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CHAPTER 5

Emerging halogenated flame retardants in the indoor environment

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ABSTRACT

Indoor environments are considered an important contributor to external human exposure to halogenated flame retardants (HFRs) due to the large amounts of chemicals currently incorporated in indoor equipment and the time humans spend every day in indoor environments. In this chapter, the presence and use of novel brominated flame retardants (NBFRs), dechlorane plus (DPs), chlorinated organophosphorus flame retardants (Cl-PFRs) and chlorinated paraffins (CPs) in indoor dust, air and consumer products collected from different indoor microenvironments (homes, public indoor spaces, and vehicles) are discussed. While data on the concentrations of HFRs in indoor dust and air are widely available, figures are still scarce for consumer products, such as textiles and foams, furnishings, flooring, electric and electronic products and building materials. This knowledge gaps still represents the biggest obstacle in linking eventual sources of contamination to the presence and chemical patterns in indoor dust and air.

KEYWORDS

Emerging halogenated flame retardants; novel brominated flame retardants; dechlorane plus; chlorinated phosphorous flame retardants; chlorinated paraffins; indoor dust; indoor air; consumer products

INTRODUCTION

Flame retardants (FRs) are chemicals added to products such as furniture, textiles, electric and electronic devices and building materials, both to prevent combustion and to delay the spread of fire after ignition [19,82]. Due to their high-performance efficiency and low cost, brominated FRs (BFRs) have been one of the largest groups of additive flame retardants on the market. Because they are not chemically bound to polymers, BFRs may easily leach from the products into the environment [57]. Among BFRs, polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and 3,3',5,5'-tetrabromobisphenol A (TBBPA) have been the most important and widely used groups of additives. As a consequence, PBDEs have become widespread environmental pollutants and, due to their persistent, bioaccumulative and toxic properties [43], the use and production of technical PBDE mixtures (i.e. Penta-, Octa- and Deca-BDE) have been phased-out, restricted or regulated by both the European Union (EU) and North America [82]. These restrictions have led to a shift in the current usage of BFRs, consequently opening the way for the introduction of other/emerging halogenated flame retardants (HFRs), used as replacements to comply with fire safety regulations in commercial products [19,84]. These replacements include:

- *Novel brominated flame retardants (NBFRs)*, increasingly used as substitutes for certain banned PBDE commercial formulations. Among them, decabromodiphenylethane (DBDPE) is used as an alternative for the now restricted Deca-BDE in different polymeric materials and textiles; 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) as a replacement for Octa-BDE in ABS, thermoplastics, polycarbonate and coatings; bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) as a replacement for Penta-BDE in polyvinyl chloride (PVC) and neoprene, PUF, soft foams, wire and cable insulation, carpet backing, coated fabrics, and wall coverings [19,38], and important components of the Firemaster 550 product with a ratio 4:1 respectively [2]. Hexabromobenzene (HBB) is mainly used as an additive BFR to woods, textiles, electronic and plastic goods, while pentabromoethylbenzene (PBEB) is mostly used in thermoset

polyester resins (circuit boards, textiles, adhesives, wire and cable coatings and polyurethane foam). These two compounds are classified as low production volume chemicals [19].

- *Dechlorane Plus (DP)*, a highly-chlorinated FR used in cable coating, computer monitors, furniture and plastic roofing materials [38,77]. The technical formulation is composed of two isomers, *syn*- and *anti*-DP, in a ratio of about 1:3. DP has been identified by the European Commission as a possible replacement for the Deca-BDE technical mixture and has become an emerging compound due to its use and high production volume, ubiquitous presence in the environment and susceptibility to long-range atmospheric transport [77].
- *Halogenated organophosphorus FRs*, mainly used for their flame-retardant properties (henceforth called chlorinated phosphorus flame retardants, Cl-PFRs) as alternatives for BFRs. Tris(1-chloro-2-propyl)phosphate (TCIPP) represents approximately 80% of the Cl-PFR market in Europe and is, by volume, the most important PFR. Tris(1,3-dichloro-2-propyl)phosphate (TDCIPP) is used as an additive FR in resins and foams, mostly in the automotive and furniture industry. Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate (V6) is chemically similar to TCIPP and TDCIPP and has a similar usage pattern, mainly applied to polyurethane foam commonly found in furniture and vehicles [25]. Tris(2-chloroethyl)phosphate (TCEP) has been mostly used in the PVC industry. The Cl-PFRs are considered carcinogenic and have proven to have other negative effects on human health, suggesting that these PFRs would not be suitable alternatives for BFRs [82].
- *Chlorinated paraffins (CPs)*, a complex mixture of thousands of individual compounds used as plasticizers, FRs and additives in rubbers, plastics, paints, coatings, sealants and adhesives [63]. Manufactured since the 1930s, CPs are high production volume chemicals classified by carbon chain length as short (SCCPs; C₁₀-C₁₃), medium (MCCPs; C₁₄-C₁₇) and long (LCCPs; C_{>17}) and by the degree of chlorination (30-70% w/w) [30,62]. Because of their widespread presence in the environment [62,89,92], as well as their persistent, bioaccumulative and toxic properties, SCCPs were classified in May 2017 as persistent organic pollutants (POPs) by the UN Environment Stockholm Convention with few exemptions [81].

To date, the timing, location, degree and pathways of human exposure to these pollutants are considered strictly related to human activities [51]. In addition, the importance of activity pattern data has increased more and more with the realization that exposure to environmental pollutants likely occurs indoors and is mainly related to indoor pollutant sources [51,60,65]. The time people spend at home or in public places, as well as the number of studies which evaluates the quality of these indoor environments, has significantly increased during the past decades [38,56]. According to the American National Human Activity Pattern Survey (EPA-NHAPS), people spend an average of 92% of their time indoors (i.e. 87% in enclosed buildings, such as at home and in public spaces, and about 5% in vehicles) and only about 8% of their time outdoors (Fig. 5.1) [51].

In this chapter, an overview of the main classes of emerging HFRs present or used in different matrices (dust, indoor air, and consumer products) and measured in the three major categories of indoor microenvironments (homes, public indoor spaces, and vehicles) is reported and discussed.

Insert Figure 5.1 here.

EMERGING HALOGENATED FLAME RETARDANTS IN INDOOR DUST

The term indoor dust generally refers to particles with diameters in the μm -mm range that are deposited in indoor spaces [68]. Acting as a repository for organic compounds, indoor dust is often used to evaluate levels of HFRs [42] and is generally collected by suction with a plain filter or with a commercially available vacuum cleaner bag, by surface wiping, or by passive sampling with collecting devices [68]. The most common technique is to collect floor dust, although elevated surface dust can also be used, potentially affecting the levels of contamination detected [3,42,83]. However, while reading this chapter, it is necessary to keep in mind that most studies covering single/multiple indoor environments do not account for this difference and, in order to limit the influence of spatial heterogeneity, single dust samples are often considered representative of whole-room or even whole-building conditions [3].

Homes

Novel brominated flame retardants and Dechlorane Plus

The main contributor to the concentration levels of NBRs in household dust was DBDPE, detected in 100% of the reviewed studies. With its production volume continuously increasing near to 80% per year, DBDPE expectantly dominates over the other NBRs [88]. Black hard plastic material, mainly found in electrical and electronic equipment, insulation foams and rubber kitchen utensils were suggested as possible primary sources of DBDPE contamination, while imported electronic products from Japan and China could be mostly related to the high levels of the other NBRs [58]. High concentrations of DBDPE were reported in home dust from Australia (median: 1.6 µg/g) [58]. In this study, DBDPE concentrations were measured 2-3 orders of magnitude higher than the other considered NBRs (BTBPE, EH-TBB, HBB, PBT and PBEB) and generally 1-2 times higher than the concentrations of the same compound in other studies worldwide [21,52,76]. BTBPE is another NBR frequently detected in indoor dust, though typically at lower concentrations than DBDPE [58]. BTBPE is the main additive in the FF-680 product [53]. Possible emission sources for the indoor environment are the hard-plastic parts of electronic equipment. These materials are mostly fabricated from acrylonitrile butadiene styrene polymers (ABS) to which BTBPE is frequently added [2,58]. Homes located in Turkish urban areas presented high levels of BTBPE (median: 0.4 µg/g) [53]. Remarkable TBPH levels were reported in China (median: 1.6 µg/g) with values that, surprisingly, exceeded those of DBDPE [10]. DP concentrations were reported in urban areas of Canada (Vancouver) and USA (California) (mean: 30 ng/g; median not available – n.a.) [23,72], in Chinese dormitories (median: 60 ng/g), homes in Nepal (median: 0.5 ng/g) and Turkish homes in urban (median: 0.3 ng/g) and suburban regions (median: 0.3 ng/g) [53,76,95].

Chlorinated PFRs

Concentrations of Cl-PFRs were measured in household dust samples collected from 63 homes in Canada, the Czech Republic and the United States. Among the three countries, the highest concentrations of Cl-PFRs were found in US dust, with medians of 3.7 µg/g (TDCIPP) and 2.8 µg/g (TCIPP), while the lowest median

concentrations were measured for TCEP in the Czech Republic (0.16 µg/g) [86]. Similar levels of Cl-PFRs were investigated in 39 residential home dust samples collected in Beijing, China, where TCIPP was measured at a median concentration of 1.4 µg/g, followed by TCEP (0.8 µg/g) and TDCIPP (0.12 µg/g) [11]. Comparable Cl-PFR median levels were also measured in living room floor dust from Australia, Canada, Germany and Kazakhstan [31]. TCIPP was the most abundant Cl-PFR in Australia (1.8 µg/g), Canada (1.2 µg/g), and Germany (1 µg/g), while TCEP was the main contaminant in Kazakhstan (1.4 µg/g) [31]. The median concentration of TCIPP was of the same order of magnitude (5.2 µg/g) in floor dust (n=92) collected from Texas, US [6], and in indoor dust from 20 apartments and houses in Araraquara-SP (Brazil), where TDCIPP was measured at a median concentration of 2.3 µg/g [20].

Significantly higher concentrations were instead measured in floor dust collected from UK living rooms (n=32), with TCIPP being the predominant Cl-PFR (median: 21 µg/g), followed by TCEP (0.81 µg/g) and TDCIPP (0.71 µg/g) [8]. The elevated concentrations of TCIPP in UK living room dust were linked by the authors to the favoured use of these PFRs in UK couch foam. Similarly, the TCIPP median concentration in indoor dust samples from UK houses (64 µg/g) was found to be 30 times higher compared to Norwegian household dust (2 µg/g) [44]. These findings were attributed by the authors to higher TCIPP usage in the UK as a replacement for TCEP, while the use of TCIPP in Norway has decreased during the past decade. Also the median concentrations of TDCIPP and V6 in UK house dust were higher (0.75 µg/g and 0.02 µg/g) than in Norwegian houses (0.34 µg/g and 0.004 µg/g), respectively [44].

Dust samples collected from 25 apartments in Alexandria, Egypt, reported low median concentrations of TDCIPP (0.08 µg/g) and TCIPP (0.03 µg/g) [48], similar to those measured in house dust from Nepal (TCIPP, 0.06 µg/g; TDCIPP, 0.02 µg/g; TCEP 0.015 µg/g) [97].

Chlorinated paraffins

Due to difficulties in analysing CPs with longer carbon chains (>C₁₈), most of the research to date has focused on SCCPs and MCCPs in indoor dust. SCCP and MCCP homologues have regularly been detected in dust samples from homes throughout the world and are often present at concentrations which exceed

those of other legacy HFRs, such as PBDEs [92]. The highest levels reported in the literature so far were recorded in homes surrounding an industrial park which recycles electronics, PVC and plastics in China [13]. Here, Σ SCCPs ranged from 35 to 2,030 $\mu\text{g/g}$ in homes (mean: 580 $\mu\text{g/g}$; median n.a.), while Σ MCCPs levels were approximately 2-3 times higher, ranging from 79 to 6,510 $\mu\text{g/g}$ (mean: 1,760 $\mu\text{g/g}$; median n.a.). CP concentrations in dust from control homes (i.e. >30 km away from the plant) were significantly lower, with Σ SCCP levels ranging from 28 to 173 $\mu\text{g/g}$ (mean: 59 $\mu\text{g/g}$; median n.a.) and Σ MCCPs ranging from 74 to 539 $\mu\text{g/g}$ (mean: 185 $\mu\text{g/g}$; median n.a.). The mechanisms of CP transfer from recycling processes to the interior of nearby homes are unclear but may be related to atmospheric transport through ventilation systems and windows or via direct transfer into homes on the clothing of workers from the plant. The concentrations in control homes were, in any case, also among the highest in the world. Levels in the dust of Chinese homes have typically exceeded those of samples from North America or Europe, perhaps due to China's role as the world largest CP manufacturer. Gao et al. (2018) [29] reported similarly elevated mean Σ SCCP and Σ MCCP levels combined from Chinese homes, workplaces and dormitories of 148 and 139 $\mu\text{g/g}$, while Σ SCCPs averaged 49 $\mu\text{g/g}$ in dust from Chinese apartments (medians n.a.) [55]. Interestingly, levels of MCCPs measured in dust from homes in Germany were of the same order as those from China, ranging from 8 to 892 $\mu\text{g/g}$ (median: 176 $\mu\text{g/g}$), while SCCPs were much lower, ranging just <LOQ-27 $\mu\text{g/g}$ (median: 5 $\mu\text{g/g}$) [36]. The comparatively low levels of SCCPs may be related to regulations and restriction on the usage of the shorter chain groups in the EU from as early as 2004 [24]. Levels were yet lower in Sweden, where combined short and medium CPs ranged from 3.2 to 18 $\mu\text{g/g}$ with a median of 7.5 $\mu\text{g/g}$ [27].

One study of Canadian dust samples found concentrations to be, overall, similar to those of the European studies, with Σ SCCPs ranging from 4 to 57 $\mu\text{g/g}$ (median: 6.2 $\mu\text{g/g}$) and Σ MCCPs ranging from 6 to 901 $\mu\text{g/g}$ (median: 19 $\mu\text{g/g}$) [70]. A separate study on 4 Canadian samples however, suggested higher levels with Σ CPs ranging 280-392 $\mu\text{g/g}$ [92]. This work revealed that the relative abundance of short-, medium- and long-chained homologues ranged 6-17 %, 48-50 % and 33-44 %, respectively. Conversely, LCCPs were the least prevalent homologue group in dust from homes in Australia (n=27), averaging 3 $\mu\text{g/g}$ (range; <0.0014-15 $\mu\text{g/g}$), while SCCPs had a mean of 13 $\mu\text{g/g}$ (range; 1.0-42) and MCCPs 110 $\mu\text{g/g}$ (range; 8.8-380 $\mu\text{g/g}$)

(median n.a.) [34]. These studies indicate that LCCP usage varies between countries but may be present at substantial levels and thus should be included in analyses wherever possible.

Indoor public spaces

Novel brominated flame retardants and Dechlorane Plus

The NBFR with the highest concentration level was TBB in fire stations from California (median: 2.7 µg/g) [9]. However, this was attributed by the authors to the “tracking back” event that frequently occurs in fire stations, i.e. the importation of FRs after each extinguishing fire mission which inevitably could result in higher levels of NBFRs. TBB was also the dominant FR in offices located in suburban areas of Turkey (median: 0.95 µg/g) [53], followed by HBB (median: 0.6 µg/g), whereas BTBPE was found as the main FR (median: 0.8 µg/g) in Turkish offices located in urban areas, indicating its possible specific application in professional equipment/environments [2].

DBDPE was found at high levels in Australian offices (median: 1.9 µg/g, year of collection: 2016), higher than in homes and vehicles [58]. Lower levels of DBDPE were found in Belgian offices (median: 0.7 µg/g, year of collection: 2008) [2], Spanish theatres (median: 0.65 µg/g) and universities/institutes (median: 0.6 µg/g) [21]. Interestingly, theatres were the most contaminated environments with NBFRs (DBEPE, BTBPE, TBPH and TBB) among homes, universities, institutes and schools [21]. The typology of new materials reported in this public indoor environment (e.g. polyurethane foam furniture, textiles and audio-visual electronic equipment) may have acted as a continuous emission source. However, no other studies investigating the presence of NBFRs in theatres were available for review to further support this hypothesis.

DPs were frequently measured in working environments, often at higher concentrations than in household and car dust. The highest levels were detected in Turkish (mean: 1.3 µg/g; median n.a.) and Spanish offices (mean: 1 µg/g; median n.a.) [53,67].

Chlorinated PFRs

Cl-PFRs were investigated in indoor dust collected from newly built low-energy preschools in Sweden and TDCIPP was detected in all samples at concentrations ranging from 0.014 to 10 µg/g [66]. Higher concentrations were measured in school and child day-care centre classrooms (n=28) and offices (n=61) in the UK, where the median concentrations of TCIPP (16 µg/g and 33 µg/g in classroom and offices, respectively) were significantly higher than TCEP (up to 0.8 µg/g) and TDCIPP (up to 0.5 µg/g) [8]. TCIPP was also the most relevant compound in dust samples from German offices (n=25), with a median concentration of 1.6 µg/g followed by TDCIPP (0.14 µg/g) and TCEP (0.13 µg/g), while TCEP was mostly responsible for the contamination of dust in offices in Kazakhstan (n=8) with median levels of 2.5 µg/g, followed by TCIPP (2.2 µg/g) and TDCIPP (0.9 µg/g) [31].

The presence of Cl-PFRs was also investigated in indoor dust samples from British stores (n=6) and offices (n=6). TCIPP (median 26 µg/g) was the predominant Cl-PFRs in UK occupational dust, higher than TDCIPP (1.2 µg/g), TCEP (0.9 µg/g) and V6 (0.04 µg/g) [44], while dust samples collected from 14 working places in Alexandria (Egypt) and 10 offices and primary schools in Araraquara-SP (Brazil) showed that TDCIPP had higher median concentrations than TCIPP (0.1 µg/g vs 0.05 µg/g in Egypt and 4.5 µg/g vs 1.8 µg/g in Brazil, respectively) [20,48]. The presence and levels of Cl-PFRs were investigated in 13 dormitory and 49 office dust samples collected in Beijing, China [11]. Their concentrations were significantly higher in the dust collected from offices (average sum Cl-PFRs: 9.6 µg/g) compared to the dormitories (3.3 µg/g) ($p < 0.05$). The high fraction of TCEP and TCIPP in dust from China can be related to their extensive use in floor wax, PVC coverings, textiles, and polyurethane foam [11].

Chlorinated paraffins

Investigation of CPs in the dust of office spaces may provide special insights into the fate of contaminants due to the high density of electronic equipment like computers and printers, as well as the faster replacement rate of products relative to the domestic environment. At present, however, very few wide-ranging studies on CPs have been conducted in offices spaces. Σ SCCP levels were of a similar order in Chinese offices as those observed in apartments from the same study, ranging from 41 to 81 µg/g (mean:

56.3 µg/g; median n.a.) [55]. Likewise, offices and homes had comparably low Σ SCCP concentrations ranging 5-31 and 11-14 µg/g in a limited number of Taiwanese dust samples (n=4) [16]. On the other hand, Gao et al. (2018) reported offices to be the least contaminated indoor environments amongst Chinese indoor microenvironments assessed with respect to both SCCP and MCCP homologues [29]. CP levels measured in a limited number of office samples from outside China have usually exceeded levels seen in homes. Hilger et al. (2013) determined Σ SCCP concentrations of 269-2050 µg/g in two samples from an official building in Germany, 2-3 orders of magnitude greater than those measured in German households, though MCCPs were not detected in the same samples [36]. Combined short-, medium- and long-chained CP concentrations in office dust from Australia (n=1), China (n=5), Sweden (n=3) and the UK (n=1) were 340, 590-4,750, 675-1,330 and 713 µg/g, respectively [92]. Except for the Swedish samples, MCCP homologues were typically dominant in dust, accounting for 41-65 % of CPs in most samples while LCCPs generally contributed 22-44 % and SCCPs 6-18 %. The relative abundance of homologue groups within Swedish offices samples varied greatly compared to samples from other countries, however, with relative abundances of 81-95 % for LCCPs, 5-18 % MCCPs and just 0.5-1 % SCCPs. These homologue patterns may be symptomatic of the Swedish government's efforts to reduce imports and usage of SCCPs in the country [27,92]. Mean levels of SCCPs, MCCPs and LCCPs in dust from Australian offices were each elevated by approximately 50% with respect to homes assessed in the same study at 18, 180 and 4.7 µg/g, respectively [34].

With regard to public spaces outside of offices, a study investigating CP levels in dust from a newly opened shopping mall in China found SCCP and MCCP levels to be approximately equal, ranging from 115-707 µg/g (mean: 322 µg/g, median n.a.) and 89-1,083 µg/g (mean: 277 µg/g, median n.a.), respectively [71]. Dust analysed from a building materials shop in the same study observed lower levels ranging 6-361 µg/g (mean: 113 µg/g; median n.a.) Σ SCCPs and 5-286 µg/g (mean: 116 µg/g; median n.a.) Σ MCCPs. Concentrations of SCCPs and MCCPs were strongly linearly correlated ($p < 0.01$) to suggested that they are released from similar sources and, hence, likely applied in conjunction with materials present in these two malls. SCCP

levels were lower again in a separate study assessing concentrations in dust from 22 commercial stores in China, with a mean level of 58 µg/g and range of 13-173 µg/g (medians n.a.) [55].

Vehicles

Novel brominated flame retardants and Dechlorane Plus

DBDPE was found to be the main contributor to the indoor dust car contamination, reaching high concentrations in Australian cars (median: 1.9 µg/g) [58] compared to the rest of the studies reported below, confirming the dominance of DBDPE in indoor environments. However, in the same study, TBB was the most frequently detected NBFR in dust sampled from the dashboards, floors and doors of vehicles (median: 0.021 µg/g), attributed to its presence in the commercial products FireMaster 550 and FireMaster BZ-54, used in soft polymers as parts of upholstery, door linings and floor covering [58]. Significant levels of DBDPE were also reported in cars from Greece (median: 0.9 µg/g) and Kuwait (0.2 µg/g) [1,5]. In the Greek study [5], further correlations between the levels of NBFRs and specific parameters (e.g. age of the car, type of ventilation, type of car seat, type of fuel) suggested an increasing trend of NBFRs compared to legacy BFRs (PBDEs) for the newer cars. The type of ventilation was also found to be a relevant factor influencing the NBFR contamination of cars, as the concentrations of total NBFRs were 3 times higher in cars with frequent A/C ventilation. No significant correlation was found related to the type of car seat (fabric or leather) or the fuel type (gas or diesel) [5].

High median concentrations were also reported for TBPH in Greek cars (0.09 µg/g) [5], but the ratio of TBPH/TBB was different than the expected ratio in the commercial mixture FireMaster 550, suggesting the use of TBPH as a plasticizer in PVC and neoprene, materials that can be found in various parts of the car interior, rather than as FR [5].

DP concentrations in car dust had a mean value of 0.05 µg/g (median n.a.) [35]. This study investigated the role played by the dust particle size in influencing the NBFR concentration and an increasing trend was observed along with the decrease of the particle size. Even though there was no statistical correlation reported, the authors suggested that DPs, due to their hydrophobicity ($\log K_{ow} \geq 9$) and their application as

FRs to softer materials, such as cotton and polyester, can be easily transferred to dust through abrasion [35] and this may result in high levels in car dust. Conversely, DPs were reported at low median levels in car dust in Saudi Arabia (*syn*-DP: 0.003 µg/g and *anti*-DP: 0.001 µg/g). Low median levels of DPs were also found in Egyptian car dust (*anti*-DP: 0.001 µg/g and *syn*-DP: 0.002 µg/g) [33].

Chlorinated PFRs

Particularly high median concentrations of TCIPP (53 µg/g) and TDCIPP (31 µg/g) were measured in UK car dust samples and foam particles [8] and in indoor dust from 16 cars in Araraquara-SP (Brazil) where TDCIPP had a remarkably high median concentration (up to 506 µg/g) [20]. Lower concentrations of Cl-PFRs were instead measured in car dust from Australia (n=39) and Germany (n=19) with median levels of 2 and 0.4 µg/g for TCEP and 24 and 2.9 µg/g for TCIPP, in the two countries respectively [31]. Even lower concentrations of Cl-PFRs were measured in dust samples collected from the interior of 25 private cars in Greece, with different years of manufacture (1997-2015) and continents of origin [17]. In this study, TCIPP was the most detected compound, with a median concentration of 2.6 µg/g, followed by TDCIPP (2.5 µg/g), TCEP (0.1 µg/g), and finally V6 (0.01 µg/g). V6, in particular, is used as FR in treated polyurethane foam in the automotive industry. It has similar chemical properties to TCIPP and TDCIPP and combinations of these three compounds are known to be applied in products with a higher need for meeting the safety standards [82]. Similar median concentrations of TCEP (2.7 µg/g), TDCIPP (1.4 µg/g), and TCIPP (1.2 µg/g) were measured in dust collected from 25 car cabins in Japan [80]. In Egypt, TCIPP median concentration (0.2 µg/g) in dust samples collected from 18 cars was higher than TDCIPP (0.09 µg/g) [48].

Chlorinated Paraffins

The only study to investigate CPs in dust from vehicles determined the compounds in each of seven samples from buses, trains and planes with an overall range of 2.2-370 µg/g [34]. MCCPs accounted for a substantial proportion of overall concentration with a mean of 270 µg/g (range: 110-370 µg/g), while levels of the SCCPs and LCCPs were similar with averages of 13 and 8.3 µg/g, respectively.

EMERGING HALOGENATED FLAME RETARDANTS IN INDOOR AIR

Air samples are usually collected either by active (e.g. high volume samplers) or passive samplers (e.g. PUF disks) [54]. Indoor active sampling methods are typically accurate, but also potentially intrusive, noisy, and relatively expensive [7,56]. On the contrary, passive samplers are cheap, user friendly and moderately discreet [7,56], but they primarily sample the gaseous phase, likely underestimating the concentrations of highly brominated compounds predominantly associated with particulates [22,54]. In this chapter, HFR data obtained by collecting indoor air samples by deploying either active or passive samplers are reported, without conducting any systematic investigation of the potential influence of different sampling methods on the contamination levels.

Homes

Novel brominated flame retardants and Dechlorane Plus

The occurrence of several HFRs was investigated in indoor air samples collected from 47 residential living rooms in the greater Oslo area, Norway [12]. PBEB and HBB were measured at median concentrations of 0.53 and 4.1 pg/m^3 , respectively, while TBPH, DBDPE and DP were always below the detection limits [12]. Similar HFR concentrations were obtained in indoor air samples from 15 UK homes [78]. Among them, HBB, PBEB, TBB, TBPH and BTBPE were frequently detected in air samples, with median concentrations of 4.2, 1.3, 2, 2.1 and 5 pg/m^3 , respectively, while DBDPE and DP were <LOD [78]. In the same order of magnitude, the concentrations of emerging HFRs were measured in indoor air from 63 homes in Canada, the Czech Republic and the US [83]. TBB and TBPH were among the most frequently detected non-PBDE compounds, generally higher in the US (medians: 9.2 and 6 pg/m^3 , respectively) and Canada (12 and 3.1 pg/m^3) than in the Czech Republic (5.5 and 3.2 pg/m^3), reflecting their higher usage in North America compared to Europe. The same trend was revealed by the concentrations of BTBPE measured in indoor air, with the highest median levels measured in the Canadian samples (1 pg/m^3). DBDPE was also a major alternative FR detected in North American indoor air, with a median level for the Canadian samples (9.2 pg/m^3) significantly lower than for the US (42 pg/m^3), but it was not detected in the European samples. Median

PBEB and HBB concentrations in indoor air samples from Canada (3.9 and 5.8 pg/m^3 , respectively) were generally higher than those from the US (1.9 and 4 pg/m^3) and from the Czech Republic (0.5 and 4.6 pg/m^3). Finally, DP was frequently detected in both the US and Canadian indoor air samples, with median concentrations of 0.4 and 38 pg/m^3 , respectively, but in only one Czech air sample, albeit with a higher value (65 pg/m^3) [83]. Similar results were found also for indoor air concentrations of NBRs and DP, determined at private residences located both in the urban area and nearby semi-rural areas around Brno, in the Czech Republic [59]. Here, two sampling campaigns, one in summer (n=17) and one in winter (n=20), were conducted to address the potential seasonal variability. Median indoor air concentrations of PBEB (0.04 pg/m^3 in summer vs 0.08 pg/m^3 in winter), HBB (0.94 pg/m^3 in summer vs 1.1 pg/m^3 in winter) and BTBPE (0.23 pg/m^3 in summer vs <LOD in winter) were generally constant throughout the year, while a significant difference was noticed for DP, with median values of 54 pg/m^3 in summer and <LOD in winter [59].

Conversely, higher levels of DBDPE were measured in domestic air samples, representative of the residential areas in Guangzhou, a megacity in southern China with rapid economic development [22]. Median DBDPE concentrations in indoor air samples were found between 50 and 110 pg/m^3 , most likely originating from the great number of industrial zones distributed across Guangzhou and spread over the city [22]. Even higher levels of DBDPE (median: 424 pg/m^3) were measured in indoor air from four major cities of Nepal [96] and were generally higher than those observed in the US, Canada [83], China [22], and Europe [12,78,83], suggesting its prominent use in Nepal as alternative FR. The concentrations of other NBRs measured in the same study ranged from 13.2 to 6,270 pg/m^3 (median: 316 pg/m^3), while DP was in the range 0.7-129 pg/m^3 (median: 3.3 pg/m^3) [96].

Relatively high median concentrations of HBB, TBB and TBPH were found also in Turkish indoor air from 10 homes in urban, semi-urban and rural neighbourhoods of Istanbul, Turkey [53]. HBB median concentration was much higher in urban (580 pg/m^3) than semi-urban (2.7 pg/m^3) environments, while a different behaviour was observed for the measured concentrations of TBB (150, 840 and 100 pg/m^3 in urban, semi-urban and rural areas, respectively). DP and TBPH, on the contrary, were found in similar median

concentrations in indoor air from urban (5.6 and 2.8 pg/m³, respectively), semi-urban (6 and 3 pg/m³, respectively) and rural (5.5 and 2.7 pg/m³, respectively) areas [53].

The HFR concentrations in indoor air collected from the living room of Norwegian households were measured in both stationary (total median: 220 pg/m³) and personal (410 pg/m³) air samples [79]. Also noteworthy in this study was the relatively high median concentration observed for TBB (150 pg/m³), while TBPH and DBDPE were found at lower median levels (3.8 and 1.2 pg/m³, respectively) [79]. Generally lower HFR contamination levels were instead measured in indoor air samples collected from the living rooms of rural and background residences in the Punjab province, Pakistan [49]. The sum of six NBFRs (HBB, PBEB, TBB, TBE, TBPH, and DBDPE) in rural and background areas ranged from <LOD to 13 pg/m³ and from <LOD to 1.2 pg/m³, respectively, while DP levels in the same sites were between 0.08 and 7.8 pg/m³ and between <LOD and 0.2 pg/m³, respectively [49].

Chlorinated PFRs

Concentrations of Cl-PFRs were measured in indoor air samples collected from 63 homes in Canada, the Czech Republic and the US [86]. The highest median concentrations among Cl-PFRs were measured for TCIPP, with Canadian home values (74 ng/m³) significantly higher than the US (26.3 ng/m³) and Czech Republic (16.4 ng/m³). TCEP median concentrations in Canada and US (up to 7 ng/m³) were significantly higher than in the Czech Republic (< 3 ng/m³), while no significant differences between countries were found for TDCIPP. The lower air concentrations of TCEP compared to TCIPP may be explained by the recent restrictions on the uses of TCEP and the associated rising usage of TCIPP [86]. TCIPP was also the compound with the highest measured median concentration (89 ng/m³) in air samples from houses in Sapporo, Japan [46]. A comparable median concentration of TCIPP (42 ng/m³) was measured in air from the living room of 47 Norwegian households [12], while lower Cl-PFR concentrations were measured in indoor air samples from private homes (n=7) in the Rhine/Main area, Germany (median concentration of 5.2 ng/m³) [100] and in home air samples from Beijing, China, with TCIPP as the dominant compound (mean concentration 3.8 ng/m³) [11]. Cl-PFRs generally dominated also in indoor air from 16 apartments in Alexandria, Egypt, but

with much lower concentrations, with TCIPP (median: 5 pg/m³) and TDCIPP (median: 3 pg/m³) as major compounds [48].

Chlorinated paraffins

Short- and medium-chained CPs have been reported in the indoor air of homes in a small number of studies. Fridén et al. (2011) [27] detected CPs in 89% of 44 samples from the living rooms of apartments in Sweden, with combined SCCP and MCCP concentrations ranging from <5-210 ng/m³ (median: 65 ng/m³). SCCPs were dominant in samples overall, while homologues with carbon chain lengths of C₁₀ and C₁₁ were the most prevalent. Fridén et al. (2011) [27] noted that concentrations were highly variable in air samples between buildings, but also between apartments sampled from the same building. This suggests that, while building materials may contribute to CP levels indoors, the contents of individual homes provide putative local sources of contamination. In contrast to the dominance of SCCPs reported by Fridén et al. (2011) in Swedish samples, however, Σ MCCP levels were approximately twice that of Σ SCCPs across samples from 24 Chinese homes [102], which ranged 5.4-182 ng/m³ and 2.9-52 ng/m³, respectively. Findings by Zhuo et al. (2019) [102] also showed levels of CPs in indoor air to be two times those measured in outdoor air, further suggesting household goods and materials to be likely sources of CP release to the indoor environment. Congeners of the C₁₄ homologue deriving from MCCP technical mixes contributed a mean of 27% to total CPs, while the SCCP C₁₁ homologue was the next most abundant, with an average of 18% in samples. Another study investigating Chinese homes determined very similar homologue distributions with C₁₄ MCCPs dominating total CP levels followed by C₁₀ and C₁₁ SCCPs [101]. Concentrations ranged 11-18 ng/m³ for Σ SCCPs and 16-41 ng/m³ for Σ MCCPs across 5 samples, which were broadly comparable to the levels in Swedish homes.

The size-distribution of particle-bound CPs in indoor air has also been investigated to reveal that both SCCPs and MCCPs tend to be associated with smaller particles. Zhuo et al. (2019) determined 50-100% of SCCPs in 40 of 46 samples to be associated with particulates of less than 2.5 μ m diameter (PM_{2.5}) [102]. Indeed, Zhou et al. (2018) assessed SCCP and MCCP distribution across 11 different particle size fractions to

find that the greatest concentrations occurred in particles of 0.6-1.0 μm [101]. Seasonal effects to CP concentrations in indoor air have also been indicated by one study which found concentrations of SCCPs and MCCPs in Chinese homes and offices to be generally higher in summer than winter [29]. Although particle- and gas-phase partitioning of CPs has not yet been explored in indoor air, this appears to suggest that higher temperatures cause a greater release of SCCPs and MCCPs from dust or treated products [29]. Partitioning of CPs between the gas-phase and particulates of different sizes are important considerations for ongoing assessment of human exposure to indoor contamination via inhalation.

Indoor public spaces

Novel brominated flame retardants and Dechlorane Plus

The occurrence of several HFRs was investigated in indoor air samples collected from six primary school classrooms in the greater Oslo area, Norway [12]. TBPH, DBDPE, and HBB were measured at median concentrations of <LOD, 8 and 4 pg/m^3 , respectively, while PBEB and DP were not detected in any of the analysed samples [12]. Similar indoor air levels of emerging HFRs were measured from three offices in Beijing, China [64]. The most commonly detected HFR was HBB (97% detection frequency), but it was found at low concentrations (median: 3.6 pg/m^3). TBB and DP were measured on average between <0.6 and 1.7 pg/m^3 and between 17 and 260 pg/m^3 , respectively, while DBDPE was always <LOD [64]. In the same order of magnitude, Tao et al. (2016) measured the concentrations of 27 emerging HFRs in indoor air samples from 20 UK offices [78]. Among them, HBB, PBEB, TBB, TBPH and BTBPE were frequently detected in air samples, with median concentrations of 9.4, 1.7, 5.3, 1.4 and 11 pg/m^3 , respectively, while DBDPE and DP were <LOD. Higher levels were instead observed for DBDPE measured in indoor air samples from two offices in Guangzhou (southern China), with median concentrations of 22 pg/m^3 and 121 pg/m^3 [22]. These relatively high levels of DBDPE were largely attributed to its release from local industrial activities. More recently, HFR concentrations were measured in indoor air from four rooms of a newly constructed university building in the Czech Republic during equipment and furniture installation [85]. The concentrations of $\sum_{23}\text{HFRs}$ (including HBB, PBEB, TBB, TBE, TBPH, DBDPE and DP) ranged from 12.3 to 1820 pg/m^3 , with a median of 158 pg/m^3 . Interestingly, in this study, the highest median concentration was

measured for HBB at 97 pg/m³. Similarly, the total median concentrations of fifteen HFRs in 23 indoor urban air collected from laboratory building on the Stockholm University campus, Sweden, was 120 pg/m³ [93]. Here, TBB had the highest median concentration (70 pg/m³) and was detected in all samples, while HBB (2.9 pg/m³), DBDPE (0.9 pg/m³) and BTBPE (0.55 pg/m³) were detected in much lower concentrations [93].

Relatively higher median concentrations of HBB, TBB and TBPH were found in Turkish indoor air from 9 offices in urban and semi-urban neighbourhoods of Istanbul, Turkey [53]. TBB (480 pg/m³), HBB (190 pg/m³) and TBPH (140 pg/m³) were prevalent in urban areas, while the same compounds in semi-urban environments were significantly lower (26, 1.3 and 2.5 pg/m³, respectively). DP, on the contrary, was found in similar median concentrations in indoor air from urban (5.4 pg/m³) and semi-urban (5 pg/m³) areas [53]. Lower levels of HFRs in indoor air samples were instead collected from working rooms/stores or processing units in industrial zones located in the Punjab province, Pakistan [49]. Here, the sum of six NBFRs (HBB, PBEB, TBB, TBE, TBPH, and DBDPE) ranged from 0.2 to 54 pg/m³, while DP levels in the same sites were between 1.8 and 44 pg/m³ [49].

Chlorinated PFRs

The occurrence of Cl-PFRs in indoor air was investigated in three university buildings in Uppsala, Sweden, including laboratory rooms, lecture rooms, dining areas, a computer room and eight offices. TCEP was the most frequently detected halogenated PFR, with a detection frequency of 73% in all air samples and an average concentration of 120 ± 210 pg/m³ (median n.a.) [69]. In another Swedish city, Stockholm, the presence and levels of Cl-PFRs were measured in 23 indoor air samples, collected from a university office [93]. Here, TCIPP and TCEP in indoor air were found at higher concentrations than in Uppsala, with absolute concentrations of 330 ng/m³ and 11 ng/m³, respectively. Indoor air samples from a different typology of the indoor environment, newly built low-energy preschools, were investigated in Sweden for the presence of Cl-PFRs, added to several building materials (e.g. age-resistant plastics, insulation, adhesives, and sealants) as flame retardants and plasticizers. TCIPP (0–42%) was the most frequently detected compound,

with concentrations varying among the preschools and up to an average of 21 ng/m³ (median n.a.) [66]. Similarly, the occurrence and profiles of Cl-PFRs were investigated in indoor air collected from various indoor public microenvironments (n=54) in the Albany area of New York State, US. Here, TCIPP was the main contributor to the general contamination (median: 17 ng/m³), followed by TCEP (2.2 ng/m³) and TDCIPP (1.5 ng/m³) [50]. In the Rhine/Main area in Germany, comparable concentrations of Cl-PFRs were determined in indoor air samples collected from several different microenvironments (including floor/carpet stores, building material markets, schools, offices and day care centres) [100]. Offices were the most generally contaminated microenvironments, with a median Cl-PFR concentration of 34 ng/m³, while day care centres had the lowest level (median: 13 ng/m³). Also in this case, TCIPP was the major compound (median: 34 ng/m³) in office indoor air [100].

Chlorinated paraffins

Both SCCPs and MCCPs were detected in each of 10 suspended particulate samples collected from office spaces in China with concentrations ranging from 6.2 to 18 ng/m³ and from 5.6 to 36 ng/m³, respectively [101]. Overall, concentrations in the air of the offices were not statistically different to levels found in homes by the same study, indicating similar sources of CPs to air in the two indoor environments. MCCP concentrations were, on average, marginally higher than those of SCCPs. A second study of CPs in the air of Chinese offices, which reported concentration in conjunction with samples from dormitories and homes found the shorter chained homologues to be dominant, with Σ SCCP concentrations ranging from 9.8 to 966 ng/m³ (mean: 181 ng/m³; median n.a.) and Σ MCCPs ranging from <LOD to 613 ng/m³ (mean: 42 ng/m³; median n.a.) [29]. SCCPs were again the most prevalent CPs in air sampled repeatedly from a single office in China over a number of weeks [39]. Σ SCCP concentrations ranged from 38 to 88 ng/m³, while Σ MCCPs ranged from 3.2 to 9.6 ng/m³. The greatest abundance was observed for C₁₀ and C₁₁ homologues with Cl₇ and Cl₈.

Vehicles

Chlorinated PFRs

Concentrations of Cl-PFRs in the indoor air of cars from the Albany area of New York State, US, were measured in relation to the car production period. TCIPP was found at the highest level in cars older than 5 years (17 ng/m³), while TDCIPP was higher in recently bought cars (10 ng/m³). Lower levels were generally measured for TCEP (<5 ng/m³), independent from the age of the vehicle [50]. Higher median concentrations of Cl-PFRs were instead determined at 127 ng/m³ in indoor air collected from private cars (n=5) in the Rhine/Main area in Germany [100], and in 9 unoccupied cars in Japan [80]. In both cases, TCIPP accounted for most of the contamination (111 ng/m³ and 1500 ng/m³, respectively). Similar air concentrations were measured in vehicles from Switzerland (TCIPP: up to 260 ng/m³ in a 9-year old car) [32], and those found in buses for public services from Sweden (TCIPP up to 2,300 ng/m³) [73].

EMERGING HALOGENATED FLAME RETARDANTS IN CONSUMER PRODUCTS

In consumer products such as textiles and foams, furnishings, flooring, electronics and building materials, HFRs are typically used as additive compounds to fulfil national and international fire safety standards [56]. The amounts of and types of HFRs in consumer products can vary widely even within product groupings and can often be referred to as percentage levels. Since they are not chemically bound to the material, HFRs have a great potential for release from final products during their lifecycle and accumulate in indoor dust and air [84]. However, although the link between consumer product sources and measured concentrations of HFRs has been often investigated to describe the possible mechanisms of chemical transfer, the characterization of their levels in these sources is still limited [84]. In this section, an overview of the available concentrations of HFRs in typical consumer product categories is reported.

Carpets, textiles and foams

Novel brominated flame retardants and Dechlorane Plus

The carpet and textile industry has changed substantially during the last century. Woven carpets made of cotton and wool have been gradually replaced since the 1950s by tufted carpets made of synthetic fibres, such as nylon, rayon, and acrylics, which have typically contained HFRs. The use of HFRs in fibres, textiles and clothes has also gradually increased through the same period [91].

Stapleton et al. (2012) analysed polyurethane foam from residential couches (n=102) purchased in the US from 1985 to 2010. Preliminary screening indicated that 88% of samples likely contained an FR chemical, either by comparison to authentic standards or by a significant (>90%) match to on-line available mass spectral databases. Thirteen foam samples contained TBB and TBPH, with a combined average concentration of 19.7 mg/g and range of 5.2 to 37 mg/g. In addition, 5% of these samples were purchased in 2002 and 2003, suggesting that the use of FM 550 started at least three years prior to the phase-out of Penta-BDE (2005) [75]. Similar values for these compounds were measured in polyurethane foam collected from baby products [74]. Lower levels were instead measured in Belgium, where Ionas et al. (2015) studied 47 curtains and 14 carpets from 4 different stores finding high concentrations of DBDPE (up to 25 µg/g) and detecting TBB at a maximum level of 10 ng/g [40]. According to the authors, these low levels of HFRs suggest that it is likely that halogen-free FR treatments/solutions are preferred for the textiles on the Belgian market.

Chlorinated PFRs

Due to the enhanced exposure toddlers experience from mouthing of potentially flame retarded goods, a number of studies have documented the occurrence of Cl-PFRs in children's products and toys. Stapleton et al. (2011) conducted a wide-ranging study of foam children's products (n=101) including car seats, changing table pads, sleep positioners, portable mattresses and baby carriers, identifying Cl-PFRs in ~60% of samples [74]. TDCIPP was the most prevalent FR, with a mean concentration of 39 mg/g (median n.a.), while concentrations of TCEP and TCIPP were generally much lower, averaging 5.9 and 5.5 mg/g, respectively. The authors reported no associations between compounds and specific product types, except for the occurrence of V6, which was present in 10 of 11 nursing pillows analysed. A follow-up study quantified V6 in the same samples and reported levels ranging from 25-59 mg/g with an average of 47 mg/g (median n.a.) [25]. Cl-PFRs were also detected in 114 toy samples, with TCIPP, TDCIPP and TCEP present in 42, 33 and 28% of samples [41]. Toys were categorized by material type to reveal that Cl-PFRs were present in each of hard plastics, soft plastics and rubber, wood, and foam and textile product groups while samples originating

from China typically contained concentrations 1-2 orders of magnitude above those from other regions. Median concentrations of TCIPP, TDCIPP and TCEP were just 1, 5 and 4 µg/g to suggest that such compounds were unintentionally incorporated into toys via recycling processes, since these levels are too low to provide flame retardancy.

Wu et al. (2019) [94] analysed Cl-PFRs in fabrics and foams from 18 children's car seats (n=36) and found TCEP, TCIPP and TDCIPP to be present in 25, 8 and 19% of samples, respectively. Each of the compounds was detected in fabric samples, while only TCIPP was detected in the foam. Overall Cl-PFR concentrations were again low, reaching a maximum of 0.9 µg/g for TDCIPP. A shift towards TCIPP usage in foams was also observed in a broad screening study of more than 1,000 polyurethane samples in which usage of TDCIPP decreased in samples purchased after 2014, while TCIPP increased through the same time period [18].

Electrical and electronic appliances

Novel brominated flame retardants and Dechlorane Plus

Electronic device technology has evolved considerably in the past decades, leading to an increased prevalence of such products in indoor environments and a higher potential for the emission of chemicals into these spaces [91]. BTBPE was measured with relatively high concentrations (ranging from µg/g to mg/g) in electronic wastes [4]. The occurrence of DBDPE was examined in household products (n=55) in the Pearl River Delta, South China, including electronic appliances, furniture and upholstery, and identified in 20% of samples ranging from 0.3 to 268 µg/g. In the same study, DBDPE was detected at concentrations between 0.4 and 1.2 µg/g in 2 raw materials for electronics [15].

Chlorinated PFRs

The presence of Cl-PFRs in electronic and electrical items has rarely been studied. Kajiwara et al. (2011) assessed TCEP, TCIPP and TDCIPP levels in the individual components of two LCD televisions and a laptop computer [45]. TCIPP was detected in all components (n=17) and was the most prevalent Cl-PFR in most items, while TCEP was present in 11 samples and TDCIPP below detection limits in all cases. Overall concentrations were yet very low, mostly in the low ng/g range. The maximum concentration of TCIPP was

150 ng/g in the AC adapter of the laptop computer, while TCEP reached a maximum of 120 ng/g in the cooling fan and speaker of the same device.

Chlorinated paraffins

In conjunction with experiments to determine human exposure to CPs via emission from hand blenders, Yuan et al. (2017) dismantled and analysed separate components of 16 blender products. Although absolute concentrations were not computed, CPs were detected in 13 of the 16 hand blenders, with each of the SCCP, MCCP and LCCP homologue groups represented within the samples [98]. MCCPs were the most prevalent group identified in components, while the chlorination degree ranged from 53-56% in the self-lubricating bearings and 54-57% in 3 out of the 5 polymer washers analysed. A similar study investigating the release of CPs from household ovens detected the contaminants in 10 of 21 fat residue samples from the interior of the appliances [28]. High levels of Σ SCCPs ranging from <LOQ-93 mg/g (mean: 12 mg/g; median n.a.) and Σ MCCPs ranging from <LOQ-1.9 mg/g (mean: 0.2 mg/g; median n.a.) in the fat samples suggest that CPs were released from interior components of the ovens. Investigators dismantled one oven to assess concentrations of CPs on the surface of individual components via surface wipes which indicated that the contaminants were likely emanating from the circuit board housing and being redistributed within the appliance at high temperature [28].

Building materials and flooring

Novel brominated flame retardants and Dechlorane Plus

Many existing building materials emit HFRs into the indoor air. The content of FRs in building material, mainly insulating foams, was investigated in 2003 [47]. The presence of DBDPE, BTBPE, DPTE, TBB, and TBPH in extruded polystyrene (XPS) construction board, wallpaper, parquet underlay, drainpipes, vapor barrier, polyurethane foam and other building material samples was reported [26]. In various consumer products, including building materials and wastes (n=137), the lowest NBFR concentrations were observed in electrical and electronic equipment wastes, with a median value of 0.4 μ g/g [84]. The two DP isomers were detected in ~30% of samples at concentrations up to 40 μ g/g, while HBB had low concentrations and

low detection frequencies. NBRs and DPs were also analysed in seven categories of building and decoration materials in China [37]. Relatively high NBR median concentrations were detected in PVC materials (387 ng/g), followed by wallpaper (33 ng/g). The median concentration of DBDPE (14.3 ng/g) is consistent with its recorded use in China, while lower levels were measured for DPs (median: 0.7 ng/g in PVC wallpaper) [37]. Results from this study suggested that NBRs in the decoration materials may be added as an auxiliary or unintentionally. Higher DBDPE concentrations were measured instead in electrical outlets (320 - 6100 ng/g) in Japan [45], potentially reflecting market differences.

Chlorinated PFRs

Aside from household consumer products, the materials used in the construction and decoration of indoor environments may also be treated with Cl-PFRs. Cl-PFRs were identified regularly among 47 curtain samples and 14 carpets, with detection frequencies of 54 and 28% for TCIPP and TCEP, respectively [40]. The maximum individual concentration among Cl-PFR compounds was 1.8 µg/g TCEP, though other measurements were typically much lower. In curtains (n=40), TDCIPP was the only Cl-PFR detected at a concentration of 4.3 mg/g in just one sample [61]. On the other hand, TCEP was the only Cl-PFR present in two curtain samples at very low concentrations of 4 and 6 ng/g [45]. Kajiwara et al. (2011) also determined Cl-PFRs in each of four wallpaper samples and two XPS insulation boards used for construction. TCIPP was identified in all the wallpaper samples ranging from 60-100 ng/g while TCEP ranged from <4-80 ng/g. TCEP, TCIPP and TDCIPP were each detected in the insulation boards at concentrations in the low ng/g range [45]. The use of TCEP, TCIPP and TDCIPP in a range of 18 building and decoration materials (n=56) was evidenced by the presence of Cl-PFRs in all samples which included wallpaper, powders, paints, boards, sealing materials PVC line and foams [90]. Concentrations of Cl-PFRs were significantly higher in foams than other materials, with levels ranging from 2-121 µg/g TCEP, 170-9510 µg/g TCIPP and 7-65 µg/g TDCIPP. Cl-PFR relative abundances varied with the material, but were typically dominated by TCIPP.

Chlorinated paraffins

Concentrations of CPs in building and construction materials have not been studied widely, though findings from very few samples indicate high levels of application within individual articles. Two sealing mass samples taken from the walls of an official building in Germany reportedly contained levels of 50.1 and 50.3 mg/g Σ SCCPs although MCCPs were not detected in the materials [36]. C₁₁ homologues accounted for 50% of SCCPs followed by C₁₂ forms at 35% and smaller proportions of C₁₀ and C₁₃. Each of the sealing mass samples was calculated to contain a chlorine content of 63% w/w. Hilger et al. (2013) also analysed sealing mass from windows in the same building, but no SCCPs or MCCPs were detected [36]. Flooring made from 60-70% PVC and 30-40% additives purchased in China contained 2.3 mg/g SCCPs and negligible levels of MCCPs [99]. The authors' noted that the flooring sample had been treated with the technical mixture CP-52, with a chlorine content of 52% w/w.

Polymeric domestic products and toys

Novel brominated flame retardants and Dechlorane Plus

Toy samples (n=69) from the two largest toy markets in Guangzhou City, China, were analysed for NBFs, including BTBPE and DBDPE [14]. Median concentrations in the hard plastic toys were 5.5 µg/g and 0.1 µg/g, respectively, which were notably higher than values in other toys (foam toys, rubber/soft plastic toys and textile and stuffed toys) [14].

Chlorinated paraffins

A wide ranging study of CP concentrations in 108 domestic polymeric materials from Chinese markets and waste recycling stations provides perhaps the best indication of CP application in consumer products, to date [87]. Samples included items such as lunch boxes, PVC tubes, plastic bottles, flooring, tires and cable sheathes and were categorized and reported according to polymer types. The detection frequencies of SCCPs and MCCPs across all sample groups were 81 and 63%, respectively, while concentrations of the two groups were significantly linearly correlated ($p = 0.01$, $R=0.708$) to suggest the two homologue groups are often employed concomitantly. CP concentrations were significantly higher in PVC products than in other matrices with mean levels of 41 mg/g Σ SCCPs and 28 mg/g Σ MCCPs. Average concentrations of Σ SCCPs

were the next highest in polypropylene (PP) at 4 mg/g, followed by food packaging, rubber, polyethylene terephthalate (PET) and polyethylene (PE) at 1.9, 0.6, 0.2 and 0.15 mg/g, respectively. The second highest mean Σ MCCP concentrations were also recorded in PP, 3 mg/g, though levels of the remaining polymers were ordered rubber > food packaging > PE > PET at 1.3, 0.6, 0.2 and 0.04 mg/g. Homologue distributions among the different polymer groups were varied for SCCPs though the C₁₀ and C₁₁ groups were generally dominant. Higher proportions of C₁₃ were, however, present for rubber and PVC samples. Less variation was observed in the homologue patterns of MCCPs, with the C₁₄ group dominating across all polymers, followed by C₁₅ and then smaller proportions of C₁₆ and C₁₇. Congener groups containing 7 and 8 chlorines were dominant across all polymers.

GENERAL DISCUSSION

Studies focusing on the presence, levels and contamination patterns of emerging halogenated flame retardants in indoor dust and air were mostly representative of their worldwide distribution, with South America and Africa being the less investigated areas (Fig. 5.2A and 5.2B). On the contrary, fewer studies were available on the presence and content of HFRs in consumer products and were mostly carried out in Asia (e.g. China and Japan), the US, and Europe (e.g. Belgium, Sweden and Germany) (Fig. 5.2C).

Differences among countries in concentration levels of the considered FR classes could be related to their diverse applications in consumer products, the large variety of compounds available on the market, differences in safety legislation (e.g. complying to stricter conditions in Europe and North America) and to a slower turnover time from legacy to new FRs [1]. In addition, caution should be recommended when comparing literature data, as they are often collected using dissimilar sampling techniques in various microenvironments and analysed with different analytical methods, which may also explain the discrepancies.

For both indoor dust and air, the most investigated microenvironments were houses, apartments, offices, schools and day-care centres. Overall, the concentrations of HFRs in indoor dust and air samples collected from public spaces were higher compared to homes, mostly due to the presence of different types of equipment (e.g. higher number of professional electronic devices), heterogeneity of chemical sources in

consumer products, frequent replacement of indoor equipment by newer ones, frequency of cleaning and stricter fire-safety regulations in public buildings. Fewer studies were generally available for vehicle interiors compared to homes and indoor public spaces despite the typically higher levels of HFR contamination determined in cars. These higher levels are mostly due to the extremely high temperatures that may occur in vehicle interiors, causing a significant release of halogenated compounds from synthetic materials (e.g. electronic parts, seat PUF fillings, etc.) [5]. The scarcity of data on concentrations of HFRs in consumer products still hampers the linking between sources of chemicals and their presence in indoor dust and air.

Insert Figure 5.2 here.

In general, the contamination profile of the considered HFR groups was dominated by the chlorinated PFRs and CPs, reaching the highest concentrations in air, dust and consumer products as expected due to the typically higher vapor pressures of PFRs and their higher production volumes than NBFRs or DPs. CP homologue profiles have been relatively consistent in dust samples across studies, with SCCPs dominated by carbon chain lengths of C₁₃ followed by C₁₂ and then smaller amounts of C₁₁ and C₁₀, while the lighter C₁₀ and C₁₁ groups tend to predominate in air. Carbon chains of C₁₄ length have been the most prevalent of MCCPs, followed by C₁₅ and then the C₁₆ and C₁₇ homologues. Congeners with 7 and 8 chlorines have been consistently the most prominent forms across both the SCCP and MCCP groups. In indoor air, concentrations varied between low pg/m³ for NBFRs and DPs to high ng/m³ for Cl-PFRs and CPs (Fig. 5.3A). In indoor dust, the chemical concentrations were reported in a higher range, from low ng/g to high µg/g, with the highest levels detected especially in indoor public spaces and vehicles (Fig. 5.3B). The largest variation in contamination was finally observed for consumer products, where the concentration of all groups of chemicals stretched from low ng/g to tens of mg/g, as expected due to the variety of analysed goods and their composition materials (Fig. 5.3C).

Insert Figure 5.3 here.

In this chapter, the presence of four groups of HFRs was reported in indoor dust, indoor air, and consumer products. Considering the substantial amount of time we spend in indoor environments, this highlights the potential risk of exposure for humans during our everyday life. However, the shortage of data on HFR levels in consumer products still represents the biggest obstacle in linking eventual sources of contamination to the presence of HFR chemicals in indoor air and dust. For this reason, and to increase our understanding of chemical indoor concentrations, it is essential to continue investigating the presence, distribution, levels and patterns of these parameters in indoor microenvironments.

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FIGURES

Figure 5.1 Pie chart showing the mean percentage of time spent by people indoors. Data were taken from the American National Human Activity Pattern Survey (NHAPS) [51].

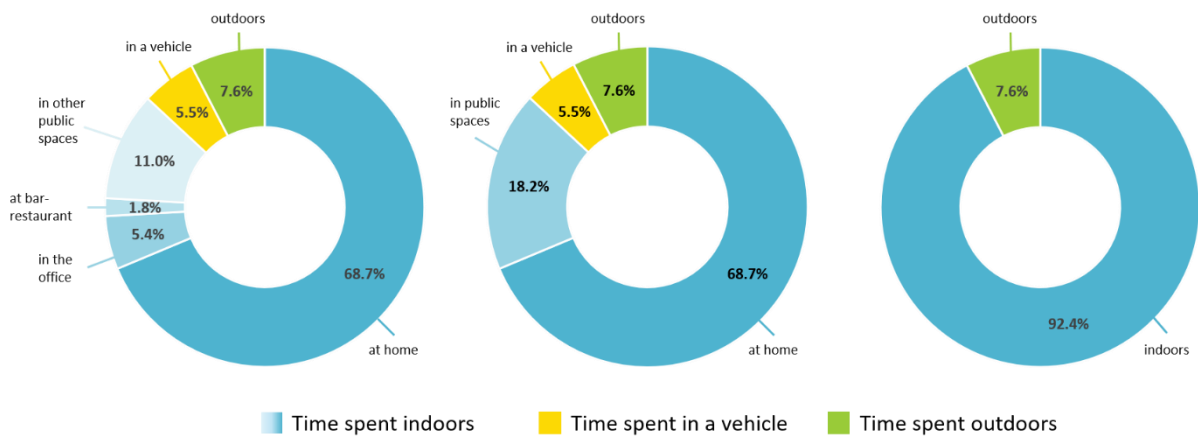


Figure 5.2 World map representing the distribution of studies investigating the HFR contamination in A. indoor dust, B. indoor air, C. consumer products.

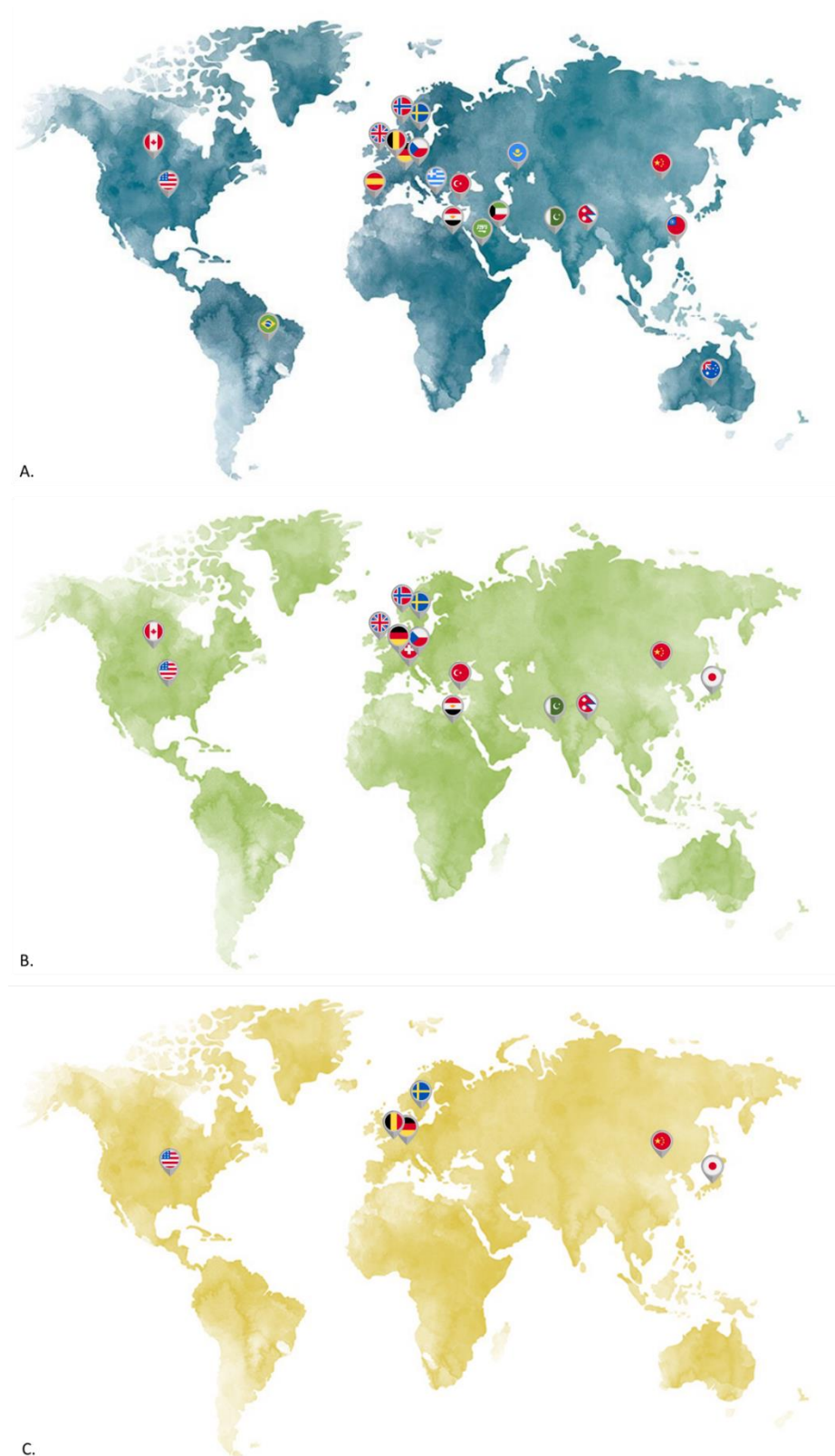


Figure 5.3 Ranges of median concentrations of the selected groups of HFRs in A. indoor air, B. indoor dust, C. consumer products.

