100	4100±7300	350 (100-23500)	100	6000±11620	310 (70-35550)
s-DP	100	3.5±2.5	2.5 (1-8)	100	5±8	3 (2-35)	93	6±10	3 (LOQ-40)
a-DP	40	2±2.5	0.5 (LOQ-8)	56	2.5±4	1 (LOQ-20)	20	5±15	1 (LOQ-65)
BTBPE	93	6±4.5	5 (LOQ-18)	75	6±8	4 (LOQ-33)	73	10±20	3 (LOQ-70)
TBB	93	45±70	16 (LOQ-250)	100	450±1350	25 (10-5500)	100	760±2300	12 (3-8700)
TBPH	100	50±80	25 (LOQ-330)	100	13±13	10 (2-55)	93	200±550	32 (LOQ-2120)
DBDPE	100	850±450	800 (110-1650)	100	670±300	650 (250-1200)	100	850±1500	3275 (45-6020)
∑Emerging Br/Cl FRs	100	950±500	950 (120-1850)	100	1150±1450	750 (275-6400)	100	1800±3050	450 (70-11100)

491 **Table 2.** Spearman's correlation data between floor and AC filter dust. **Bold** shows significantly
492 positive correlation.
493
494

Analytes	*r*	*p*
BDE 47	**0.602**	**0.008**
BDE 100	**0.647**	**0.005**
BDE 99	**0.583**	**0.010**
BDE 154	**0.561**	**0.010**
BDE 153	**0.472**	**0.038**
BDE 183	0.080	0.390
BDE 209	**0.700**	**0.001**
TEHP	-0.297	0.140
TnBP	0.118	0.337
TCEP	**0.440**	**0.049**
TBEP	0.385	0.780
TPhP	0.343	0.110
EHDPP	0.073	0.399
TDCPP	0.232	0.202
TCPP	0.225	0.211
BTBPE	0.155	0.290
TBB	**0.480**	**0.035**
TBPH	0.330	0.117
DBDPE	-0.254	0.180

Table 3. Assessment of human exposure to FRs *via* dust ingestion, all values are provided in ng/kg bw/day.

Analytes	RfD values	Toddlers						Adults					
		Median exposure		Low end exposure		High end exposure		Median exposure		Low end exposure		High end exposure	
		High	*Mean*	*High*	*Mean*	*High*	*Mean*	*High*	*Mean*	*High*	*Mean*	*High*	*Mean*
TCEP	22,000	10	2	2.5	0.5	135	35	0.3	0.1	0.1	<0.1	6	2.5
TDCPP	15,000	50	12	4.5	1.5	670	170	2	1	0.2	0.1	30	12
TCPP	80,000	30	7	3.5	1	155	40	1.5	0.5	0.1	0.1	7	3
BDE 47	100	0.6	0.1	0.1	<0.1	**55**	15	<0.1	<0.1	<0.1	<0.1	2.5	1
BDE 100	100	0.1	<0.1	<0.1	<0.1	**25**	6	<0.1	<0.1	<0.1	<0.1	1.5	0.5
BDE 99	100	0.6	0.2	0.1	<0.1	**125**	30	<0.1	<0.1	<0.1	<0.1	5.5	2.5
BDE 209	7,000	4	1	1.1	0.5	15	4	0.2	0.1	<0.1	<0.1	0.6	0.2
DP		0.1	<0.1	<0.1	<0.1	0.5	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BTBPE	243,000	0.1	<0.1	<0.1	<0.1	0.5	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TBB	20,000	0.5	0.1	0.1	<0.1	8	2	<0.1	<0.1	<0.1	<0.1	0.5	0.1
TBPH	20,000	0.2	0.1	<0.1	<0.1	1	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DBDPE	333,333	12	3	4	1	22	6	0.5	0.2	0.2	0.1	1	0.5

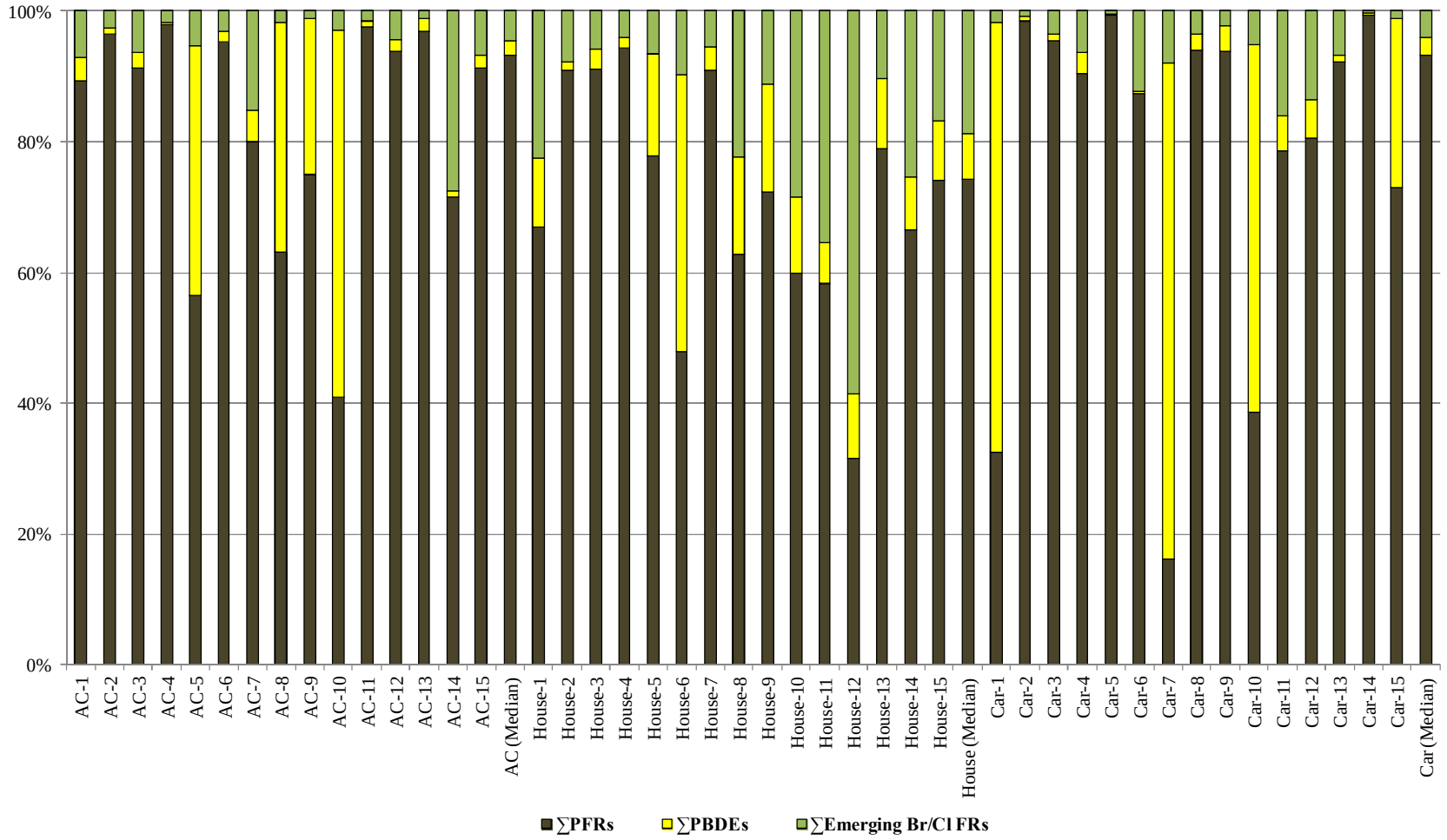


Figure 1. Percentage contribution of different classes of FRs in dust from different microenvironments of KSA.

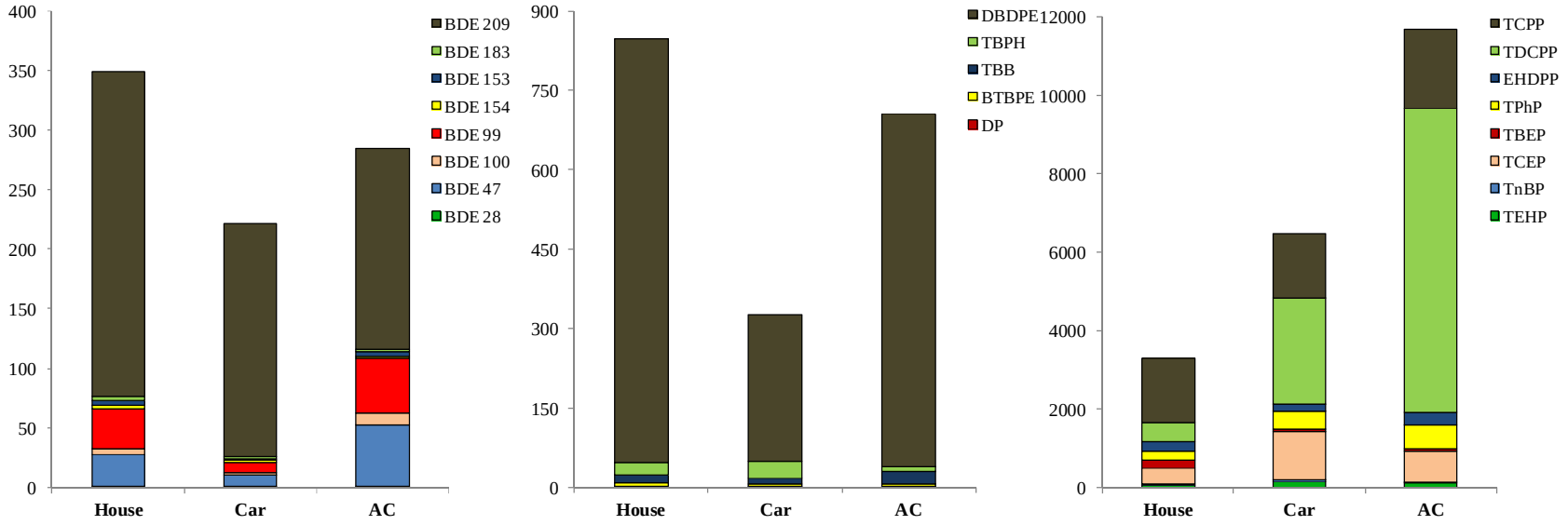
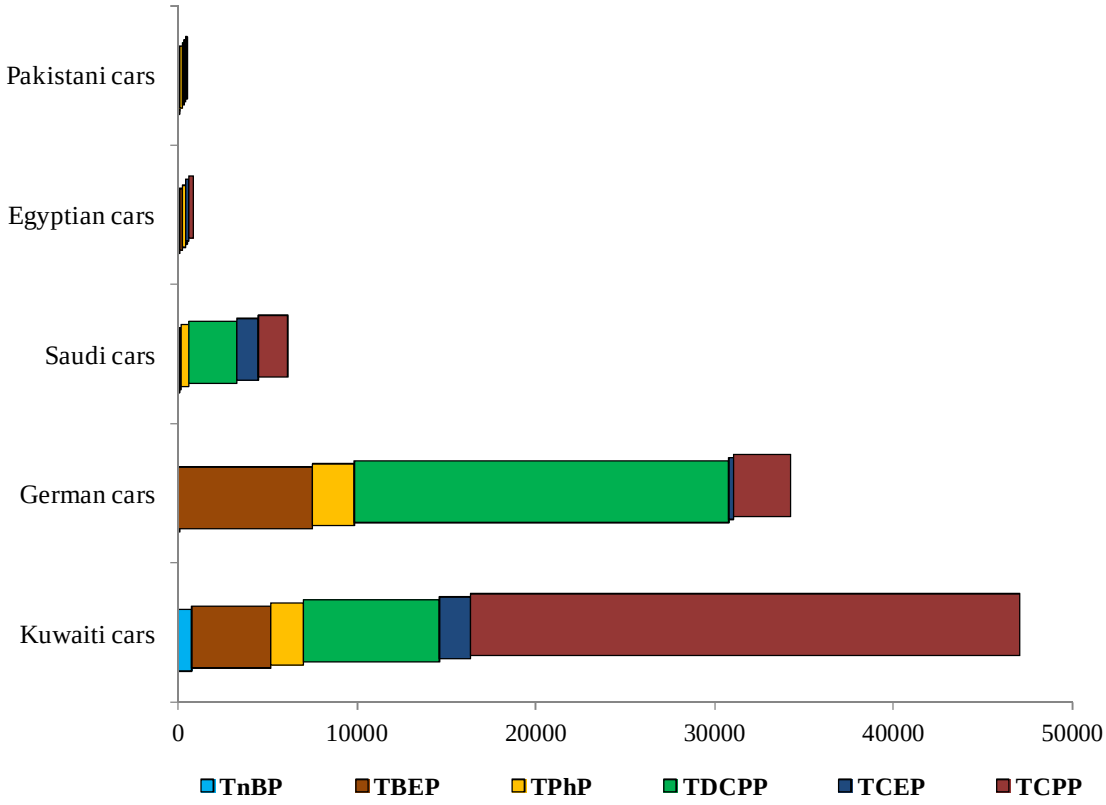


Figure 2. Levels and comparative profile of analyzed FRs in household floor, AC-filter and car dust.



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507 **Figure 3.** Comparison of selected PFRs levels and profile between Saudi cars and car
508 dust data from other countries [(a). Ali et al., 2013a; (b). Brommer et al., 2012, (c).
509 Current study, (d). Abdallah et al., 2014]. Levels on the Y-axis are given in ng/g of dust.

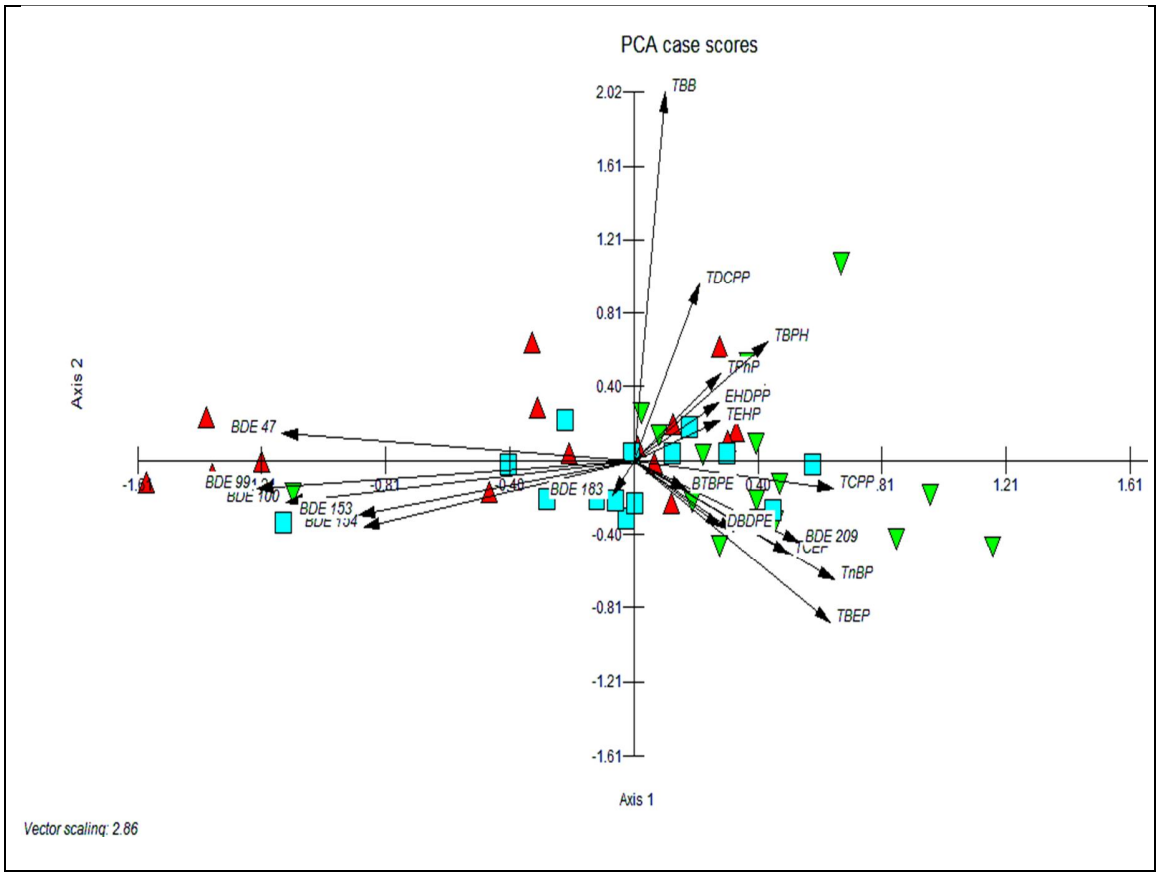

Figure 4. Two-dimensional principal component score plot showing the chemical patterns of analyzed FRs in studied dust samples collected from different microenvironments.

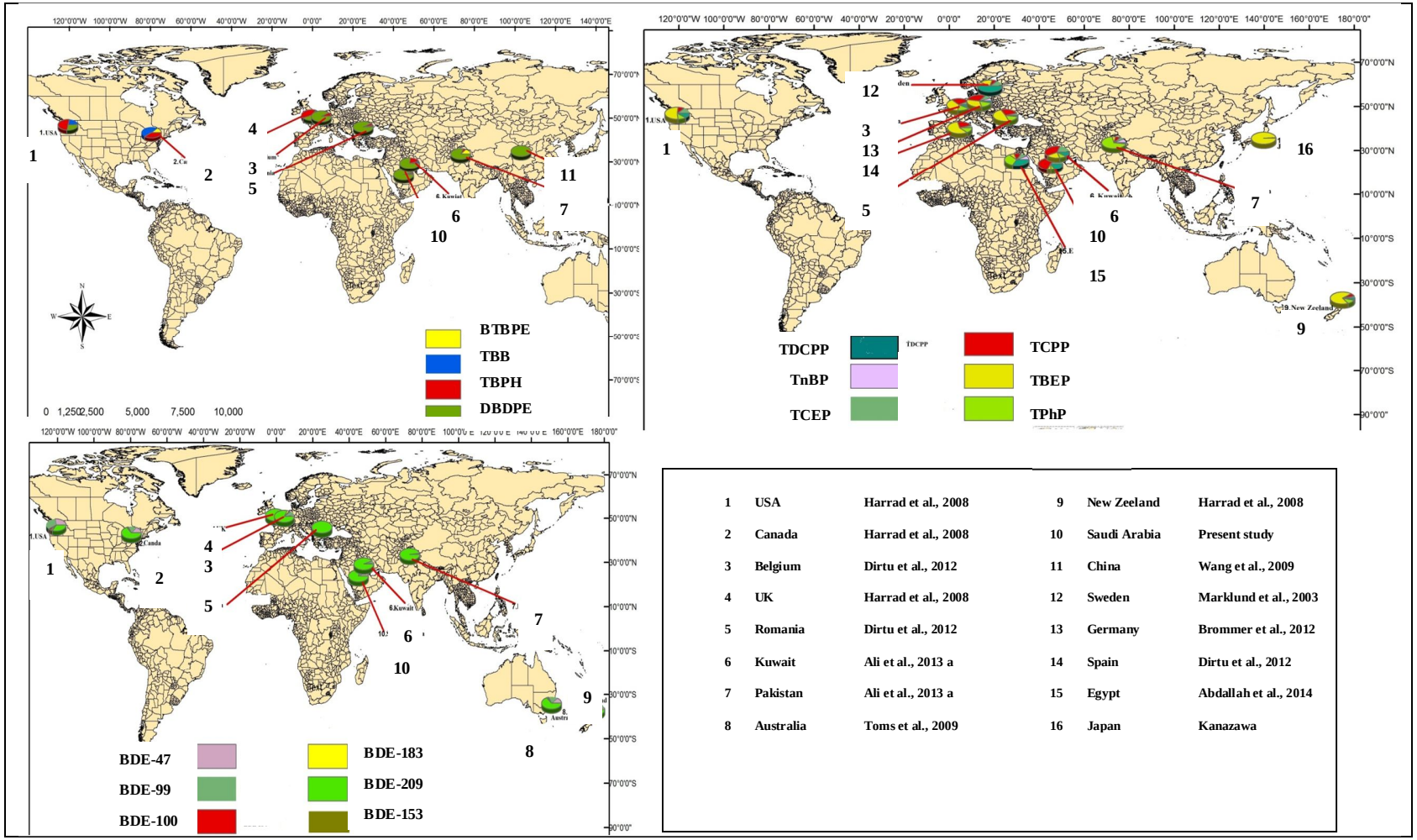

Figure 5. Comparison of selected PBDEs, emerging BFRs, PFRs levels and profile in dust from KSA (10) with data from other countries.