UNIVERSITY OF BIRMINGHAM

FACTORS INFLUENCING HUMAN EXPOSURE ASSESSMENT OF ORGANOPHOSPHORUS FLAME RETARDANTS (OPFRS) VIA INDOOR DUST INGESTION.

By

Yessica Patricia Ortiz Carrizales

M.Sc.

A thesis submitted to the University of Birmingham

for the degree of

DOCTOR OF PHILOSOPHY (PhD)

Division of Environmental Health and Risk Management
College of Life and Environmental Science
The University of Birmingham
Edgbaston, B15 2TT
United Kingdom

September 2017

ABSTRACT

Concentrations of selected organophosphate flame retardants (PFRs) were determined in samples of living room dust from Spain, Jordan, the Czech Republic, Greece, Finland, USA, and Mexico, with international differences in absolute concentrations and relative abundance of different PFRs highlighted and discussed. When previous data from the UK were considered, TCIPP was found to be the most abundant target PFR, with concentrations of TCIPP highest in the UK, followed by the USA and Mexico. Other substantial international differences were observed that are likely attributable to variations in flame retardant legislation and use between different countries. Within-room, within-home, and between-home temporal and spatial variation in concentrations of PFRs in floor dust and elevated surface dust was studied in 3 homes from Birmingham, UK. Of particular note are the seasonal variations in PFR concentrations whereby higher concentrations were observed in spring and summer especially for TCIPP; and that between-home spatial variation was largely attributable to differences in flooring composition (carpeted or tile). Moreover, higher concentrations were generally found in elevated surface rather than floor dust. Concentrations of PFRs were determined in indoor air from houses and offices in Birmingham, UK. The relative order of abundance of PFRs in air was TCEP, TCIPP, TnBP and TPhP. This contrast with the order in dust samples from the UK where the order of abundance was TDCIPP, TPhP, EHDPP and TnBP. TCEP has the highest vapor pressure of the chlorinate PFRs. TCEP is about six orders of magnitude more volatile than TDCIPP and as a result, binding of TDCIPP to dust or soil particles is much likely than TCEPP and TCIPP. Finally, controlled chamber experiments were conducted to examine the magnitude and rate of PFR transfer from a treated fabric to dust via direct fabric-dust contact.

A key finding was that source-to-dust transfer via direct contact occurs and over the time period of our experiments was proportional to the duration of contact; with the majority of PFRs, transfer from fabric to dust via direct contact occurs within the first 4 days of contact.

DEDICATION

To my father

Héctor Javier Ortiz Rodríguez

ACKNOWLEDGEMENTS

First of all, thanks so much to God and the Universe for support, guidance and inspiration throughout this work.

This work would not be possible without the help of several people. Those, who share their knowledge and experience whit me, special thanks to my supervisor Dr. Stuart Harrad for his help, orientation and advice to see the big picture to understand and expand my vision.

Thank so much to Dr. Yuning Ma and Dr. Mohamed Abdallah for their invaluable advice in the laboratory. This gained knowledge will be with me forever. And thanks to my fellows in room 216 for all the good times, fun and dinners shared. I treasure all these memories.

Very special thanks to PROMEP Mexico for believing in me and funding my Ph.D. I feel very committed to contributing my experiences to the next Mexican generations.

Thanks so much to my new and old friends, especially to Eva López y Bárbara Macias who listened to me in my weak moments, but also for all the fun, travels and breakfast, lunch and dinners I will retmain as good memories forever.

I would like to say thanks to my family for all their support, encouragement and unconditional love throughout my life especially my mom Maria Guadalupe Carrizales Sanchez, for her I am who I am.

Finally, thanks so much to my husband who is the best man to share my life, thanks, Cesar Cruz Melo for your love, support, and patience. I would not have been able to complete this journey without you. I love you.

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ABBREVIATIONS

%RSD	Relative Standard Deviation (%)
%IS Rec	Internal standard recovery
BFRs	Brominated flame retardants
bw	Bodyweight
EHDPP	2-Ethylhexyl diphenyl phosphate
EPA	Environment protection agency
ES	Elevated surface
EU	European Union
F	Floor
GC	Gas chromatography
H1	House number 1
H2	House number 2
H3	House number 3
Hc	Henry's constant
HBLV	Health based limit value
ISTD	Internal Standard
Kow	Octanol - water partition coefficient
LOD	Instrument limit of detection
LOQ	Sample limit of quantification
MS	mass spectrometry
m/z	Mass to change ratio
NAT	Native compound
nd	Not detected
OSHA	Occupational Safety and Health Administration
PFRs	Organophosphate ester flame retardants
POP	Persistent organic pollutant
PUF	Polyurethane foam
QA/QC	Quality assurance/quality control
RDS	Recovery determination standard

RfD	Reference dose
RPM	Revolutions per minute
RRFs	Relative response factors
RRTs	Relative retention times
RSD	Relative standard deviation
SD	Standard deviation
SRM	Standard Material Reference
T	Temperature
t1/2	Half life
TCP	Tri-cresyl phosphate
TCEP	Tris (2-chloroethyl) phosphate
TCIPP	Tris (chloroisopropyl) phosphate
TDCIPP	Tris (1,3-dichloro-2-propyl) phosphate
TnBP	Tri-n-butyl-phosphate
TPHP	Triphenyl phosphate
UK	United Kingdom
USA	United States of America
Vp	Vapor pressure
WHO	World Health Organization

CHAPTER I. INTRODUCTION

1.1 Organophosphate flame retardants

Since the discovery of fire, multiple advantages have accrued: food can be cooked, houses heated, and combustion has also transformed transportation. On the other hand, this amazing discovery also presented disadvantages related to the danger that fire represents, such as human life loss caused by fire; according to the European Flame Retardant Association (2012a). Furthermore crops, goods, houses and offices may also be damaged by fire; in 2009 alone, the UK reported losses of £1,800 million due to fire damage (The Geneva Association, 2012).

Flame retardants (FR) are chemicals added to materials to impart resistance to fire. Fire is a chemical reaction and flame retardants interrupt it by physical dilution, chemical interaction, inert gas dilution, thermal quenching and protective coatings (Kemmlein et al., 2003). The relative role played by these mechanisms will depend on the flame retardant used and material. Flame retardants can be divided into additive and reactive flame retardants. Additive flame retardants are those added but not bonded chemically to the raw material. By comparison, reactive flame retardants are those that are chemically bound to the raw material. Organophosphate flame retardants (PFRs) are additive FRs and thus are susceptible to release into the environment (EPA, 2005).

Chemically, FRs can be divided into four broad groups: halogenated (containing chlorine or bromine for example: TCEP, TDCIPP, and TCIPP), inorganic (based on metals such as aluminium trihydrate (ATH) and magnesium hydroxide (Mg_2OH_4), other non-halogenated organic species like TnBP, EHDPP, TPhP and TCP (Coelho et al., 2016) and nitrogen compounds which their main applications are melamine for polyurethane flexible foams, melamine cyanurate in nylons, dicyandiamide in intumescent paints and sulfamate for wallpapers. Their advantages are the absence of dioxine and halogen acids as well as their low evolution of smoke. (Horacek and Grabener, 2016).

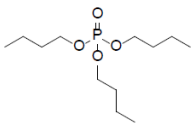
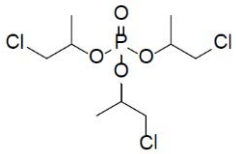
1.2 Organophosphorus flame retardants: usage volumes and applications

At the turn of the 21st century, the most commonly used organic flame retardants (OFRs) were brominated flame retardants (BFRs) like polybrominated diphenyl ethers (PBDEs) but over the last decade, scientific research has established the toxicity, persistence and bioaccumulative tendencies of PBDEs and other BFRs such as hexabromocyclododecane (HBCD) as well as evidence of water, air and soil contamination (Harrad et al., 2009b; Harrad et al., 2010a). Such findings have led to restrictions and bans on the use of different PBDE formulations across the world (Reemtsma et al., 2008); Stapleton et al., 2009; USEPA, 2005). This is exemplified by the listing of HBCD and the Penta- and Octa-BDE formulations under the UNEP Stockholm Convention on Persistent Organic Pollutants (European Flame Retardant Association, 2008). Moreover, the most extensively used PBDE formulation, Deca-BDE has recently been listed under this Convention.

Due to restrictions on manufacture and new use of these “classic” BFRs, alternatives are sought and hence the use of organophosphorus flame retardants (PFRs) has increased substantially (Ven der Veen et al., 2012).

According to Stapleton et al. (2012) 50 % of the sofas in American homes have been treated with TDCIPP with a similar frequency of application reported in Japan by Takigami et al., (2009). Meanwhile in Europe the use of TCIPP in domestic and office furniture foam is more widespread due to the high price of TDCIPP (almost double that of TCIPP). As a result, in Europe TDCIPP use is largely confined to applications requiring a greater degree of flame retardancy such as in the automobile industry (EU RAR, 2008c). Table I-1 summarises the seven most commonly-used PFRs studied and their applications. And table I-2 summary of the relative production volumes of the major PFRs in different countries.

Table I-1Shows the seven most common PFRs studied and their applications as well their name and formula.

PFR	Applications and uses:
Tri-n-butyl phosphate TnBP 	Manufacture of plastics and vinyl resins, fire-resistant aircraft hydraulic fluids (ACG,1999)
Tri(2-chloroisopropyl) phosphate TCIPP 	Rigid polyurethane foams, spray systems for building insulation as well as clock and panels for the same purpose, flexible polyurethane foams for furniture and its upholstery and mattresses, polyurethane carpet backing, principally in the United Kingdom and Ireland. The rest of Europe and USA have limited its use. (WHO, 2009) also been reported in PVC, glass fibre wallpaper use, wood preservation coating (Ni et al., 2007)

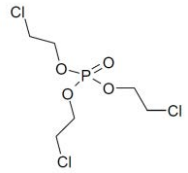
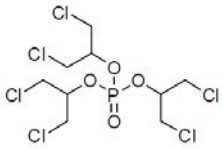
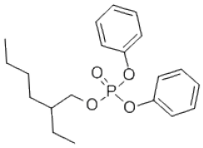
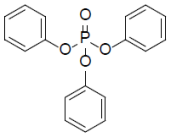
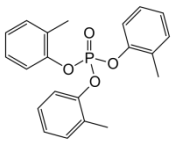
PFR	Applications and uses:
Tri(2-chloroethyl) phosphate TCEP 	Flame retardant plasticiser in furniture, flexible polyurethane foams, PVC materials, textile, and floor covering. Other uses in minor grade are flame resistant paints, cars, aircraft and trains manufacture. High levels in ceiling coating (EFRA. 2010 a, b; Stapleton et al., 2009).
Tri(1,3-dichloropropyl) phosphate TDCIPP 	In flexible and rigid polyurethane foams, mattresses, and upholstery (EFRA. 2010 a, b; Stapleton et al., 2009)
(2-ethylhexyldiphenyl phosphate) EHDPP 	PVC plasticizer, rubber, photofilms, paints, pigments, adhesives and textile coatings, food packing. (Weil, E.D., 1993; NTP 2013; USFDA, 2006).
Triphenyl phosphate TPhP 	Plastic (PVC) and rubber preparations, coatings and adhesive products, commercial mixtures such as FM® 550 from Chemtura, application in linoleum floor and plastic of computers. (Marklund et al., 2003; Van den Eede et al., 2011).
Tri-cresyl phosphate TCP 	PVC, artificial leather, tents, tarpaulins, electrical cables, conveyor belts, cellulosic polymers, thermoplastics & synthetic rubber, lubricants, hydraulic fluids, engine oil for motorcycle and automobiles. (EFRA, 2010 a, b)

Table I-2 Summary of the relative production volumes of the major PFRs in different countries.

PFR	Production/usage Volume (t/year)	Country	Year
TnBP	33.8	Norway	2008
TCIPP	22950	Europe	1995
	2750	UK	1995
	40000	Worldwide	1997
	50	Norway	2001
	42.7	Norway	2008
	177	Denmark	2008
	16429	Finland	2008
	132	Sweden	2008
TCEP	2040	Europe	1995
	400	UK	1995
	1286	Norway	2003
	798.5	Norway	2004
	1598	Finland	2004
	227–454	United States	2006
	261.3	Norway	2008
	0.1	Denmark	2008
	198	Finland	2008
TDCIPP	8000	Worldwide	1997
	4500–22700	United States	1998
	<10000	Europe	2000
	134.1	Denmark	2002
	4500–22700	United States	2006
EHDPP	2.8	Norway	2002
	30.1	Norway	2005
TPhP	4500–22700	United States	1998
	4500–22700	United States	2002
	55	Norway	2004
	1592	Sweden	2005
	4500–22700	United States	2006
	18.4	Norway	2008
	2.3–16.7 $year^{-1}$	Denmark	2004–2008
	9.8–57.1 $year^{-1}$	Finland	2004–2008
	46.0–88.0 $year^{-1}$	Sweden	2003–2008
TCP	454–4500	United States	1998
	454–4500	United States	2006
	0.8	Norway	2008
	0.6	Denmark	2008
	3.6	Finland	2008
	5.0	Sweden	2008

WHO (1997), UNEP (2002), US-EPA (2002), US-EPA (2006), EU (2008a, 2008b), Green et al. (2008) and SPIN (2011).

One of the major components of the flame retardant formulation FM-550 that has found widespread application in furniture PUF in North America is TPhP (Stapleton et al., 2008). According to Stapleton et. al, (2012) the increasing use of PFRs is further demonstrated by a study of 102 US sofas where 24 % of sofas purchased before 2005 contained TDCIPP versus 52 % in sofas purchased after 2005. Overall, Table I-2 shows the PFRs for which there is the greatest demand are: TPhP, TDCIPP and TCIPP.

1.3 Physicochemical properties and mechanism of action

1.3.1 Physicochemical properties

It is evident that there will be substantial variation in environmental fate and behaviour between different PFRs. For example, those like TCP and EHDPP with high K_{ow} values will likely partition preferentially to dust, sediment and soil rather than air and water, compared to TCEP which with its low K_{ow} and comparatively high vapour pressure, is more likely to partition to air and water than soil or dust.

PFRs with higher vapour pressure also undergo more facile volatile emission from treated goods. TCIPP has a low K_{ow} making it more soluble in water with similar considerations applying to TDCIPP. Meyer et al (2004) reported that chlorinated alkyl phosphates such as TCEP, TCIPP and TDCIPP may be persistent as a result of their resistance to degradation and affinity for soil and dust organic carbon, a conclusion supported by estimates that the half-lives of TCEP and TDCIPP in groundwater range from 20 to 45 years (Regnery et al., 2011).

Table I.3 summarises values of key physicochemical properties for selected PFRs. Of note the half-life of EHDPP in different environmental compartments are: water 50 days, atmosphere 9.7 hours, and soil and sediment 300 days (Environmental risk evaluation report: CAS no. 1241-94-7, 2009). This suggests EHDPP to be more persistent in particles than air.

Table I-3 Values of key physicochemical properties of PFRs of interest (ATSDR, 2012).

PFR	State at room temperature	Solubility in Water (mg L^{-1}) at 25 °C	Log K_{ow}	Vapour Pressure (mm Hg) at 25 °C	Henry's Law constant (atm^{-3} $mole^{1}$) at 25 °C
TnBP	Liquid	280	4	1.1×10^{-3}	1.5×10^{-7}
TCEP	Liquid	7.0×10^{3}	1.4	1.1×10^{-4}	3.3×10^{-6}
TCIPP	Liquid	1.60×10^{3}	2.6	0.75	6.0×10^{-8}
TDCIPP	Liquid	1.50	3.8	7.4×10^{-8}	2.6×10^{-9}
TPhP	Liquid	1.9	4.6	1.2×10^{-6}	3.3×10^{-6}
EHDPP	Liquid	0.067	5.7	6.29×10^{-5}	2.48×10^{-7}
TCP	Liquid	0.36	5.1	1.8×10^{-7}	9.2×10^{-7}

1.3.2 Mechanism of action

The general mechanisms of action of flame retardants are of two broad types: One mechanism is via preventing ignition it reduces the capability of the product to catch fire. The second mechanism is by reducing the formation of no-combustible gases to stop the spread of fire.

In the case of PFRs, the mechanism of action depends on the chemicals involved, for halogenated PFRs in the gas phase $OH^{\cdot}$ and $H^{\cdot}$ radicals are removed and replaced with Cl, thereby retarding the burning reaction and thus the fire spread. The benefit of this mechanism is that halogen atoms as well as phosphorus offer additional flame retardancy as they both act independently in the polymer molecule (Van der Veen et al., 2012).

On the other hand, for non-halogenated PFRs, during the fire phosphorus from the PFR component is transformed into phosphoric acid forming a char on the burned material that limits further combustion (European Flame Retardants Association, 2012b).

1.4 Environmental contamination with PFRs

As a result of the widespread use of PFRs as additive FRs they may be released easily through volatilization and abrasion from treated goods and accumulate in indoor and outdoor environments (Wensing et al., 2005). Marklund et al. (2005) reported concentrations of EHDPP in municipal sludge to range from 0.32 to 4.6 µg/g in Sweden.

Meanwhile, Andersen et al., (2004) and Stachel et al., (2005) reported concentrations of TCIPP between 100 to 350 ng/L in surface water and up to 311 ng/g on sediments.

There are also reports of concentrations of PFRs in indoor air as well as in house dust (Kim et al. 2011), (Van den Eede et al. 2010) (Ali et al 2012) (Brommer et al 2012) (Van den Eede 2011). PFRs have also been detected in drinking water (Stackelberg et al., 2007), in sediment and in biota, including human tissues such as breast milk (Sundkvist et al. 2010; Kim et al. 2011a).

The detection of TCIPP and TDCIPP in groundwater older than 20 years indicates their persistence (Regnery el al 2011). Moreover, TCEP and TDCIPP proved resistant to photodegradation in a laboratory experiment (Regnery et al. 2010).

Overall, PFRs have been detected throughout the world, including countries such as the USA (Stapleton et al., 2009), Japan (Kanazawa et al., 2010b), Belgium (Van den Eede et al 2010), Spain, Romania and Belgium (Van den Eede, et al., 2011), Germany (Brommer et al 2012), the Philippines (Kim et al 2012), New Zealand (Ali, et al. 2012), Kuwait, and Pakistan (Ali, et al. 2013).

1.4.1 Dust

Cao et al (2014) studied dust from 56 offices in Beijing, concluding that concentrations of PBDEs and NBFRs were minor compared to those of PFRs likely as a result of phasing out of BFRs. Such a higher concentration of PFRs compared to BFRs has also been reported in indoor environments in Japan (Mizouchi et al., 2015).

Moreover, according to Van den Eede et al. (2011), the median concentrations (μg/g) of PFRs in Belgian indoor dust samples were significantly higher (20 to 30 times) than those of PBDEs and HBCD in Belgian dust reported by Roosens et al. (2010), suggesting that exposure to PFRs through dust ingestion is significantly higher than for BFRs.

Over the last 15 years concentrations of PFRs have been determined in indoor dust from different micro environments such as: homes, work places, daycare centres, cars and so on (Brommer et al., 2012, 2015; Abdallah et al., 2014; Luongo et al., 2015; He et al., 2015; Araki et al., 2014; Cequier et al., 2014; Ali et al., 2013). Table I.4 summarises the available data on key PFRs, highlighting the difference in concentrations of PFRs between the EU and the US, in particular for TCEP where in Europe (Romania, Belgium, Spain, Netherlands) concentrations are lower than in the US and Japan (Van den Eede et al., 2011b; Dirtu et al., 2012, Brandsma et al., 2014). Such international differences in concentrations are thought to be due to the difference in use and type of FR in each country (Kim et al., 2013).

Temporal variation in PFR contamination of indoor dust is an important factor influencing human exposure assessments and according to Cao et al., (2014) the major seasonal variation concentration occurs in late winter and early spring because of the sensitivity of PFRs to temperature changes as they are more volatile than PBDEs or NBFRs.

In winter, low ventilation and temperatures decrease PFR concentrations in contrast with the conditions in early spring and summer that favor emission of PFRs from products to indoor environments with subsequent accumulation in dust (Cao et al., 2014). There are three main factors that may contribute to temporal variation in PFR concentration in indoor environments: 1) the introduction or removal of a possible FR source such as carpet, furniture, television or other FR treated product, 2) temperature variation which may influence the release from treated products (Zhang et al., 2009) as well as air: dust partitioning (Hazrati and Harrad, 2006) and 3) ventilation (Cao et al., 2014). In one study, spatial variability was studied in three homes and three offices finding a variation in dust contamination depending on the proximity to the possible source. Specifically, the highest concentration of ΣHBCD and γ-HBCD was observed closest to a TV, whilst lower concentrations were detected in dust sampled floor areas of the same room sampled further away from the TV (Harrad et al., 2009). The same study also reported within-room temporal variability in concentrations of HBCD in dust.

In particular, the introduction to and temporary withdrawal of a TV from one room resulted in changes in HBCD concentrations in monthly dust samples of up to a factor of 2.5 that matched the temporal change in presence/absence of the TV in the room (Harrad et al., 2009).

TCIPP has been reported as the predominant PFR in living room dust in countries such as UK, Japan and other European countries, in contrast to North America where TDCIPP and TPhP are the most abundant (Brommer et al., 2015). Meanwhile, in office dust TCIPP is predominant in the UK and Germany, while TPhP was the major PFR detected in Kazakhstani dust (Brommer et al. 2015).

Studies of PFRs in indoor dust from other countries such as Kuwait have attributed high PFR concentrations to the import of furniture from Japan, China and USA (Ali et al., 2013). In Egyptian indoor dust TDCIPP, TCIPP and TCEP were detected at average concentrations of 233, 229 and 144 ng/g respectively (Abdallah et al, 2014). Meanwhile in the same study, TPhP was the most frequently detected and most abundant PFR which was attributed to the wide use of TPhP as a plasticizer in addition to its application as an FR in different consumer goods; while concentrations (average 50 ng/g) of EHDPP in Egyptian dust were lower than reported from other countries (Abdallah et al., 2014). Further afield, countries like Mexico import a substantial mass of goods from the US that may contain high concentrations of PFRs. In addition, Mexico has an important flame retardant manufacturing industry. For example, Mexico is home to the following companies: Thor (an international company originally from UK, who manufacture and distribute PFRs to South America from Mexico, e.g. the commercial product AFLAMMIT ®); WSFR (Zhejiang Wansheng Co. LTD) another international company originally from China, which manufactures and distributes FRs for use in plastics, flexible and rigid polyurethane from Mexico to South America; and Polyrob Plastics, S.A. de C.V. - a Mexican company that distributes FR for different applications throughout South America.

1.4.1.1 Differences between PFR concentrations in elevated surface versus floor dust.

Tajima et al., (2014) reported higher concentrations of TPhP, TCIPP, TCEP and TnBP in elevated surface dust than in floor dust and attributed this potentially to more frequent cleaning of floors than elevated surfaces. Concentrations of TCIPP in floor dust and elevated surface dust were significantly correlated ($r=0.886$, $p<0.001$) suggesting that floor material might be a possible source for this compound, especially where the dominant floor surface material was wall-to-wall carpet and PVC rather than wood floors (Tajima, et al., 2014). TCEP is used in carpet and PVC floor material (ECHA, 2010). In elevated surface dust, the TnBP, TCEP and TPhP were more abundant than in floor dust, with one possible explanation being lower cleaning frequency of elevated surfaces compared to floors in some houses (Tajima, et al., 2014).

Van den Eede et al., (2011) also report similar concentrations of TnBP, TPhP, and TDCIPP in Belgian and Spanish indoor dust, but detected TCEP at higher concentrations in Spain. Meanwhile concentrations in indoor dust from Portuguese houses were low compared to those reported in other European countries and the US (Coelho et al., 2016). TPhP and TCIPP were the most abundant PFRs reported in five sampled sites in China, with concentrations of TCIPP comparable to those in other countries such as Kuwait, Pakistan, Belgium, Romania and Spain.

In contrast, high levels of TPhP were found in indoor dust from the US (Zheng et al., 2015), presumably attributable to the widespread use of FM-550 in furniture.

Also in the US, high levels of TDCIPP were found in living areas compared to bedrooms, indicating the presence of more upholstered furniture in living areas than bedrooms (Wei et al., 2015). On the other hand, concentrations of TnBP and TPhP in bedrooms in New Zealand implied mattress dust as a common emission source to floor dust (Ali et al., 2012). Variations in concentrations between house dust from different countries are likely attributable to differences in the numbers and types of putative sources such as floor materials, electronics, and furniture, as well as the degree and type of ventilation with low concentrations observed in houses with a high frequency of window opening (Araki et al., 2014).

Table I-4 Median concentrations (μg/g) of PFRs in indoor floor house dust reported in selected studies.

Country	n	year	TnBP	TCEP	TCIPP	TDCIPP	TPhP	EHDPP	TCP	Reference
Spain	8	2007	0.23	0.50	3.8	0.12	1.9	N/A	N/A	(Garcia et al., 2007)
Belgium	33	2011	0.13	0.23	1.4	0.36	0.50	N/A	0.20	(Van den Eede et al., 2011)
Sweden	10	2011	0.3	2.1	1.6	10	1.2	0.5	N/A	(Bergh et al., 2011)
Romania	47	2010	0.04	0.10	0.86	0.06	0.50	N/A	N/A	(Dirtu et al., 2012)
US	16	2006	<0.08	5.1	2.1	2.8	3	0.61	N/A	(Dodson et al., 2012)
New Zealand	34	2011	0.08	0.15	0.35	0.23	0.6	N/A	0.12	(Ali et al., 2012)
Kuwait	15	2011	0.05	0.71	1.46	0.36	0.43	0.19	N/A	(Ali et al., 2013)
Pakistan	15	2011	<0.02	0.15	<0.02	0.25	0.16	0.06	N/A	(Ali et al., 2013)
Japan	148	2014	1.0	5.8	8.7	2.8	4.5	N/A	<0.4	(Araki et al., 2014)
Japan	48	2014	N/A	N/A	0.74	<0.59	0.9	N/A	<0.4	(Tajima et al., 2014)
Egypt	20	2014	0.017	0.022	0.028	0.072	0.067	0.042	N/A	(Abdallah et al., 2014)
Norway	48	2014	0.06	0.41	2.68	0.50	0.98	0.62	0.31	(Cequier et al., 2014)
China	6	2015	N/A	2140	720	110	600	N/A	N/A	(He et al., 2015)
China	56	2015	0.15	0.35	2.17	0.49	0.36	0.61	N/A	(Zheng et al., 2015)
China	25	2015	0.14	1.93	1.22	0.15	1.09	0.31	N/A	(He et al., 2015)
China	11	2015	0.08	3.78	0.75	0.75	0.13	0.15	0.36	(He et al., 2015)
Sweden	62	2015	5.6	4.0	11	2.0	4.3	2.7	2.7	(Luongo et al., 2015)
Portugal	28	2016	0.02	0.01	N/A	0.02	0.66	0.62	N/A	(Coelho et al., 2016)
UK	32	2015	0.03	0.81	21	0.71	3.3	1.6	N/A	(Harrad et al., 2016)
Australia	42	2015	0.06	0.60	1.8	0.32	1.2	0.38	N/A	(Harrad et al., 2016)
Canada	14	2015	0.13	0.69	1.2	1.1	1.6	0.39	N/A	(Harrad et al., 2016)
Germany	22	2015	<0.03	0.21	1.0	0.08	0.23	0.14	N/A	(Harrad et al., 2016)
Kazakhstan	9	2015	0.11	1.4	1.0	0.11	3.8	0.27	N/A	(Harrad et al., 2016)

N/A Not available/not investigated

Table I-5 Concentrations of PFRs in indoor dust in different microenvironments and countries (μg/g dust).

Country	Place	TnBP	TCEP	TClPP	TDClPP	TPhP	TCP	Reference
Kuwait	Car	N/A	1.76	3.07	7.63	1.76	N/A	Ali et al. (2013)
New Zealand	Mattress	0.07	0.04	0.25	0.11	0.24	0.16	Ali et al. (2012)
Belgium	Shop	0.21	0.59	2.94	0.76	1.97	0.2	Van de Eede et al. (2011)
Sweden	Public place	0.4	1.4	2.4	1.1	3.1	N/A	Marklund et al. (2003)
	Day care centres	1.2	30	3.1	9.1	1.9	N/A	Bergh et al. (2011)
	Work places	0.2	6.7	19	17	5.3	N/A	
Germany	Cars	0.11	0.95	3.10	130	3.0	0.24	Brommer et al. (2012)
	Offices	0.22	0.12	3.00	0.15	2.5	0.37	

N/A not applicable

Generally speaking TCIPP and TCEP are the most important PFRs in indoor dust not just with respect to their frequency of detection, but also due to their absolute concentrations in different microenvironments such as hotels, offices, day care centers, hospitals, and shops etc.

1.4.2 Air

PFRs are reported to be persistent in the atmosphere and be capable of medium or long-range transport (Lui et al., 2014). However, only a few studies of their presence in outdoor air exist. In La Coruña, Spain, Quintana et al. (2007) reported TCEP and TCIPP to be present in outdoor air at 0.52 ng m^{-3} and 1 ng m^{-3} respectively. Meanwhile, concentrations of TCEP (0.0016 ng m^{-3}), TCIPP (0.81 ng m^{-3}) and TDCIPP (0.02 ng m^{-3}) were reported for Finland (Marklund et al., 2005). In pine needles (used as a natural passive sampler) in the Sierra Nevada Mountains, USA, concentrations of TCEP (1950 ng/g), TCIPP (763 ng/g) and TDCIPP (1320 ng/g) were reported (Aston et al., 1996).

With respect to indoor air, PFRs may arise as a result of volatilization from putative sources and subsequently partition between gas and particulate phases (Van den Eede et al., 2011). Air samples from 169 apartments in Stockholm were analysed for PFRs, revealing median concentrations of TCEP (4 ng m^{-3}), TCIPP (14 ng m^{-3}) and TPhP (<3.1 ng m^{-3}) (Bergh et al., 2011). Concentrations of PFRs in urban outdoor air from Toronto, Canada were measured by Shoeib et al. (2014) during 2010-2011, reporting a yearly mean (2.64 ng m^3) of ΣPFRs. The same study reported significant positive correlations between TCEP and both TCIPP and TPhP indicating similar sources of these compounds.

According to Staff et al. (2005) PFRs are established as ubiquitous indoor air pollutants, with concentrations in the range of 1-870 and 1-2300 ng m^{-3} for TCIPP and TCEP respectively and for TPhP and TnBP 1-220 ng m^{-3} and 1-170 ng m^{-3} respectively. The observation that homes contain lower concentrations than offices has been attributed to the existence of more sources of contamination in offices than in homes as a result of more stringent fire safety regulations in public spaces (Staaf et al. 2005). The offices sampled were almost new and modern with acoustically damped ceilings, new computers, and new polyurethane foam upholstery, suggesting greater emissions from such new goods and materials than from older ones (Staaf et al. 2005). Related to this, chamber experiments have documented TCIPP volatilisation from upholstery, insulating material and foam (Kemmlein et al., 2003).

1.4.3 Fabrics as a source of PFRs to indoor environments

The majority of current commercial FRs used to treat textiles originate from those developed before 1980 such as Fyrol 6 and 51 (containing TDCIPP and TPhP), which were specifically recommended for textile applications (Horrocks, 2011). The widespread use of such FRs to meet flame retardancy regulations (such as the UK's Furniture and Furnishings (Fire Safety) Regulations 1988) has substantial relevance as textiles and fabrics constitute a substantial proportion of the surface area in many indoor microenvironments (Molander et al., 2012). Thus, there is substantial potential for FRs present in such fabrics to transfer to indoor dust via: volatilization with subsequent partitioning to dust; by abrasion of an FR-containing fabric resulting in direct transfer of FR-laden fibres to dust; and transfer via direct contact between treated fabric and dust (Suzuki et al., 2009; Webster et al., 2009; Wagner et al., 2013; Cao et al., 2014; Rauert et al., 2016).

In the US, the California legislature recently approved a law (SB1019) requiring labels in furniture to indicate if a product contains FR or not. TDCIPP is more commonly used as flame retardant in US furniture, as evidenced by Stapleton et al. (2012), who report the presence of TDICPP in 50 % of residential furniture PUF samples analysed. In a recent study, 40 samples of furniture (foam, fabric covers, synthetic fibres and beads) were analysed finding the following concentrations of PFRs: cover fabrics (TCIPP 6.26 ppm, TCEP 5 ppm, and TPhP 4.6 ppm) synthetic cover pad and batting (TCIPP <6.25 ppm, TCEP 4.6 ppm) foam (TCIPP 6.3 µg g, TCEP <4.6 ppm, TDCIPP 3.8 ppm). The study observed that products manufactured before 2013 displayed the highest concentrations (Petreas et al., 2016).

A recent study was conducted in the UK to measure FR concentrations in carpets, curtains, mattress fabric, furniture foam, and furniture upholstery textile. It found that 8 of the 9 furniture foams analysed were treated with PFRs at a mean concentration of 1.9 % w/w TCIPP, and 1.1% and 0.5% of TDCIPP and TCEP respectively (Stubbings et al., 2016).

1.5 Toxicity

Evidence of the presence of elevated concentrations of PFRs in indoor environments has raised concerns about human exposure. Such exposure concerns are exacerbated by evidence of PFR toxicity. Toxicology studies to date have included long-term exposure in laboratory animal tests (WHO, 2000B, 1998) to TCIPP, TDCIPP, and TCEP that demonstrate adverse effects including potential carcinogenicity in rats and mice, mutagenic, teratogenic, haemolytic effects and neurotoxicity which some have suggested render them inappropriate substitutes for BFRs (Van de Veen et al 2012).

Exposure to TnBP has also been linked to sick building syndrome (Kanazawa et al., 2010), while TPhP has been linked to dermatitis as well as respiratory problems, as well also associated with altered prolactin levels and decreased sperm count in men (Camarasa et al., 1992; Kim et al., 2013; Dodson et al., 2012).

Table I-6 Summary of knowledge of the toxicity of PFRs.

PFR	Reported effects
TnBP	Possible neurotoxicity and carcinogenicity, as well as testicular, kidney and liver damage. (Meeker and Stapleton, 2010; NTP, 1990; WHO, 1991, 1998).
TCIPP(tri(2-chloroisopropyl) phosphate	Ni et al., 2007 considered it potentially carcinogenic. Leisewitz et al., 2000 reported chronic toxicity, accumulation in liver & kidneys. As well as skin and eye irritation in rats, Dishaw et al., 2011 found that TCIPP diminishes cell numbers & alters neurodifferentiation.
TCEP (tri(2-chloroethyl) phosphate	WHO (1998) report TCEP to be carcinogenic to animals. Chapin et al., 1997 report TCEP reduces fertility, sperm mobility, and sperm density in humans. In the EU, it is classified as a “potential human carcinogen” and was classified by the Californian EPA as a “known carcinogen” in 1992.
TDCIPP (tri 1,3dichloropropyl) phosphate)	Andersen et al., 2004 & WHO 1998 report TDCIPP to be a possible carcinogen and in the EU, it is classified as a level 2 carcinogen (EURAR, 2008c). Also reported to be associated with decreased thyroid hormone levels (Meerker et al., 2010). Additionally, linked to inhibited DNA synthesis and decreased cell number alternating neurodifferentiation. (Dishaw et al., 2011).
EHDPP	Possible human skin irritant, with prolonged exposure resulting in eye irritation and conjunctivitis. Neurotoxicity reported in rats as well as reproductive toxicity (Sprague et al., 1981, IARC 1990, NTP 2010a).

PFR	Reported effects
TPhP (triphenyl phosphate)	Andersen et al 2004 reported TPhP displays possible neurotoxicity, but Pakalin et al., 2007 reported low neurotoxicity. Meeker and Stapleton 2010 sampled house dust and related TPhP with diminution of sperm concentration. Camarasa et al., 1992 reported it linked to dermatitis.
TCP (tri-cresyl phosphate)	McPherson et al 2004 found a possible relationship between TCP and reproductive effects. Bolgar et al., 2008 reported CNS toxicity.

1.6 Pathways of human exposure to PFRs

While a study of PFRs in indoor dust and blood serum showed concentrations of TCIPP, TCEP and TDCIPP to be detected in dust only, evidence for human exposure to PFRs is provided by recent studies that have detected metabolites of chlorinated PFRs in urine samples suggesting urine to be an important human exposure biomarker. (Dodson et al., 2014; Hoffman et al., 2015). Likewise, EHDPP was detected in pooled breast milk samples of Swedish women, at levels ranging from 3.5 - 7.9 ng/g lipid. In the one individual breast milk sample that was analysed, EHDPP was found at a concentration of 13 ng/g lipid. (Sundkvist et al., 2010).

While such biomonitoring studies provide irrefutable evidence that humans are exposed to PFRs, they do not explain via pathways such exposure occurs.

The widespread presence of PFRs in various goods and materials leads to contamination of indoor air and dust and consequent potential for human exposure via contact with these matrices in indoor environments (Cao et al., 2014). Of particular concern is the recognition that exposure to PFRs via indoor dust is especially important for young children partly because of the greater hand-to-mouth

behaviour of young children compared to adults, but also because given equal intakes, their exposure will exceed that of adults on a body weight-normalised basis (Harrad et al 2008). With respect to dust contact rate, while definitive data has yet to be generated the USEPA (2005) estimated that children between 1 to 5 ingest on average 100-200 mg dust/day, while adults ingest about 20-50 mg dust/day (Jones-Otazo et al. 2005). Moreover, dermal uptake of PFRs has been demonstrated (Abdallah et al, 2016).

With respect to inhalation exposure, airborne particles can be divided between inhalable particles (<4 mm nominal diameter) that deposit in the upper respiratory tract, and respirable air particles which are capable of penetrating deep inside the lung´s gas-exchange region (Schreder et al., 2015). TCIPP and TDCIPP were detected in inhalable particles at mean concentrations of 371 ng/m^3 and 19.1 ng/m^3 respectively in indoor air from Washington, US (Schreder et al., 2015). In Sweden, Marklund et al (2005) reported TCIPP concentrations to range between 38 and 210 ng/m^3 in houses, with a maximum concentration of 570 ng/m^3 TCIPP in a prison corridor, with concentrations in offices reaching as high as 730 ng/m^3 (Marklund et al., 2005).

FRs are used in a large variety of consumer products. These compounds are continuously released into the aquatic environment from sources such as wastewater treatment plants, where aquatic organisms tend to accumulate these contaminants in their body (Richardson, 2008).

Kim et al., (2011) report in fish, mean concentrations of TCP (2.14 ng/g) and of TPhP and EHDPP (23.9 and 3.9 ng/g) respectively. Andresen et al. (2004) reported that in 2004 in the River Ruhr in Germany, concentrations of TCIPP were between 20-200 ng/L, while those of TCEP and TDCIPP were ~50 ng/L and those of TnBP and TPhP were 30-40 ng/L and 10-30 ng/L respectively.

With respect to guidelines limits on safe levels of human exposure to PFRs, Table I.7 summarises current based on a chronic no observed adverse effect level (NOAEL) divided by an uncertainty factor of 1000, HBLVs for 22,000, 80,000 and 15,000 ng/kg bw/day were derived for TCEP, TDCIPP and TDCIPP respectively (Ali et al., 2012).

Table I-7 NOAEL (ng/ (kg bw)/day) for different PFRs

PFR	**NOAEL ng/ (kg bw)/day**	**Comments**
TnBP	24000	NOAEL based on carcinogenic effects (Pharmaco LSR Inc, 1994 Report No. 89-3533).
TCEP	22000	NOEL based on relative liver and kidney weight (Matthews et al., 1990).
TCIPP	80000	NOAEL of male rats based on changes in liver weight and cellular changes in kidney (Stauffer report, 1981).
TDCIPP	15000	NOAEL based on relative liver weight (Kamata et al., 1989).
TPhP	70000	NOEL based on liver weight and depression of weight gains (Sutton et al., 1960).
TCP	13000	LOAEL 13–15 mg/kg (NOAEL 7 mg/kg based on lesions in adrenal gland, ovary and liver) (NTP, 1994).

1.7 Aims of this study

Against the backdrop of current knowledge outlined above, the primary objectives of this study are to:

- Compare concentrations of seven PFRs in floor dust from a number of different countries to test the hypothesis that PFR contamination of indoor dust will be influenced by international differences in flame retardant use.
- Evaluate within-room and within-home spatial and temporal variability in concentrations of seven PFRs in floor and elevated surface dust from a number of homes in Birmingham, UK. This will test the hypothesis that such variability can exert an appreciable influence on human exposure assessments.
- Measure concentrations of seven PFRs in both indoor air and dust from offices and homes in Birmingham, UK. These data will be used to test the hypothesis that the relative significance of inhalation and dust ingestion as pathways of human exposure will vary according to the physichemical properties of the PFR.
- Use a test chamber to test the hypothesis that direct fabric-dust contact is an important pathway via which PFRs may transfer from a PFR-containing fabric to dust.

CHAPTER II. SAMPLING AND ANALYTICAL METHODOLOGY

This chapter covers the sampling, extraction and analytical methods used in this thesis to determine concentrations in indoor air and dust of 7 of the most widely used PFRs. Method validation and quality assurance/quality control data are included and explained. The methods used were optimisations of those developed previously in this research group (Brommer et al., 2015).

2.1 Sampling

2.1.1 Dust sampling

2.1.1.1 Dust sampled for the purposes of studying temporal and spatial variations in PFR concentrations.

Within-room spatial and temporal variability in PFR concentrations in dust were studied in three homes in Birmingham under normal room use conditions to reflect actual human exposure, table II.1. Dust samples were collected monthly for 1 year starting November 2013 to evaluate temporal and seasonal variability.

Sampling was conducted using a TESCO VC207 1400 W vacuum cleaner in accordance with a previously reported protocol (Harrad et al., 2008b). For floor dust, a 1 m^2 area was vacuumed for 2 minutes where the floor is carpeted, while for bare floors (e.g. wood or tiled) a 4 m^2 area was sampled for 4 minutes. (Harrad et al., 2008 a, b). Samples were collected using nylon sample socks (25 μm pore size) that were mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie, sealed in a plastic bag and stored until analysis.

Table II-1 Areas sampled in houses in this study.

House	Area		
House 1	Living room	1 bedroom	kitchen
House 2	Living room	1 bedroom	Kitchen
House 3	Parents' bedroom	Children's bedroom	Kitchen

To facilitate study of spatial variation in PFR concentrations, care was taken to avoid overlap of each sampling area, with study of temporal variation facilitated by ensuring that the same areas were sampled each month. Table II.1 show the areas sampled in each house. Figure II.1, II.2 and II.3 shows the sampling configuration in houses (H1, H2 and H3), while figure II.4 illustrates the dust sampling methodology used.

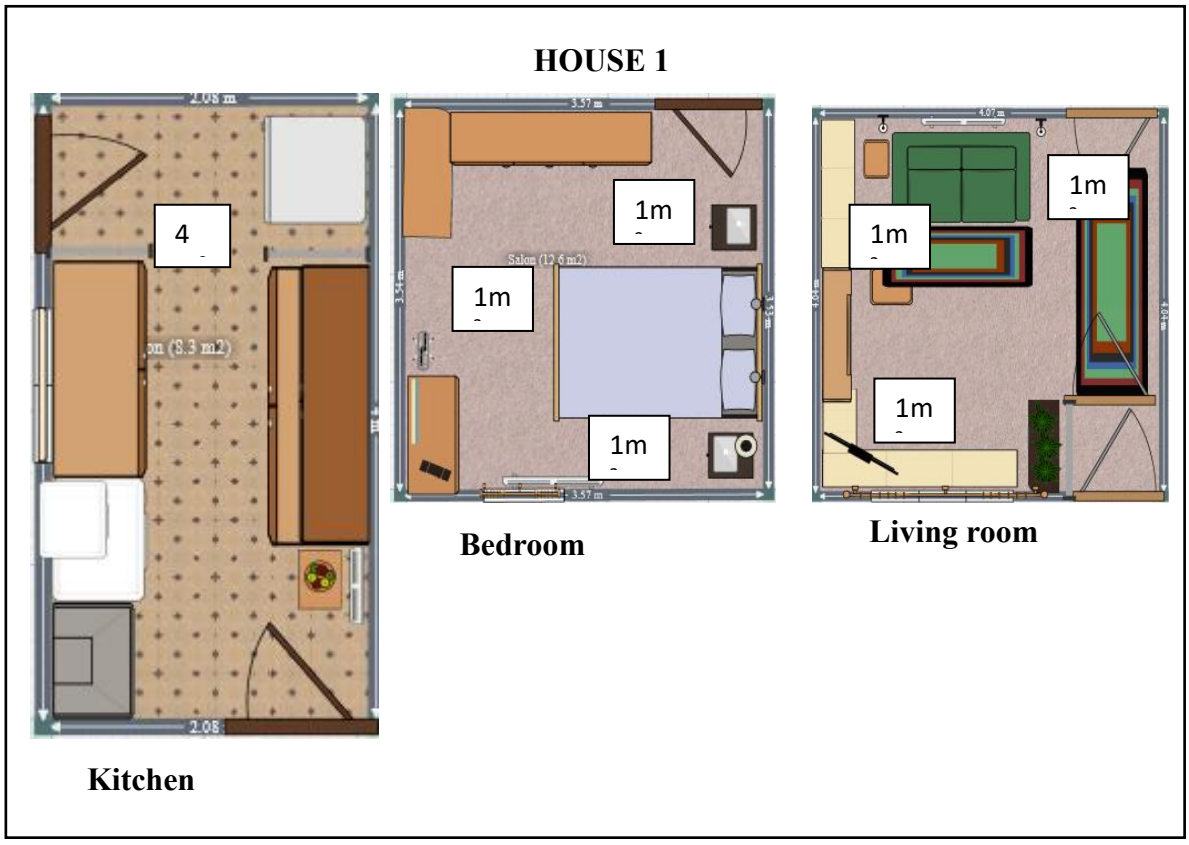


Figure II-1Floor areas and rooms sampled in H1.

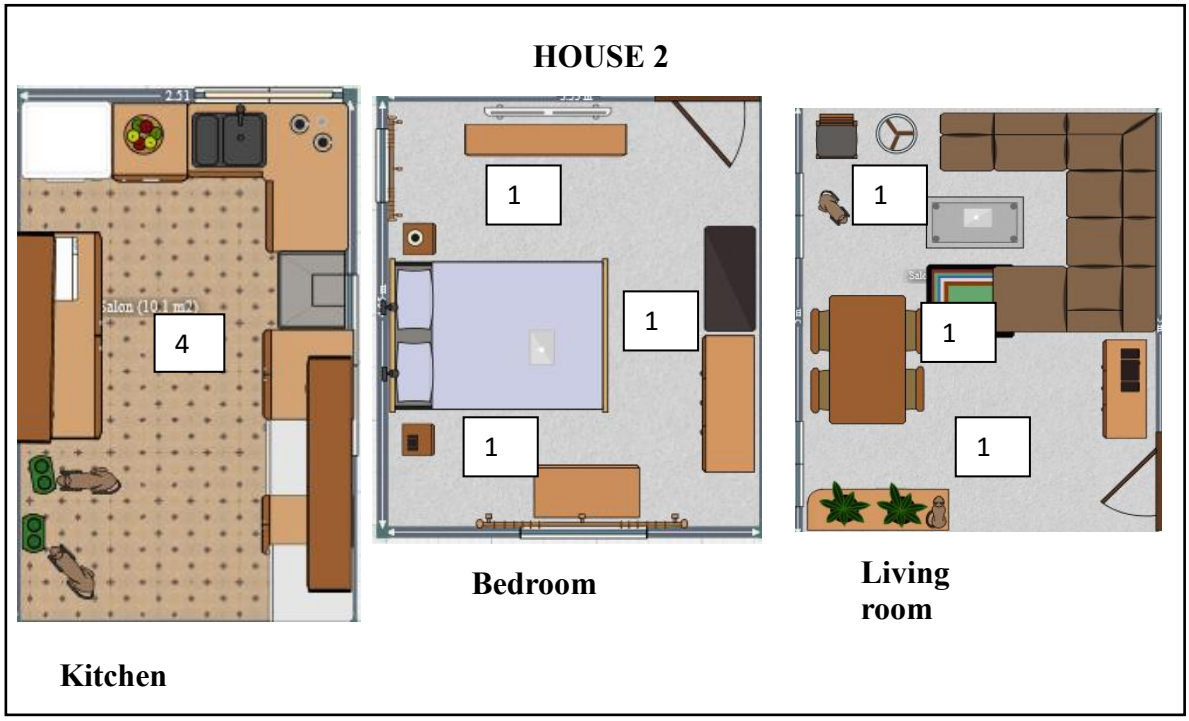


Figure II-2 Floor areas and rooms sampled in H2.

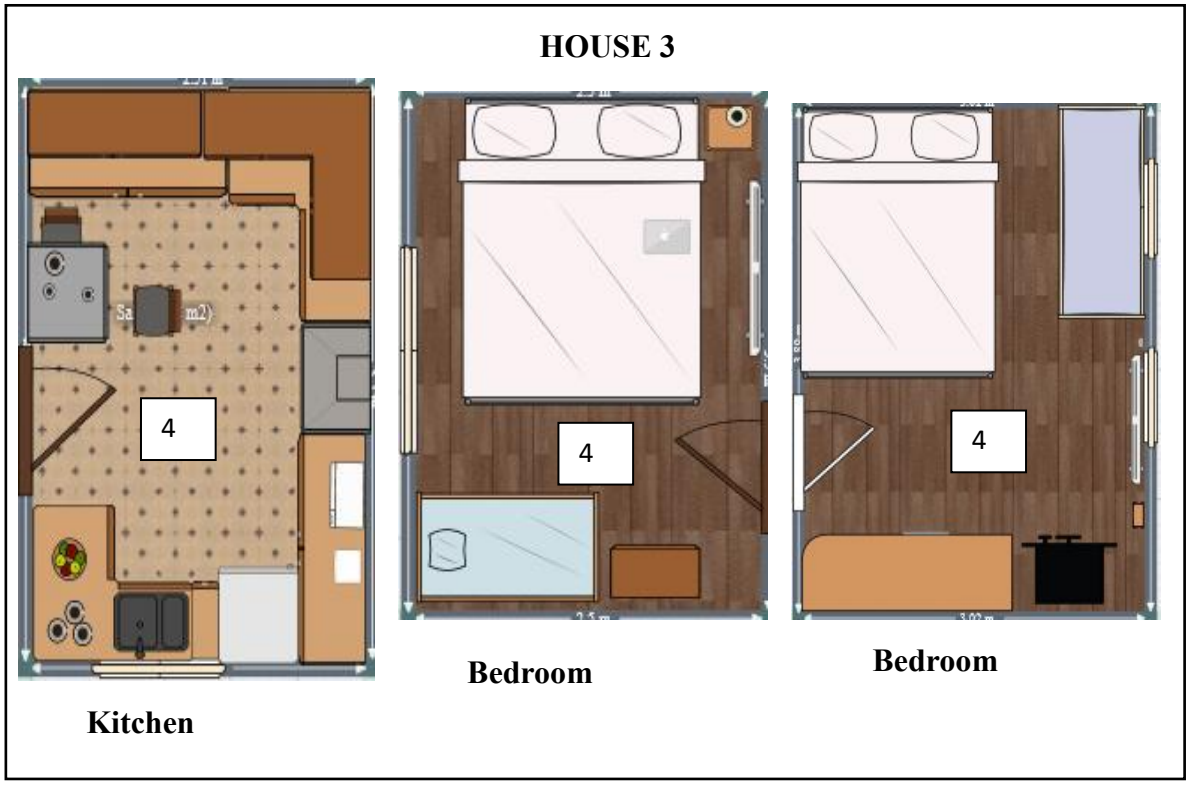


Figure II-3 Floor areas and rooms sampled in H3.

Carpet floor vacuumed

Tied Sock

Surface vacuumed

Tiled floor vacuumed

Figure II-4 Examples of sampling method.

2.1.1.2 Dust sampling to provide samples to study the relationship between PFR concentrations in indoor air and dust

In order to study the relationship between PFR concentrations in indoor air and dust collected from the same rooms over the same period; passive air samplers (see below) were deployed for one month in homes and offices in the West Midlands conurbation. Dust samples were collected at the end of each air sampling period in accordance with the protocol described in 2.1.1.1. In total, air and dust samples were collected from 21 living rooms, 21 bedrooms from the same houses as the living rooms, and 20 offices.

2.1.2 Passive air sapling

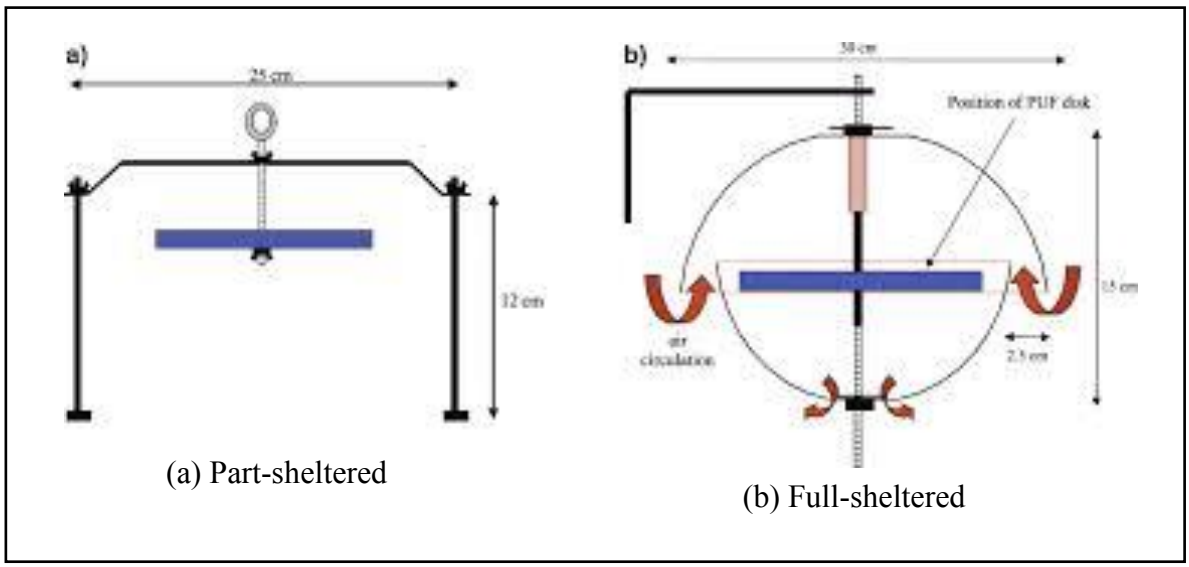
During January to May 2016, indoor passive air samplers were deployed in 20 different offices in the University of Birmingham, as well as 21 bedrooms and 21 living rooms from the same houses within the West Midland conurbation, UK. In addition, outdoor air samplers (n=7) were deployed during May 2017 at the Elms Road Observatory Site (EROS) in the University of Birmingham, UK. Table II.2 summarises the total number of air samples collected.

Table II-2:Numbers of passive air samples collected in indoor and outdoor environments

Area	Number of samples
Living rooms	21
Bedrooms	21
Offices	20
Outdoor	7

The passive air samplers deployed are illustrated in figure II.5. They comprise a pre-cleaned polyurethane foam (PUF) disk (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area 0.07 g cm^{-3} density, PACS, Leicester, UK) sheltered by stainless steel housing (18 cm diameter bottom housing –not used in the "part-sheltered" configuration deployed indoors, and a 23 cm top housing). The shelters were cleaned carefully and acetone solvent rinsed to remove potential contamination between deployments.

PUF disks were washed in tap water, dried at room temperature and pre-cleaned using pressurised liquid extraction (Dionex Europe, UK, ASE 350). PUF disks were treated with PCB 129 (1 μg/mL; 50 μL) as a sampling evaluation standard (SES) prior to field deployment. The total sampling time was one month (Newton, et. al., 2016).



(a) Part-sheltered (b) Full-sheltered

Figure II-5 PUF disk passive air samplers used to sample (a) indoor air (part-sheltered) and (b) outdoor air (full-sheltered).

2.1.3 Chamber experiments to study transfer of PFRs to dust via direct source: dust contact

A stainless-steel chamber designed at the University of Birmingham was utilized – see Figure II.6. With an internal surface area of 785 cm^2, the dimensions were 10 cm diameter and 20 cm height, and a total volume of 1,570 cm^3. A piece of upholstery fabric (30 x 20 cm) that had previously been established to contain elevated concentrations of TCIPP was vacuumed thoroughly before the experiment to remove dust as well as any loosely adhering fabric fibers (Rauert et al. 2016).

This fabric was green wool, used as a covering for a seat cushion from a desk chair sampled June 2012 in the University of Birmingham as part of a previous project within our research group. A smaller piece of the vacuumed fabric (5 x 5 cm) was cut, weighed and placed onto a (GFF that was placed onto a wire mesh 10 cm above the chamber floor. A layer of approximately ±0.13 g of pre-characterized dust (a mix from different living room floors from Ciudad Victoria, Mexico, sampled December 2014 and January 2015) was spread over the surface of the fabric, using a small spatula. The experiment was conducted at room temperature with the chamber sealed to avoid external contamination. The following contact times were investigated: 1, 2, 4, 7 and 10 days. After each sampling period, the dust was gently brushed off from the fabric, collected and weighed again prior to extraction and analysis. This entire procedure was conducted in triplicate. The dust and fabric were extracted and analysed separately.

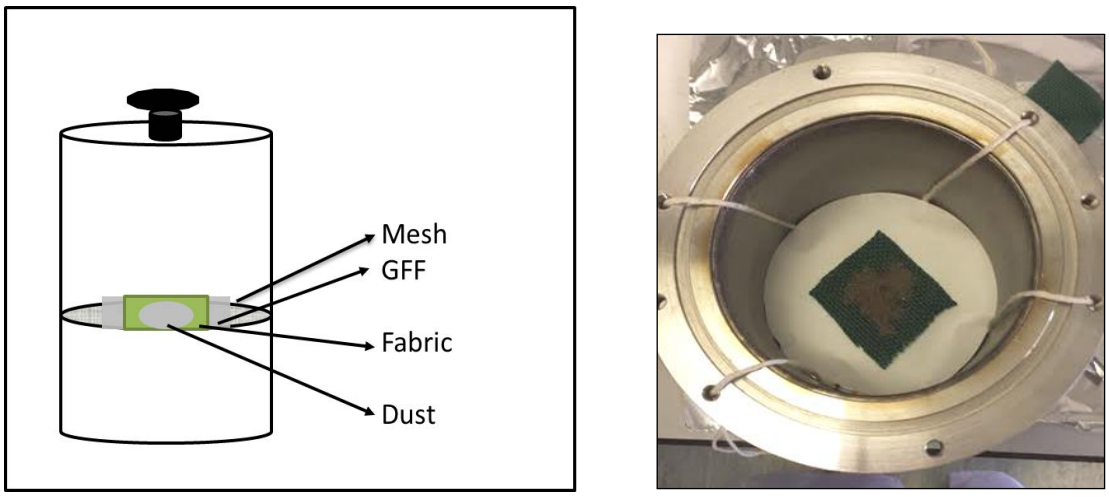


Figure II-6 Configuration of the chamber experiments studying source-to-dust transfer of PFRs via direct contact.

2.2 Sample extraction and purification

2.2.1 Chemicals

The native compounds (TnBP, TCEP, TPHP, EHDPP, TDCIPP, TCIPP and TPhP), $TnBP_{D27}$ and $TPhP_{D15}$ used as internal standards and D_{10}-anthracene and D_{12}-benz[*a*]anthracene used as recovery determination (or syringe) standards were purchased from Wellington Laboratories (Canada) as stock solutions in toluene at 1 mg/mL. The standards used are summarised in table II.3.

HPLC grade acetone and hexane were supplied by Fisher Scientific UK Ltd, while ethyl acetate, iso-octane, florisil, and glass wool were supplied by Sigma Aldrich. Nitrogen used for solvent evaporation was oxygen free and supplied by BOC Gases.

Table II-3 Native and labelled organophosphate standards used in this study.

Compound	**Abbreviation**	**Molecular formula**	**Molecular Weight**	**Purity (%)**
Native Standards				
Tri-n-butyl phosphate	TnBP	$C_{12}H_{27}O_4P$	266.32	98
Tris(2-chloroethyl) phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	285.49	98
Triphenyl phosphate	TPHP	$C_{18}H_{15}O_4P$	326.29	98
2-Ethylhexyl diphenyl phosphate	EHDPP	$C_20H_{27}O_4P$	362.41	98
Tri (2-chloroisopropyl) phosphate	TCIPP	$C_9H1_8C_{l3}O_4P$	327.57	98
Tri (1,3-dichloropropyl) phosphate	TDCIPP	$C_9H_{15}C_{l6}O_4P$	430.91	98
Tri-cresyl phosphate	TCP	$C_{21}H_{21}O_4P$	368.37	98
Internal Standards				
Tri-n-butyl phosphate $_{D27}$	TnBP $_{D27}$	$C_{12}D_{27}O_4P$		98
Triphenyl phosphate $_{D15}$	TPHP $_{D15}$	$C_{18}D_{15}O_4P$	341.38	98

Compound	Abbreviation	Molecular formula	Molecular Weight	Purity (%)
Recovery Standard				
Anthracene $_{D10}$	Ant $_{D\ 10}$	$C_{14}D_{10}$	188.29	99
Benz[a]anthracene $_{D\ 12}$	B[a]A $_{D\ 12}$	$C_{18}H_{12}$	228.29	99
Sampling Evaluation Standard				
2,2',3,3',4,5-hexachlorobiphenyl	PCB 129	$C_{12}H_4Cl_6$	360.87	99

2.2.2 Dust sample preparation, extraction and clean up

The dust samples were homogenised by sieving though 500 µm mesh aluminium sieve and removing undesirable fibres using acetonerinsed tweezers. After sieving, the dust was weighed and stored in glass jars with aluminium foil lined lids and stored at 4 ˚C until extraction.

The extraction method used followed that developed by Brommer et al (2013) in our laboratory. 50 mg of dust was spiked with 150 µL ISTD solution (100 ng each of $TnBP_{D27}$ and $TPHP_{D15}$). Then the samples were extracted with 2 mL Hex-Ac (hexane: acetone 3:1 v/v) combining vortexing for 1 min, followed by ultrasonication for 5 min (2 cycles). Between cycles the dust samples were centrifuged at 2,000 rpm for 2 min and the supernatants collected in a clean glass tube.

A baked Pasteur pipette was filled with 1 g of precleaned Florisil (baked for 1 hr at 400 °C) then subjected to ASE using hexane as solvent (1 cycle). The Florisil column was prewashed using 8 mL of methanol then 4 mL of hexane. Following addition of the sample extract, the column was eluted with 8 mL of hexane which was discarded, to remove PBDEs. The PFRs were then eluted with 10 mL ethyl acetate, the eluate evaporated to incipient dryness before resolubilization with 100 µL of iso-octane containing 100 ng of Ant $_{D10}$ and B[*a*]A $_{D12}$ as recovery determination standards ready for injection into the GC-MS. The extraction and clean-up processes followed are summarised in fig. II.5 (Brommer, et.al 2015).

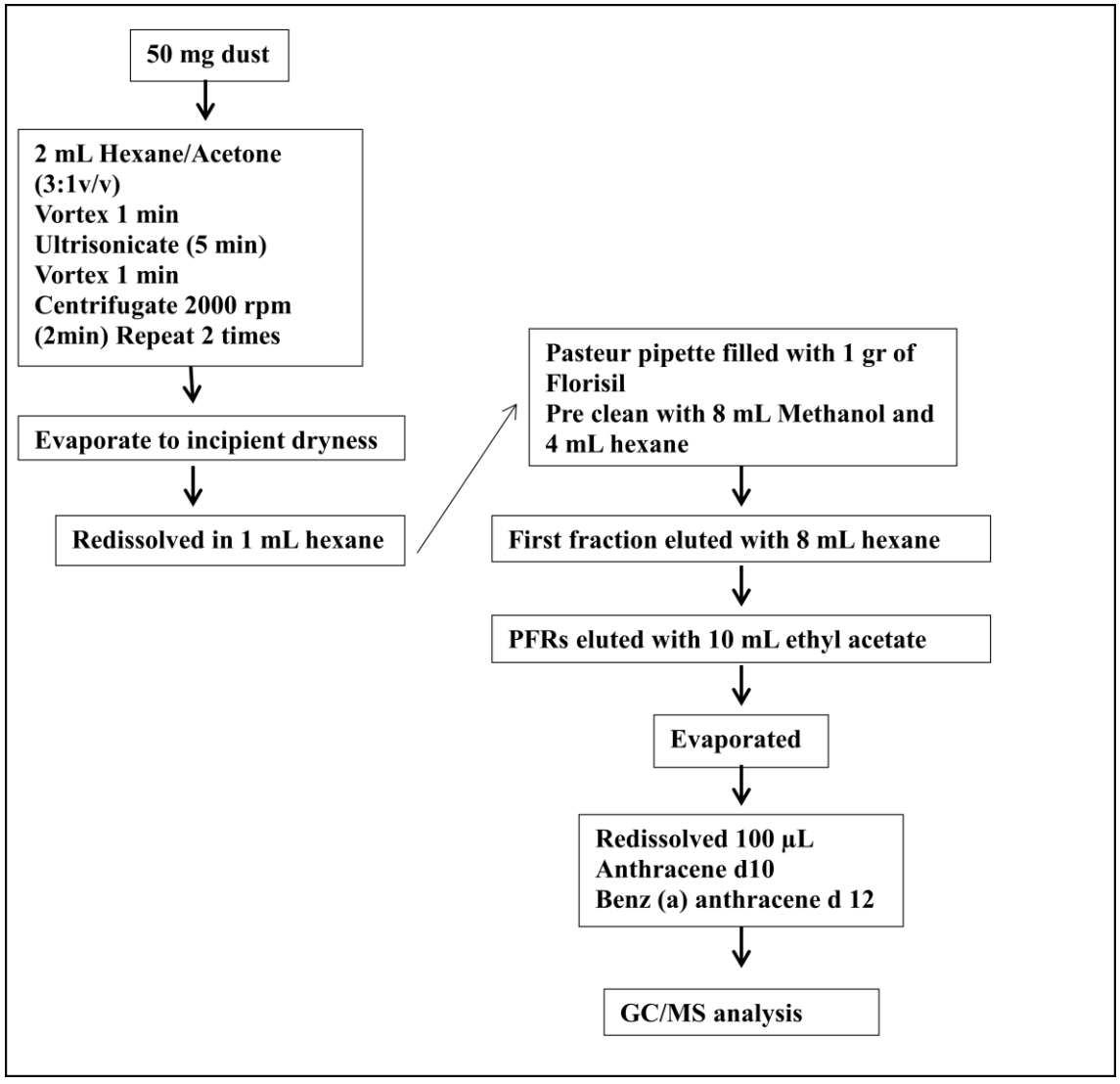


Figure II-7 Diagrammatic summary of dust extraction and extract purification processes.

2.2.3 Air samples extraction and clean up

After a month deployment, PUF disks were harvested from air samplers and loaded into precleaned ASE 350 (Dionex) cells as shown in figure II.8. The 66 mL stainless-steel cells (Thermo Scientific, UK) were spiked with (150 µL) D_{27} TnBP and D_{15} TPHP as internal standards. The ASE cells were extracted with: hexane: ethyl acetate (3:4 v/v) (15 mL hexane: 20 mL ethyl acetate) at 70 ˚C and 1500 psi. The heating time was 5 minutes static time 5 minutes, purge time 100 s, flush volume 60 % with 3 static cycles.

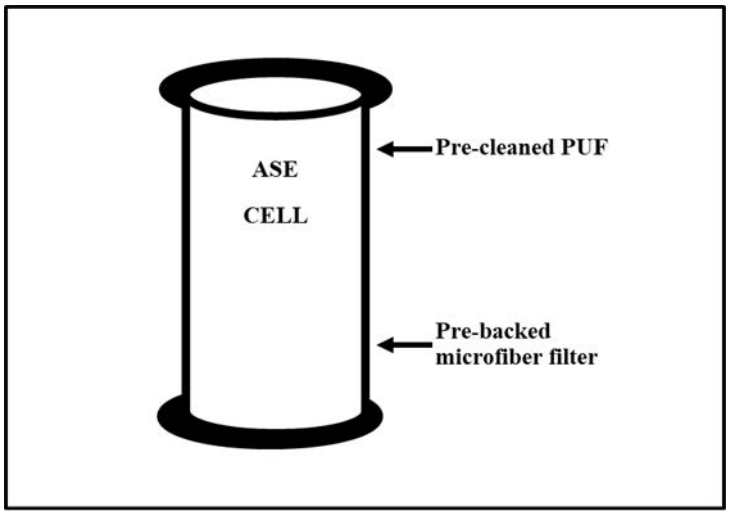


Figure II-8 Pre-packed ASE cell.

2.2.4 Fabric extraction and clean up

Fabric samples were extracted for analysis of PFRs in accordance with the soaking extraction procedure of Kajiwara et al. (2009). Approximately 0.2 g of fabric was placed in 20 mL of toluene in a glass bottle with a lid then vortexed for 2 minutes followed by storage in the dark at room temperature for 2 days.

After 2 days, a 2 *μ*L aliquot of the crude extract was injected onto the GC-MS and analysed using the procedures outlined in 2.3.1 below. The test textiles were analysed in triplicate.

2.3 Analysis

In accordance with Brommer et. al., (2015) the methodology followed was thus: the analysis was conducted on an Agilent 5975 GC/MS fitted with a 30 m DB-5 MS column (0.25 mm id, 0.25 μm film thickness). The carrier gas was helium with a constant flow rate of 1.0 mL/min. Mass spectrometer temperatures used were: injector 290 °C under splitless conditions and MS solvent delay of 3.8 min.

The ion source, quadrupole and interface temperatures were 230 °C, 150 °C and 300 °C respectively. The GC temperature programme is as shown in fig 2.5, at the beginning 100 °C, hold for 1.25 min, ramp 10 °C/min to 240 ˚C, ramp 20 °C/min to 310 °C, and hold for 5 min. Total run time estimate 23.75 min.

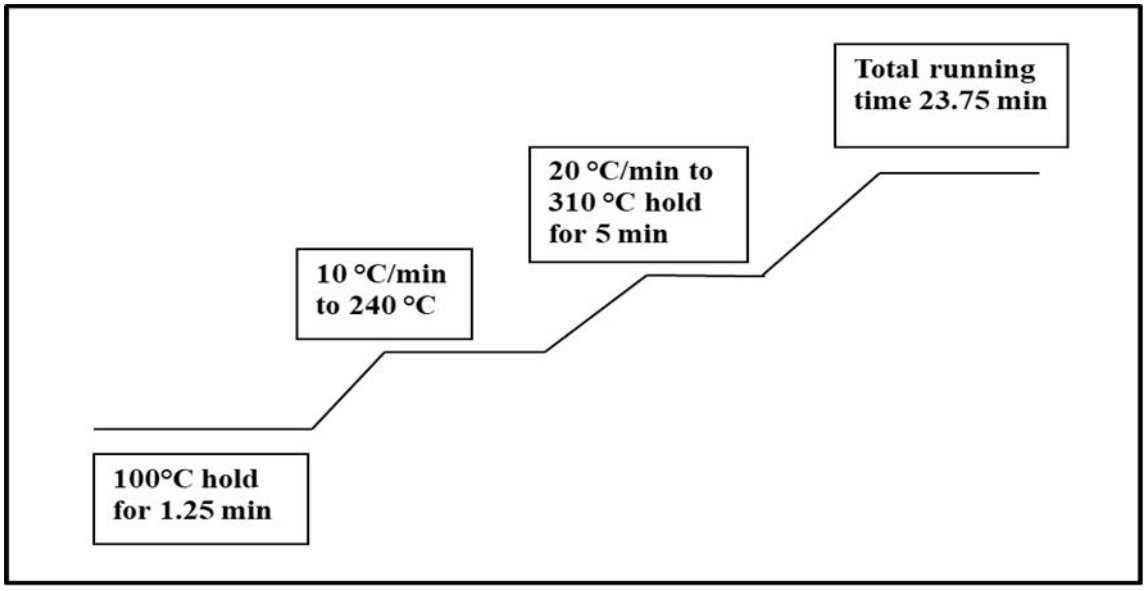


Figure II-9 GC-MS Temperature programme

The MS was operated in electron ionisation (EI) selected ion monitoring (SIM) mode. An overview of the ions monitored for identification and quantification purposes can be found in table II.4. d_{27}TnBP was used to quantify TnBP, TCP, TCIPP and TCEP while TDCIPP, TPhP and EHDPP were quantified using d_{15}TPhP. Dwell times were 30 ms.

Illustrative chromatograms are shown in the next seven figures. Specifically, these are: figure II.10 1 µg/mL mixed PFR standard, figure II.11 an extract of SRM 2858, figure II.12 a dust sample, figure II.13 a field blank, II.14 an indoor air sample, II.15 an outdoor air sample, and figure II.16 a fabric sample.

Table II-4 Ions (m/z) monitored for PFRs**.**

Compound	**Quantification Ion**	**Identification Ion**
TnBP	211	155
TCEP	249	251
TCIPP	277	279
TPhP	326	325
TDCIPP	381	379
EHDPP	251	250
TCP	368	368
D_{27} TnBP	103	167
D_{15} TPHP	341	339
Anthracene d_{10}	188	
Benz(a)anthracene d_{12}	240	

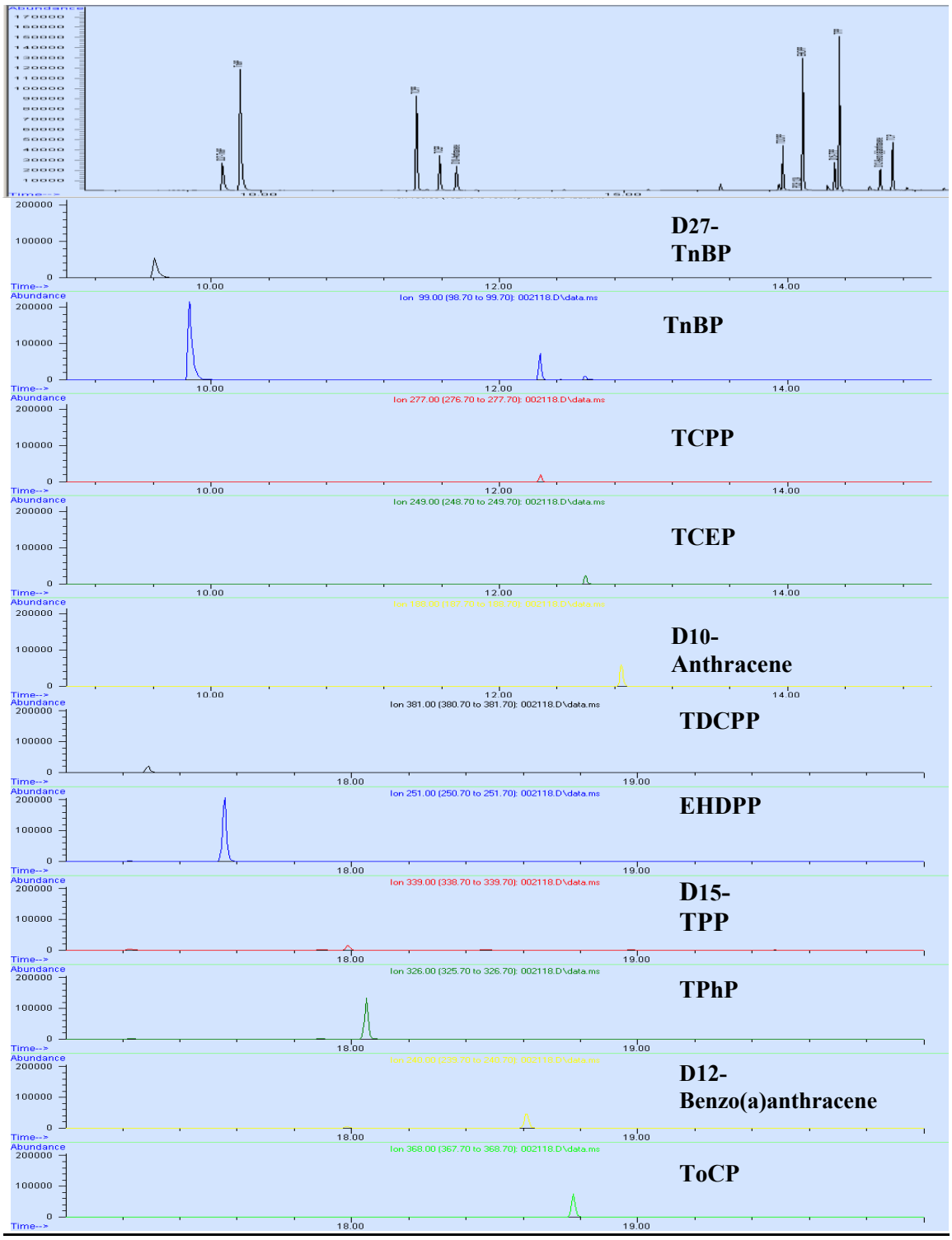


Figure II-10 GC MS chromatogram of a 1 µg/mL PFR standard mixture.

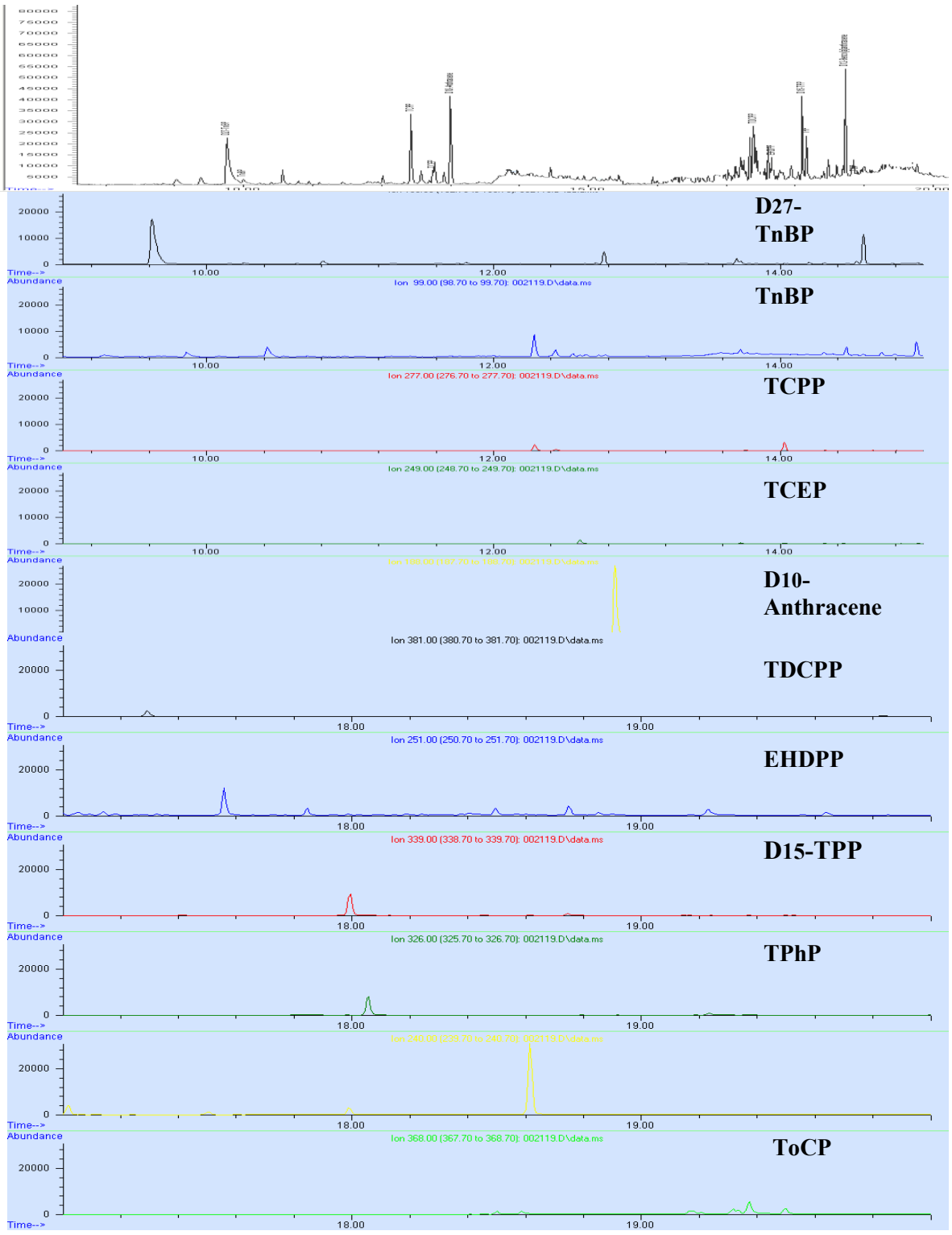


Figure II-11 GC MS chromatogram for an extract of SRM 2585.

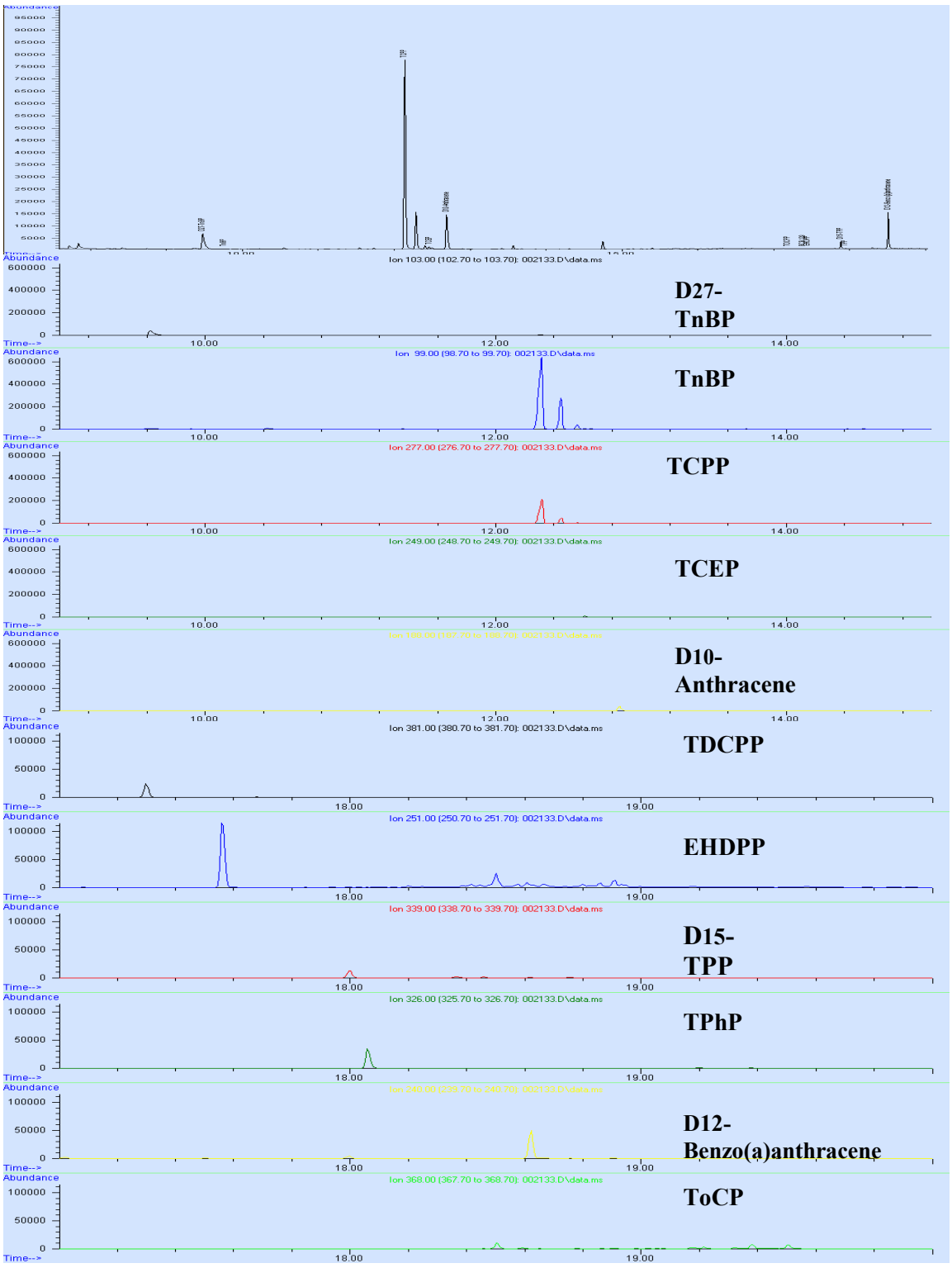


Figure II-12 GC MS chromatogram for a dust sample.

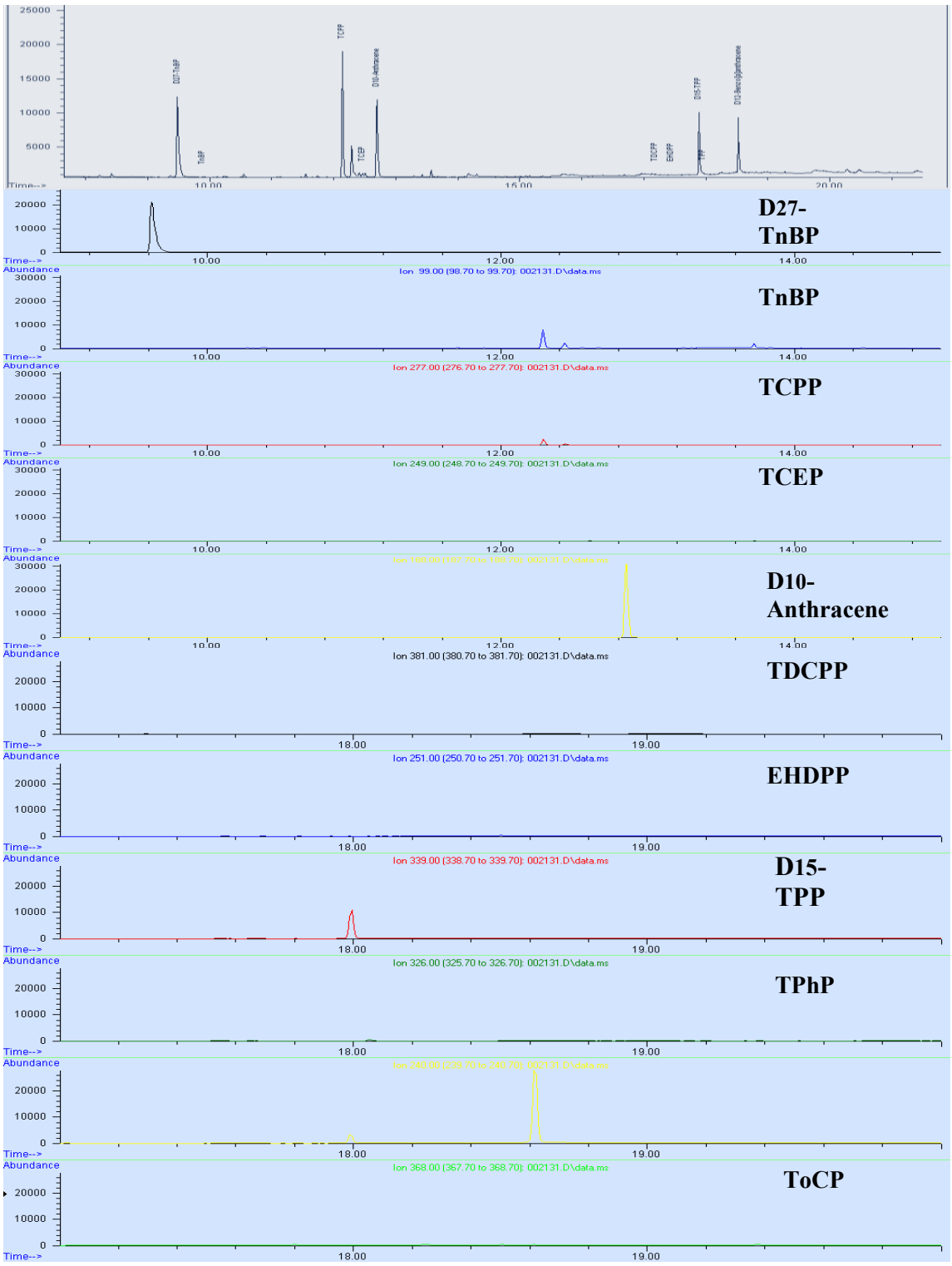


Figure II-13 GC MS chromatogram of a field blank.

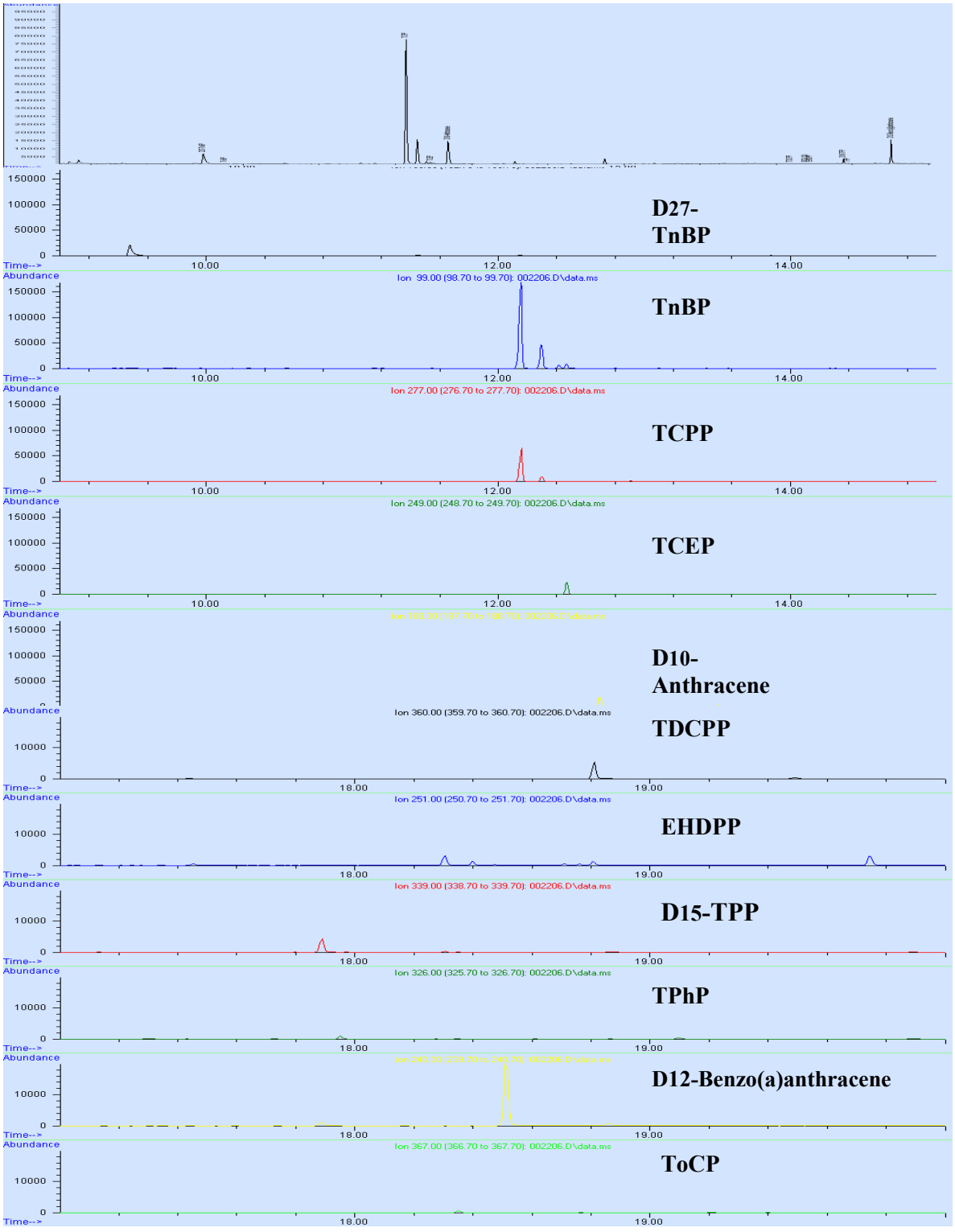


Figure II-14 GC MS chromatogram of an indoor air sample.

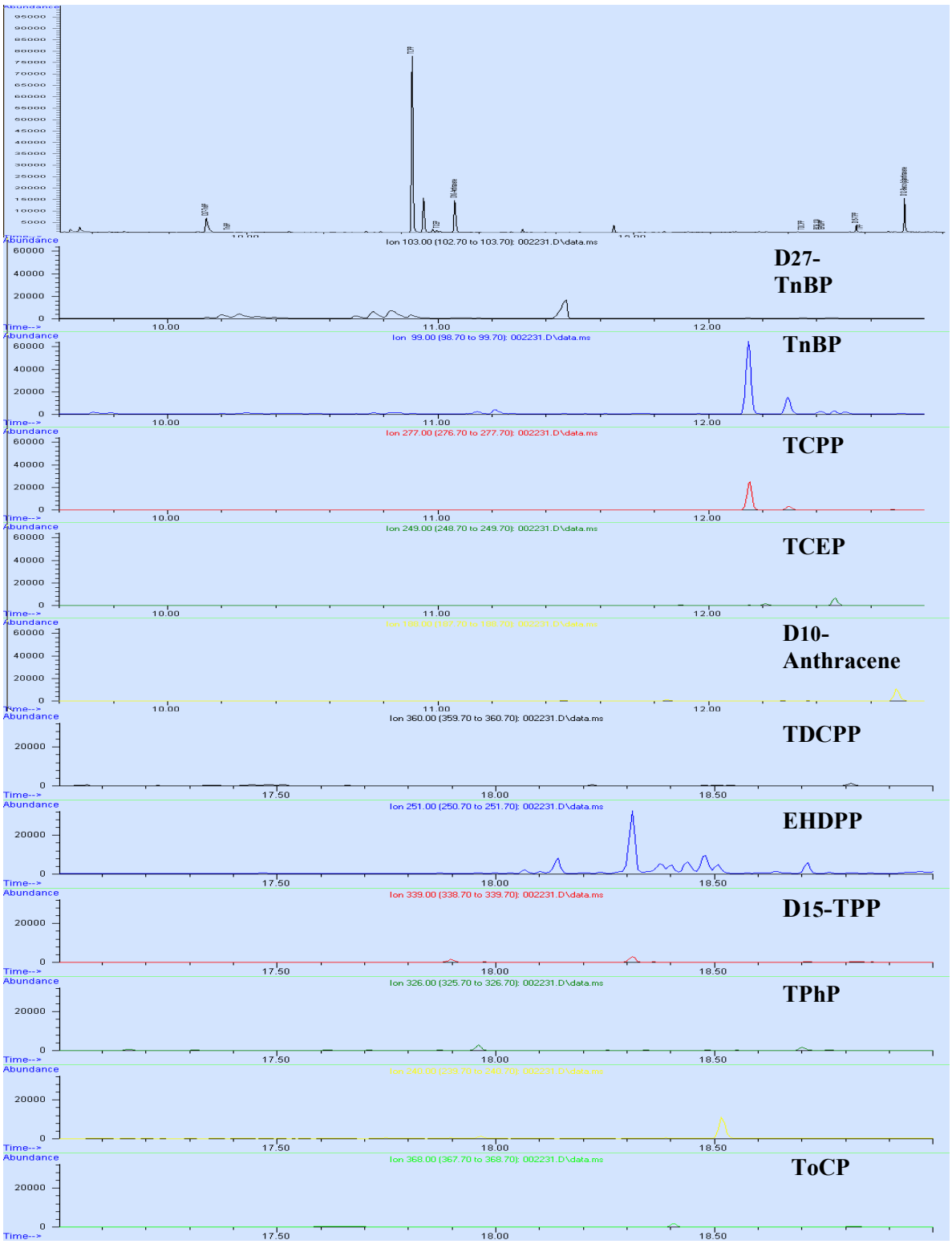


Figure II-15 GC MS chromatogram of outdoor air sample.

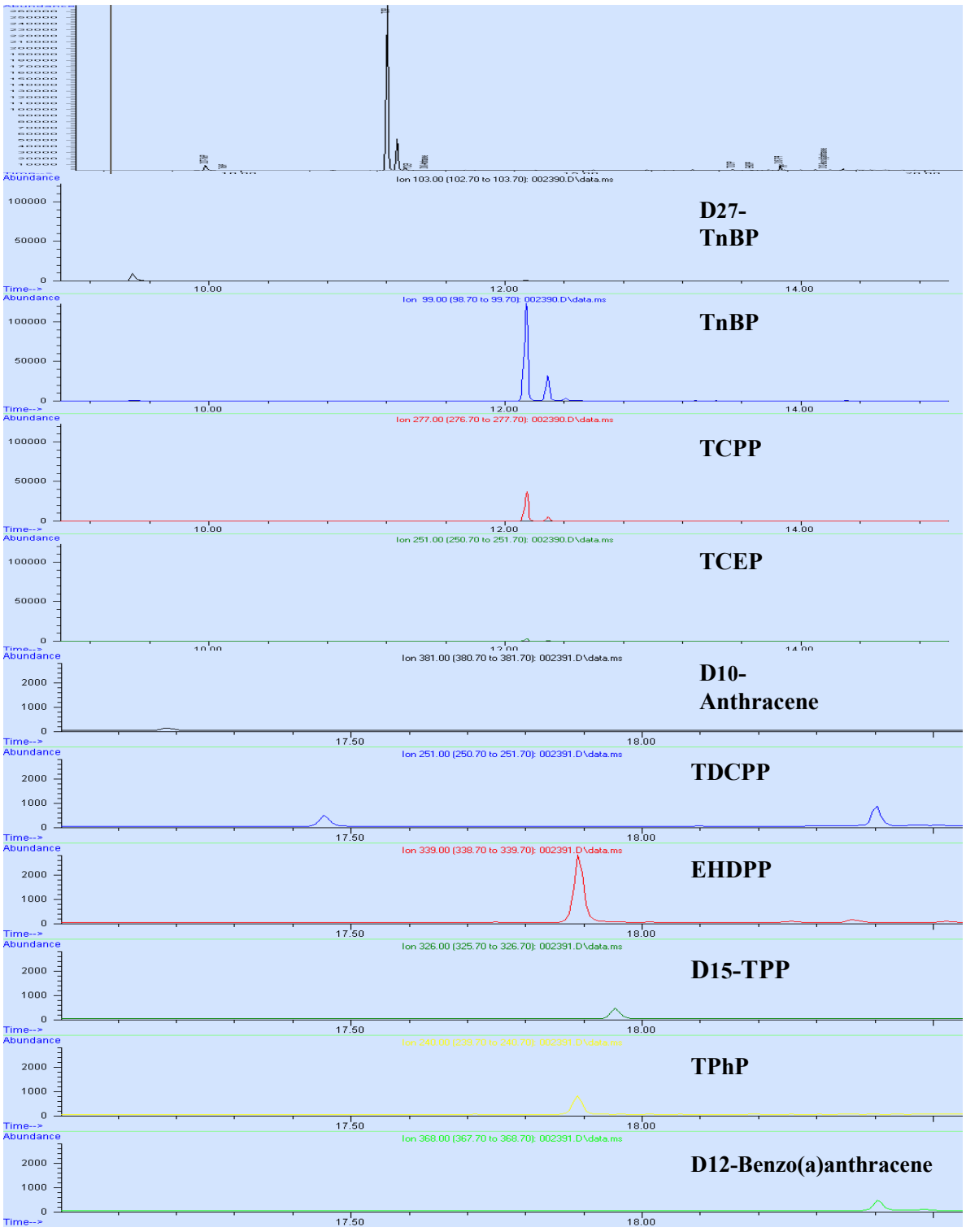


Figure II-16 GC-MS chromatogram for a fabric sample.

2.4 Validation and QA/QC criteria

2.4.1 Analyte identification and quantification criteria

A calibration plot covering 7 concentration points was conducted (0.05, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 ng μL^{-1}) to assess the linearity of the GC/MS response. Linearity was indicated by R^2>0.99 for all target compounds. Data from this calibration plot were used to calculate relative response factors (RRFs) for each of the target compounds. The RRF is defined as the instrument response for a unit amount of target pollutant relative to the instrument response obtained for the same amount of the internal standard (IS).

Equation 1 is the algorithm to calculate relative response factors (RRFs) for each of the target compounds.

Equation 1: $$\mathrm{RRF} = \frac{A_{NAT}}{A_{IS}} \times \frac{c_{IS}}{c_{NAT}}$$

Where A_{NAT} is the peak area for the native compound; A_{IS} is the peak of the internal standard; (C_{NAT}) is the concentration of the native compound; and C_{IS} is the concentration of internal standard. The relative standard deviation (RSD) of the RRFs calculated for each target compound at each concentration point of the calibration plot did not exceed 5%.

2.4.2 Sampling evaluation standard (SES)

To assess any losses during passive air sampling, pre-cleaned PUF disks were treated with 50 µL of a sampling evaluation standard (SES) (PCB 129) prior to field deployment providing a quantitative measure of the efficiency of sampling.

2.4.3 Recovery determination (syringe) standard (RDS).

The recovery of the SES and the ISs used were determined by use of a RDS added to the sample extracts just before GC-MS analysis. In this study anthracene d_{10} and benz[a]anthracene d_{12} were used.

The recoveries of the IS in each sample were calculated using equation 2.

$$\text{Equation 2 \% IS Recovery} = \left[\left\{ \frac{A_{IS}}{A_{RSD}} \right\}_S X \left\{ \frac{A_{RSD}}{A_{IS}} \right\}_{STD} X \left\{ \frac{C_{IS}}{C_{RSD}} \right\}_{STD} X \left\{ \frac{C_{RSD}}{C_{IS}} \right\}_S \right] X\ 100$$

Where $(A_{IS}/A_{RDS})_s$ = ratio of IS peak area to recovery determination standard peak area in the sample; $(A_{RDS}/A_{IS})_{STD}$ = ratio of recovery determination standard peak area to the internal standard peak area in the calibration standard; $(C_{IS}/C_{RDS})_{STD}$ = ratio of concentration of internal standard to concentration of recovery determination standard in the calibration standard; and $(C_{RDS}/C_{IS})_S$ = ratio of concentration of recovery determination standard to concentration of internal standard of the sample.

For air samples, equation 3 was used to calculate SES recoveries

$$\text{Equation 3 \% SES Recovery} = \left[\left\{ \frac{A_{SES}}{A_{RSD}} \right\}_S X \left\{ \frac{A_{RSD}}{A_{SES}} \right\}_{STD} X \left\{ \frac{C_{SES}}{C_{RSD}} \right\}_{STD} X \left\{ \frac{C_{RSD}}{C_{SES}} \right\}_S \right] X\ 100$$

Where $(A_{SES}/A_{RDS})_S$ = ratio of sampling evaluation standard peak area to recovery determination standard peak area in the sample; $(A_{RDS}/A_{SES})_{STD}$ = ratio of recovery determination standard peak area to sampling evaluation standard peak area in the calibration standard (the average of calibration standard run before and after batch samples);

$(C_{SES}/C_{RDS})_{STD}$ = ratio of concentration of sampling evaluation standard to concentration of recovery determination standard in the calibration standard and $(C_{RDS}/C_{SES})_S$ = ratio of concentration of recovery determination standard to concentration of sampling evaluation standard in the sample.

Table II-5 Statistical summary of the recoveries of the SES and ISs in all samples (µg/g).

Standard	n	SD	Median	Mean	Range	%RSD
[a]**D_{27} TnBP**	620	17	93	91	42-135	18
[a]**D_{15} TPhP**	620	16	94	92	44-137	17
[b]**Anthracene d_{10}**	620	8	67	66	59-84	12
[b]**Benz[*a*]anthracene d_{12}**	620	3	58	58	53-62	6
[c] **PCB 129**	70	17	73	72	30-73	23

a Internal Standard, b Recovery standard and c Sampling evaluation standard.

2.4.4 Accuracy and precision.

As part of the quality assurance for the entire method, aliquots of NIST standard reference material (SRM2585, organic contaminants in indoor dust) table II.6 show the results were analysed regularly to provide on-going assessment of method accuracy and precision.

As neither certified nor indicative concentration data were available for PFRs in this SRM, our data were compared to literature data (Van den Eede et al., 2011), (Bergh et al., 2012), (Brandsma et al., 2013) as shown in table II.7: RSD (<20 %) values obtained indicate the precision of the method.

Table II-6 Summary of PFR concentrations in SRM 2585 in this study (µg/g).

SRM (n=46)	TnBP	TCEP	TCIPP	TDCIPP	EHDPP	TPhP
Mean	0.23	1.07	1.06	2.02	1.06	1.09
Minimum	0.15	0.71	0.76	1.55	0.74	0.87
Maximum	0.27	1.29	1.37	2.26	1.28	1.28
SD	0.03	0.12	0.11	0.15	0.09	0.09
%RSD	13	11	11	7	9	9

Table II-7 PFR concentrations in dust SRM2585 compared with literature data (µg/g).

	TnBP	TCEP	TCIPP	TDCIPP	EHDPP	TPhP	Reference
Mean	0.18	0.70	0.82	2.00	NA	0.99	Van den
STDEV	0.02	0.17	0.10	0.26		0.07	Eede et al., 2011
Mean	0.19	0.84	0.88	2.30	1.30	1.10	Bergh et al., 2012
STDEV	0.02	0.06	0.14	0.28	0.12	0.10	
Mean	0.29	0.81	0.75	2.50	1.23	0.89	Brandsma et al., 2014
STDEV	0.01	0.04	0.02	0.01	0.02	0.04	
Mean	0.23	1.07	1.06	2.02	1.06	1.09	This study
STDEV	0.03	0.12	0.11	0.15	0.09	0.09	

2.4.5 Analysis of Blanks, LOD and LOQ

To further assess the quality of the method, every 6th sample run on the GC-MS was a reagent blank, which consisted of 50 mg pre-baked Na_2SO_4 extracted and cleaned as a sample. In the case of air samples, a clean PUF was extracted and analysed as a sample. For dust, field blanks were also collected in all countries sampled (except Mexico and the USA for logistical reasons).

These field blanks consisted of pre-baked Na_2SO_4 vacuumed from the surface of aluminium foil into a sampling sock and thereafter treated as a dust sample. Where the blank associated with a particular batch contained analyte concentrations <5 % of those present in a sample from that batch, no blank correction was conducted; however, where analyte concentrations in the blank fell between 5-20 %, concentrations in samples of the analyte in question were corrected by subtracting the blank concentration.

Finally, where blanks revealed a target PFR concentration > 20 %, all samples from that batch were discarded and re-analysed. This latter action was necessary for some of the earliest dust samples analysed due to high concentrations of TCIPP in blanks. Subsequent corrective action to minimise TCIPP contamination of blanks was successful and blank correction of further dust samples was not needed. Table II.8 summarises the levels of target PFRs detected in field blanks following corrective action to minimise TCIPP contamination. Table II.9 summarises the levels of target PFRs detected in reagent blanks. None of the target compounds were detected in field blanks (n= 16) for air samples, consisting in a pre-cleaned PUF disk, extracted and cleaned as a normal passive air sample, placed in the sampling location and immediately removed.

Table II-8 Summary of field blank concentration (µg/g) assuming 50 mg of dust analysed

Field Blank (n=92)	**TnBP**	**TCIPP**	**TCEP**	**TDCIPP**	**EHDPP**	**TPHP**	**TCP**
MEAN	0.02	0.07	0.04	0.05	0.02	0.02	0.01
MIN	0.00	0.02	0.01	0.01	0.00	0.01	0.00
MAX	0.08	0.18	0.34	0.09	0.08	0.08	0.02
SD	0.02	0.04	0.05	0.02	0.02	0.01	0.01
%RSD	11	5	12	4	9	5	3

Table II-9 Summary of reagent blank concentration (µg/g) assuming 50 mg of dust analysed.

Reagent Blank (n=92)	TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPHP	TCP
MEAN	0.01	0.06	0.03	0.03	0.00	0.02	0.01
MIN	0.00	0.04	0.02	0.01	0.00	0.02	0.00
MAX	0.01	0.08	0.04	0.04	0.00	0.02	0.02
SD	0.01	0.02	0.01	0.01	0.00	0.00	0.01
%RSD	8	4	3	6	5	4	3

Instrumental limit of detection (LOD) values were calculated for each of the studied compounds based on 3 times the standard deviation of the mass of that PFR detected in the procedural blanks. Method limits of quantification (LOQ) were then calculated based on the LOD, final extract volume (FEV), volume of final extract injected (VFEI), sample size (SS) and percentage of internal standard recovery (% IS Rec). LOQs were calculated following equation 4.

Equation 4 $$LOQ = \frac{LOD \times FEV}{SS \times VFEI} \times \frac{100}{\%\ ISRec}$$

Where FEV= 100 µL, SS = 50 mg, VFEI= 1 µL and %IS Rec= 70

Table II-10 Calculated LOD and LOQ for PFRs in this study.

Analyte	LOD	LOQ
TnBP	0.06	0.2
TCEP	0.15	0.5
TCIPP	0.12	0.4
TDCIPP	0.06	0.2
EHDPP	0.01	0.2
TPhP	0.01	0.1
TCP	0.03	0.1

2.5 Statistical Analysis

Statistical analysis was conducted using Microsoft Excel (Microsoft Office 2011) and SPSS version 22. Where concentrations were below the LOQ, concentrations were assumed to equal half the LOQ. The distribution of each data set was evaluated using Kolmogorov-Smirnov test and visual inspection; moreover, inspection of the concentration data for dust and indoor air revealed it to be log-normally distributed. Consequently, independent sample t-tests, ANOVA and Pearson correlations were performed on log transformed concentrations to evaluate statistical significance of the difference in variance between tested data sets. Confidence intervals in SPSS were preset at 95 % ($p = 0.05$).

CHAPTER III. CONCENTRATION OF PHOSPHATE FLAME RETARDANTS IN DUST FROM DIFFERENT COUNTRIES

3.1 Synopsis

The demand for PFRs has increased worldwide. Consequently, knowledge of the concentrations of these flame retardants in indoor dust and how this varies around the world is vital, given the various adverse health effects reported. In this chapter, the concentrations of seven PFRs in indoor dust from seven countries Jordan (Amman) plus 2 from North America (Victoria city, Mexico and Houston, USA) and 4 from Europe (Barcelona, Spain, Prague, Czech Republic, Athens and Crete, Greece and Helsinki, Finland) will be reported. To our knowledge, this is the first report of PFRs in indoor dust from Mexico and Jordan.

3.2 Sampling strategy

Dust from living room floors was sampled and analysed from Ciudad Victoria, Mexico and Houston, USA specifically for this project between December 2014 and January 2015. The living room floor dust samples analysed here from other countries were obtained as part of another project (HEXACOMM). Table III.1 lists the countries studied. All samples were collected in accordance with the protocol reported in section 2.1.1.1

Table III-1 Dust samples collected and analysed for PFRs in this chapter.

Country	(n) Living rooms	Country	(n) Living rooms
Ciudad Victoria, Mexico	39	**Prague, Czech Republic**	17
Houston, USA	19	**Athens and Crete, Greece**	11
Barcelona, Spain	3	**Helsinki, Finland**	10
Amman, Jordan	7		

3.3 International differences in PFRs concentrations of house dust

All seven PFRs were detected and quantified in all dust samples. A statistical summary is given in table III.2. Median concentrations were: Ciudad Victoria, Mexico = 20.83 μg ΣPFRs g^{-1}; Houston, United States = 35.36 μg ΣPFRs g^{-1}; Barcelona, Spain = 7.54 μg ΣPFRs g^{-1}; Amman, Jordan = 4.64 μg ΣPFRs g^{-1}; Prague, Czech Republic = 8.71 ng ΣPFRs g^{-1}; Athens/Crete, Greece = 12.12 ng ΣPFRs g^{-1}; Helsinki, Finland =12.17 ng ΣPFRs g^{-1}.

Table III-2 Statistical summary of concentrations (μg/g).

Location	Statistical Parameter	TnBP	TCEP	TCIPP	TDCIPP	EHDPP	TPhP	TCP	Σ Total PFRs
Mexico n= 39	**Average**	0.12	2.28	8.30	5.47	1.87	2.38	0.41	20.83
	SD	0.28	5.14	4.47	4.15	2.99	2.31	0.59	19.93
	Median	0.05	0.85	6.14	4.06	0.90	1.44	0.20	13.63
	Minimum	0.02	0.47	4.30	0.61	0.24	0.11	0.05	5.79
	Maximum	1.60	31.75	18.99	16.85	13.18	9.31	2.71	94.37
USA n= 19	**Average**	0.10	3.74	12.19	11.84	1.93	5.23	0.33	35.36
	SD	0.06	5.09	7.15	13.51	2.34	4.57	0.46	33.17
	Median	0.09	1.93	9.23	5.85	1.00	3.01	0.18	21.28
	Minimum	0.01	0.15	4.62	0.25	0.14	0.52	0.18	5.88
	Maximum	0.23	19.00	28.69	45.36	9.70	17.96	2.11	123.05
Spain n= 3	**Average**	0.01	1.13	1.45	4.05	0.50	0.35	0.05	7.54
	SD	0.01	1.50	1.95	5.26	0.70	0.47	0.07	9.95
	Median	0.14	1.51	3.27	1.25	1.44	0.84	0.16	8.61
	Minimum	0.14	0.97	2.25	0.86	0.55	0.70	0.15	5.62
	Maximum	0.16	3.79	6.01	10.16	1.93	1.56	0.27	23.89
Jordan n= 7	**Average**	0.05	0.75	1.17	0.81	0.26	0.84	0.75	4.64
	SD	0.04	0.71	0.78	0.67	0.09	0.78	0.93	4.00
	Median	0.04	0.41	1.13	0.70	0.27	0.65	0.15	3.35
	Minimum	0.03	0.18	0.21	0.13	0.14	0.16	0.15	0.99
	Maximum	0.14	1.76	2.27	1.61	0.37	2.29	2.05	10.50

Location	Statistical Parameter	TnBP	TCEP	TCIPP	TDCIPP	EHDPP	TPhP	TCP	Σ Total PFRs
Czech Republic n= 17	**Average**	0.23	1.89	2.51	1.60	0.92	1.18	0.38	8.71
	SD	0.37	1.00	0.94	0.92	0.42	0.50	0.42	4.58
	Median	0.10	1.59	2.15	1.48	0.82	1.26	0.15	7.56
	Minimum	0.02	0.52	1.46	0.42	0.32	0.46	0.15	3.35
	Maximum	1.54	4.22	4.06	3.66	1.93	1.95	1.50	18.86
Greece n= 11	**Average**	0.10	1.20	5.65	1.79	1.92	1.10	0.36	12.12
	SD	0.09	0.89	2.30	1.60	3.12	1.05	0.61	9.65
	Median	0.08	0.83	6.51	1.14	0.66	0.79	0.15	10.17
	Minimum	0.02	0.25	2.27	0.21	0.22	0.29	0.15	3.42
	Maximum	0.32	3.03	8.36	4.62	10.60	3.88	2.18	32.99
Finland n= 10	**Average**	0.14	0.98	4.08	1.35	2.73	2.27	0.62	12.17
	SD	0.08	0.56	1.05	1.38	1.85	0.65	0.60	6.18
	Median	0.12	0.71	4.04	0.70	2.32	2.04	0.39	10.31
	Minimum	0.08	0.38	2.66	0.25	0.56	1.37	0.15	5.45
	Maximum	0.33	1.87	6.21	4.04	7.37	3.31	2.16	25.27

ΣPFR concentrations in the dust from Houston, USA were the highest in this study followed by those from Mexico. With respect to individual PFRs, the predominant in the USA and Mexico, is TCIPP at median concentrations of 12.19 µg/g and 8.30 µg/g respectively, reflecting its use as a major PFR globally. The second predominant is TDCIPP that is present at a median concentration of 11.84 µg/g and 5.47 µg/g in the USA and Mexico respectively.

By comparison, Dodson et al. 2012 reported house dust sampled in California in 2006 to contain median concentrations of TCIPP of 2.1 μg/g and 2.8 μg/g of TDCIPP, with roughly similar concentrations (TCIPP 2.2 μg/g and TDCIPP 2.1 μg/g) detected in the same houses in 2011.

The higher concentrations detected in our US samples may be down to a number of factors, including: (a) small sample numbers in our case; (b) inter-state differences in FR use (our study samples were from Texas, rather than California; and (c) increased PFR use between 2011 when the latest Dodson et al samples were taken and 2015-2016 when our samples were procured – this is plausible, given the recent restrictions on BFR use that may have shifted FR use to PFRs. The country with the lowest median concentration is Jordan for which TCIPP = 1.17 μg/g and TDCIPP = 0.81 μg/g. It is thus of note that Abdallah et. al. 2014 reported dust from Egyptian houses to display among the lowest PFR levels concentrations worldwide. Our ΣPFR concentrations are consistent broadly with previous studies in both United States and Europe (Brommer et al., 2015; Araki et al., 2014; Brandsma et al., 2014; Cequier et al., 2014; Brommer et al., 2012; Van de Eede., 2011 (Table III.3). Due to the low sample numbers it is not possible to draw firm conclusions without analysing more dust samples.

Table III-3 International comparison between median concentrations of PFRs (μg/g) reported in indoor dust from houses from different countries.

Reference	Country	n	TnBP	TCEP	TClPP	TDClPP	TPhP	EHDPP	TCP
Brommer et al., 2015	**UK**	32	0.03	0.81	21	0.71	3.3	1.6	N/A
Abdallah et al., 2014	**Egypt**	20	0.01	0.02	0.02	0.07	0.06	0.04	N/A
Araki et al., 2014	**Japan**	148	1.0	5.8	8.7	2.8	4.5	N/A	N/A
Brandsma et al., 2014	**The Netherlands**		0.03	1.3	1.3	0.28	0.82	0.35	N/A
Cequier et al., 2014	**Norway**	48	0.05	0.41	2.7	0.50	0.98	0.62	N/A
Ali et al., 2012	**New Zealand**	34	0.08	0.11	0.35	0.23	0.6	N/A	0.12
Brommer et al., 2012	**Germany**	6	0.13	0.20	0.74	0.38	N/A	N/A	N/A
Van de Eede., 2011	**Belgium**	33	0.13	0.23	1.38	0.36	0.5	N/A	0.24
This study	**Mexico** **USA** **Spain** **Jordan** **ChRep** **Greece** **Finland**	39 19 3 7 17 11 10	0.05 0.09 0.14 0.04 0.10 0.08 0.12	0.85 1.93 1.51 0.41 1.59 0.83 0.71	6.14 9.23 3.27 1.13 2.15 6.51 4.04	4.06 5.85 1.25 0.70 1.48 1.14 0.70	0.90 1.00 1.44 0.27 0.82 0.66 2.32	1.44 3.01 0.84 0.65 1.26 0.79 2.04	0.20 0.18 0.16 0.15 0.15 0.15 0.39

N/A Not available/investigated

Figure III.1 shows median concentrations (μg/g) of target PFRs in dust from different counties. The similar concentrations between Mexico and USA may be because Mexico imports, uses and consumes many US goods that are likely to be flame-retarded such as chairs, sofa, TVs, and other electronic items etc. due to the North America Free Trade Agreement (NAFTA). While concentrations of PFRs in the US environment are relatively well-characterised, this study constitutes to our knowledge, the first report of PFRs in Mexican indoor dust, although Rauert et al., (2016) reported PFR concentrations in outdoor air from the southwest of Mexico. Interestingly, TCIPP was predominant in outdoor air, in line with our findings for indoor dust. Another possible source of PFR emissions in Mexico may be from the Great Lakes Chemical Corp (GLCC) production plant in Reynosa (just 3 hours drive from Ciudad Victoria) (Focusonpigments.com 2003). According to Brommer et al., (2015) TCIPP is the predominant PFR in UK, in contrast to the US where TDCIPP and TPhP predominate. Another study points out that in house dust from Australia, UK and Germany, the major PFR is TCIPP, while in the US and Canada the most abundant PFR is TPhP (Harrad et al., 2016). About 50 % of TPhP is used as a flame retardant in PVC, with other uses including as a flame retardant in other polymers (22 %), printed circuit boards (11 %) and photographic films (7 %) (Ferro, 2011). Other market names for TPhP are: Reofoss® TPP, Reomol® TPP, Celluflex TPP, Phosplex® TPP (Lassen et al., 1999; ATSDR, 2012). During 2002, the worldwide production of TPhP was estimated at between 20,000 to 30,000 tones, with 40 % produced in USA followed by 35 % from Asia and 25 % from Western Europe, i.e. production in USA exceeds that in Europe (Leonards, 2011).

Even though Spain, Finland, the Czech Republic, and Greece occupy the same continent and are subject to European Union legislation, differences in PFR concentrations might arise as a result of between-country variations in types of flame retardant products such as: textiles, plastics, furniture, mattresses, etc. According to the Freedonia Group, an acceleration in manufacturing has stimulated a global demand for flame retardants projecting an expansion of 4.6 % per year until 2018 especially in the USA, Japan and Western Europe. The enhanced increased demand in these regions might be because the construction codes are more strictly enforced there, as well as the increment in flame retardant sales for use in products such as: plastic products, automobiles, foamed plastics insulation and vinyl flooring, this study says (Additives for polymers, 2015).

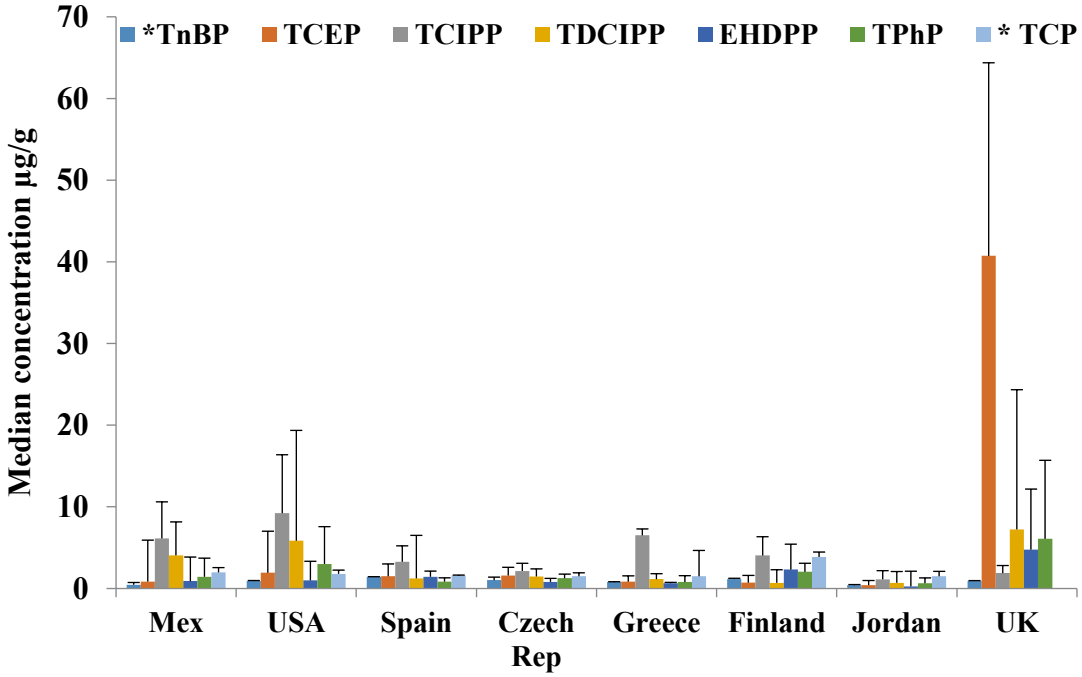


Figure III-1 Median concentrations (µg/g) of target PFRs in dust from different counties. UK PFRs concentration (see table V.5).

*Due the low concentrations of TnBP and TCP the results were multiplied by 10 for these two compounds.

Between-country variations in the relative abundance of individual PFRs – expressed as a percent contribution to PFRs - is shown in figure III.2. The major contributor in all countries is TCIPP (30-80 %) followed by TDCIPP (5-30 %) and TCEP (5-20 %), a finding consistent with data on PFR concentrations in house dust from Birmingham, UK (Brommer et al., 2015). Concentrations of PBDEs reported by the same grup (Harrad et al., 2008) in the same city reported average concentrations of ΣPBDEs in domestic dust to be 0.07 μg/g.

Dust samples from 40 dormitories in Beijing, China were analysed in 2012 and found to have an average concentration of ΣPBDEs 2.82 μg/g. The authors suggested that the low concentrations compared to PFRs might be due to the global phase-out of PBDEs (Cao et al., 2014). Indoor dust samples from Belgium were reported to contain average concentrations for PFRs of: TnBP 0.58 μg/g, TCEP 0.35 μg/g, TCIPP 0.44 μg/g, TPhP 0.69 μg/g, TDCIPP 0.24 μg/g and TCP 0.25 μg/g respectively, while the average concentration of ΣHBCDs was 0.60 μg/g (Van den Eede et al., 2012).

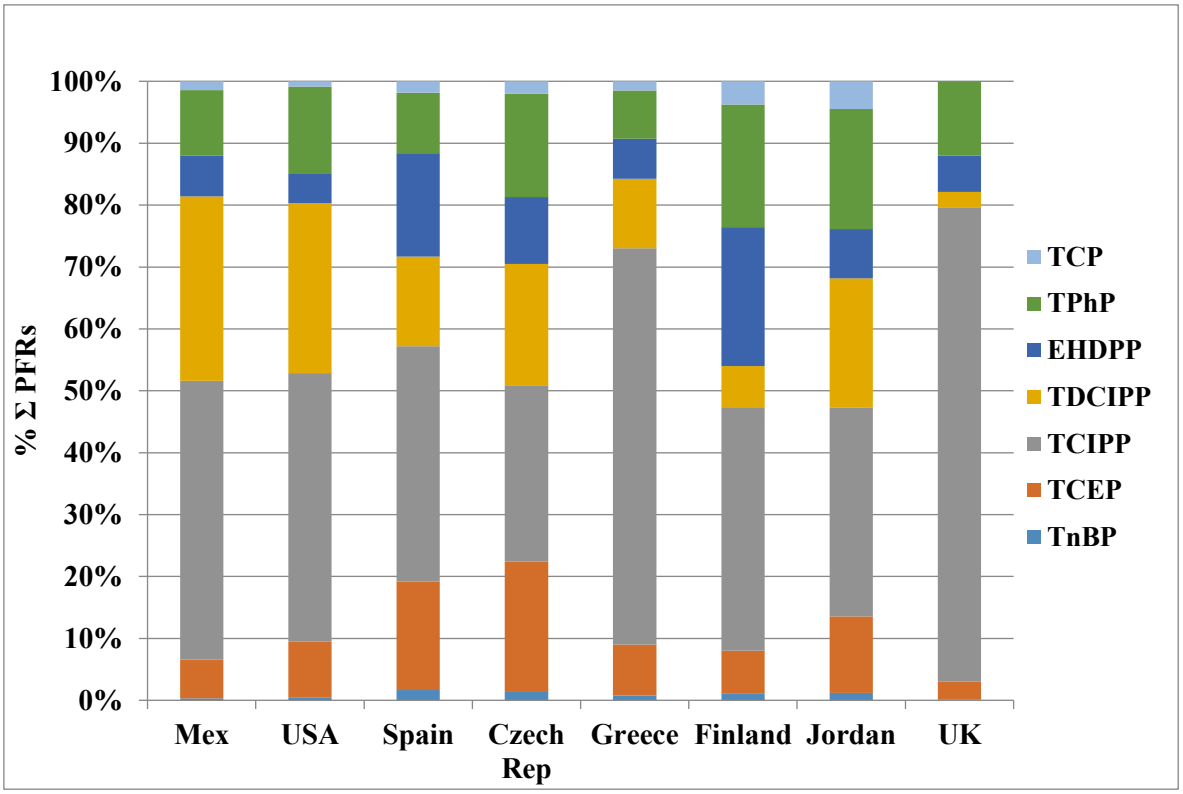


Figure III-2 Average relative contribution (expressed as % ΣPFR) of PFRs in the studied samples. UK PFR concentration data are from: Brommer et al., 2015.

The data were evaluated statistically for differences in concentrations between the different countries studied, with the exception of our data from Spain as the number of samples for this country (n=3) were too few to be of statistical validity. As a first step, the distribution of concentrations within countries was evaluated using a Shapiro-Wilks test. The data were log-transformed prior to ANOVA testing, owing to the log-normal distribution of our data. Using ANOVA with Tukey and Games-Howell test post-hoc tests, data on PFR concentrations in our study countries were analysed, finding some significant differences (p<0.05) for our target PFRs. Table III.4 summarises the statistically significant (p<0.05) differences in concentrations of PFRs in living room dust from different countries.

Table III-4 Summary of statistically significant (p<0.05) differences in concentrations of PFRs in living rooms dust from different countries.

PFR	Significant difference		
TCEP	USA	>	Jordan
TCIPP	Mexico and USA Czech Republic Greece and Finland	> > >	Czech Republic, Greece, Finland and Jordan Finland and Jordan Jordan
TDCIPP	Mexico and USA	>	Czech Republic, Greece, Finland and Jordan
EHDPP	Finland	>	Jordan
TPhP	Mexico and USA	>	Czech Republic, Greece and Jordan

For TnBP and TCP, ANOVA analysis revealed no significant (p<0.05) international differences, while TCEP concentrations in US dust significantly exceed those in Jordanian dust (p=0.08). For TCIPP, concentrations were significantly greater in Mexico and the USA than those in the Czech Republic, Greece, Finland and Jordan (p<0.01, 0.08 and 0.01 respectively). Moreover, those in the Czech Republic exceeded significantly those in Finland and Jordan (p<0.01 in both cases) with those in Greece and Finland significantly higher than those in Jordan (p<0.01). Similar observations were made for TDCIPP, with concentrations in Mexico and the USA significantly exceeding those in the Czech Republic, Greece, Finland and Jordan (p<0.01, 0.02, 0.01, 0.01 respectively).

Meanwhile, concentrations of EHDPP were significantly greater in dust from Finland than in dust from Jordan (p< 0.01) while concentrations of TPhP in Mexico and USA exceed significantly those in the Czech Republic, Greece and Jordan (p<0.01 in all cases).

3.4 Implications for human exposure.

Human exposure to the seven PFRs of interest was estimated for adults and toddlers from the 7 countries studied using the concentration of house dust from each individual country and assuming average weights of 70 kg and 12 kg for adults and toddlers respectively, along with mean dust ingestion rates of 50 and 20 mg day^{-1} and high-end dust ingestion rates of 200 and 50 mg day^{-1} for adults and toddlers respectively, and assuming 100 % absorption of intake (Jones-Otazo et al., 2005). Various possible dust ingestion exposure scenarios were estimated, using 5^{th} percentile, median, average and 95^{th} percentile concentrations in dust samples reported in this experiment.

As toddlers spend most of their times indoors, the assumption is that domestic indoor dust was the only source of dust exposure (Harrad et al., 2008). It is important to state that the estimates provided here are only an indication of the likely population-level exposure due to the relatively small number of dust samples analysed and the uncertainties in our assumed dust ingestion rates, also it is important to mention that these estimates here are based only on house dust and that dust from other microenvironments such as cars, nurseries or offices are not included in these estimates. Table III.5 shows estimated daily exposures for adults and toddlers based on the 5^{th} percentile, arithmetic mean and 95^{th} percentile from average and high rates concentrations of our seven target PFRs.

Table III-5 Daily exposure to ΣPFRs via dust ingestion (ng kg body weight per day) of adults and toddlers

	Average dust ingestion rate		High dust ingestion rate	
	Adults	**Toddler**	**Adults**	**Toddler**
Mexico				
5th percentile	2	30	5	119
Median	6	87	10	227
95th percentile	18	263	45	1053
USA				
5th percentile	2	25	4	98
Median	10	147	15	355
95th percentile	35	513	88	2051
Spain				
5th percentile	2	25	4	99
Median	4	53	6	143
95th percentile	6	93	16	372
Greece				
5th percentile	1	15	3	62
Median	3	50	7	170
95th percentile	8	114	20	456
Finland				
5th percentile	2	25	4	99
Median	3	51	7	172
95th percentile	6	94	16	377
Czech Republic				
5th percentile	1	17	3	67
Median	2	36	5	126
95th percentile	5	66	11	264
Jordan				
5th percentile	0	5	1	19
Median	1	19	2	56
95th percentile	3	41	7	165
UK (Brommer et al 2012)				
5th percentile	0	5		
Median	7	106		
95th percentile	31	459		

Table III-6 Comparison of assessment of human exposure to PFRs via dust ingestion using mean dust intake rates (ng per kg body weight per day) for adults and toddlers from somewhere reports.

Reference		TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPhP	TCP	ΣPFRs
Belgium									
Van den Eede et al., 2011.	**Toddler**								
	Average	0.05	5.6	1.0	1.5		2.0	1.0	11.1
	High	6.4	92	19	9.8		40	9.6	176
	Adult								
	Average	0.05	0.5	0.1	0.3		0.1	0.1	1.15
	High	0.9	10	1.5	7.7		5.1	2.5	27
New Zealand									
Ali et al., 2012.	**Toddler**								
	Average	0.31	1.37	0.34	0.73		1.5	0.54	4.79
	High	10	39	6.8	25		23	7.2	111
	Adult								
	Average	0.02	0.09	0.02	0.04		0.1	0.04	0.31
	High	0.46	1.7	0.29	1.1		1.0	0.31	4.86
Philippines									
Kim et al., 2013.	**Toddler**								
	Average	0.82		1.5		4.7	3.8	0.78	11.6
	High	3.3		5.9		19	15	3.1	46
	Adult								
	Average	0.24		0.43		1.4	1.1	0.23	3.4
	High	0.61		1.1		3.5	2.8	0.57	8.58
Egypt									
Abdallah et al., 2014.	**Toddler**								
	Average	1.3	4.7	3.2	7.5	2.4	7.5		22.5
	High	5.2	18	13	30	9.6	30		90
	Adult								
	Average	0.5	1.9	1.3	3	1	3		9
	High	1.3	4.7	3.2	7.5	2.4	7.5		22.5
China (Nanjing City)									
He et al., 2015.	**Toddler**								
	Average		51	161	241		20		473
	High		20	626	1396		39		2081
	Adult								
	Average		2.3	6.7	9.1		1.1		19
	High		8.8	27	51		2.3		89
China (Guangzhou City)									
He et al., 2015.	**Toddler**								
	Average	0.28	2.7	13.7	0.47	1.32	0.53	0.00	23.5
	High	0.54	7.3	34.6	23.5	11	2.64	15	110
	Adult								
	Average	0.02	0.24	1.20	0.04	0.12	0.05	0.00	2.06
	High	0.05	0.64	3.03	2.06	0.97	0.23	0.35	9.61

Our data are consistent with previous reports that indoor dust ingestion represents a substantial pathway of human exposure to PFRs. This is especially so in the USA and Mexico, for which our exposure estimates (see Table III.7), are similar to those reported by Brommer et al (2012) for the UK.

Elsewhere, Van den Eede et al., (2011) reported exposure in Belgium via dust ingestion. Other countries with lower exposures than the USA are Egypt and the Philippines; according to Abdallah et al., (2014) and Kim et al., (2013) exposures in these countries are similar to those reported in this work for toddlers (assuming average dust ingestion and median dust concentrations) in Jordan, the Czech Republic, and Spain.

Table III-7 Summary of average and high-end estimates of daily exposure to PFRs via dust ingestion (ng/kg b/w per day) of adults and toddlers in seven countries.

		TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPhP	TCP	ΣPFRs
MEXICO									
Mean Adults	**P5**	0.01	1.24	0.13	0.52	0.07	0.06	0.01	2.03
	Median	0.03	2.37	0.65	1.56	0.53	0.68	0.12	5.95
	P95	0.26	5.26	2.16	4.30	3.19	2.31	0.58	18.0
Toddler	**P5**	0.08	18.0	1.96	7.53	0.99	0.94	0.21	29.7
	Median	0.49	34.5	9.50	22.8	7.80	9.91	1.71	86.8
	P95	3.72	76.6	31.4	62.6	46.5	33.7	8.52	263
High Adults	**P5**	0.01	3.10	0.34	1.29	0.17	0.16	0.04	5.1
	Median	0.08	5.93	1.63	3.91	1.34	1.70	0.29	14.8
	P95	0.64	13.1	5.39	10.7	7.99	5.78	1.46	45.1
Toddler	**P5**	0.31	72.2	7.85	30.1	3.96	3.74	0.83	119
	Median	1.96	138	37.9	91.2	31.1	39.6	6.85	347
	P95	14.8	307	126	251	186	135	34.0	105

		TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPhP	TCP	ΣPFRs
USA									
Mean Adults	**P5**	0.00	1.32	0.04	0.07	0.04	0.15	0.05	1.68
	Median	0.03	3.48	1.07	3.38	0.55	1.49	0.09	10.1
	P95	0.06	8.20	5.43	12.9	2.77	5.13	0.60	35.1
Toddler	**P5**	0.05	19.2	0.63	1.06	0.60	2.17	0.75	24.5
	Median	0.40	50.7	15.6	49.3	8.04	21.8	1.38	147
	P95	0.94	120	79.1	189	40.4	74.8	8.80	513
High Adults	**P5**	0.01	3.30	0.11	0.18	0.10	0.37	0.13	4.20
	Median	0.07	8.71	2.67	8.46	1.38	3.74	0.24	25.2
	P95	0.16	20.4	13.5	32.4	6.93	12.8	1.51	87.8
Toddler	**P5**	0.20	76.9	2.54	4.23	2.40	8.70	3.00	98.0
	Median	1.59	203	62.3	197	32.1	87.2	5.50	589
	P95	3.77	478	317	756	162	299	35.2	205
SPAIN									
Mean Adults	**P5**	0.04	0.67	0.29	0.26	0.18	0.20	0.04	1.69
	Median	0.04	1.10	0.60	1.17	0.37	0.30	0.06	3.63
	P95	0.04	1.64	1.02	2.65	0.54	0.43	0.07	6.38
Toddler	**P5**	0.59	9.79	4.28	3.74	2.66	2.96	0.63	24.6
	Median	0.62	16.0	8.71	17.0	5.43	4.31	0.81	52.9
	P95	0.66	23.9	14.8	38.6	7.82	6.22	1.09	93.1
High Adults	**P5**	0.10	1.68	0.73	0.64	0.46	0.51	0.11	4.23
	Median	0.11	2.75	1.49	2.92	0.93	0.74	0.14	9.08
	P95	0.11	4.10	2.54	6.62	1.34	1.07	0.19	15.9
Toddler	**P5**	2.37	39.1	17.1	14.9	10.6	11.8	2.52	98.6
	Median	2.47	64.0	34.8	68.1	21.7	17.2	3.23	212
	P95	2.62	95.6	59.3	154	31.2	24.8	4.23	373

Continuation estimated daily exposure to PFRs via dust ingestion (ng per kg body weight per day) of adults and toddlers in seven countries.

		TnBP	TClPP	TCEP	TDCIPP	EHDPP	TPhP	TCP	ΣPFRs
CZECH REPUBLIC									
Mean Adults	**P5**	0.01	0.44	0.23	0.13	0.12	0.16	0.04	1.14
	Median	0.07	0.72	0.54	0.46	0.26	0.34	0.11	2.49
	P95	0.23	1.15	0.97	0.82	0.50	0.54	0.31	4.52
Toddler	**P5**	0.11	6.45	3.40	1.88	1.81	2.40	0.63	16.6
	Median	0.96	10.4	7.87	6.68	3.82	4.93	1.56	36.2
	P95	3.42	16.7	14.1	12.0	7.24	7.84	4.53	65.9
High Adults	**P5**	0.02	1.11	0.58	0.32	0.31	0.41	0.11	2.86
	Median	0.16	1.79	1.35	1.14	0.66	0.85	0.27	6.22
	P95	0.59	2.87	2.43	2.06	1.24	1.34	0.78	11.3
Toddler	**P5**	0.45	25.8	13.6	7.53	7.25	9.60	2.50	66.7
	Median	3.83	41.8	31.4	26.7	15.2	19.7	6.25	145
	P95	13.6	66.9	56.7	48.0	28.9	31.3	18.1	264
GREECE									
Mean Adults	**P5**	0.01	0.67	0.11	0.07	0.07	0.09	0.04	1.05
	Median	0.03	1.62	0.34	0.51	0.55	0.31	0.10	3.46
	P95	0.08	2.35	0.82	1.26	2.14	0.82	0.35	7.82
Toddler	**P5**	0.11	9.75	1.57	1.04	1.04	1.28	0.63	15.4
	Median	0.42	23.5	4.99	7.45	7.99	4.58	1.49	50.4
	P95	1.10	34.2	11.9	18.3	31.2	11.9	5.17	114.0
High Adults	**P5**	0.02	1.67	0.27	0.18	0.18	0.22	0.11	2.65
	Median	0.07	4.04	0.86	1.28	1.37	0.79	0.26	8.66
	P95	0.19	5.88	2.05	3.15	5.36	2.05	0.89	19.5
Toddler	**P5**	0.44	39.0	6.28	4.17	4.15	5.13	2.50	61.6
	Median	1.69	94.2	19.9	29.7	31.9	18.3	5.97	202
	P95	4.38	137	47.7	73.5	125	47.7	20.6	456
FINLAND									
Mean Adults	**P5**	0.02	0.76	0.12	0.08	0.25	0.42	0.04	1.69
	Median	0.04	1.17	0.28	0.38	0.78	0.65	0.18	3.48
	P95	0.08	1.61	0.53	1.15	1.67	0.94	0.47	6.46
Toddler	**P5**	0.33	11.1	1.73	1.13	3.58	6.17	0.63	24.7
	Median	0.58	17.0	4.09	5.61	11.3	9.45	2.58	50.6
	P95	1.20	23.5	7.74	16.7	24.3	13.7	6.86	94.1
High Adults	**P5**	0.06	1.91	0.30	0.19	0.61	1.06	0.11	4.24
	Median	0.10	2.91	0.70	0.96	1.95	1.62	0.44	8.69
	P95	0.21	4.04	1.33	2.88	4.17	2.35	1.18	16.1
Toddler	**P5**	1.30	44.5	6.91	4.52	14.3	24.7	2.50	98.8
	Median	2.33	68.0	16.3	22.4	45.4	37.8	10.3	203
	P95	4.80	94.1	30.9	67.1	97.3	54.7	27.4	377

Continuation estimated daily exposure to PFRs via dust ingestion (ng per kg body weight per day) of adults and toddlers in seven countries.

		TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPhP	TCP	ΣPFRs
JORDAN									
Mean Adults	**P5**	0.01	0.08	0.05	0.04	0.04	0.06	0.04	0.32
	Median	0.02	0.33	0.22	0.23	0.08	0.02	0.21	1.11
	P95	0.03	0.61	0.49	0.46	0.10	0.56	0.57	2.82
Toddler	**P5**	0.12	1.16	0.77	0.54	0.63	0.80	0.63	4.65
	Median	0.23	4.88	3.14	3.36	1.09	3.52	3.13	19.3
	P95	0.50	8.97	7.12	6.68	1.52	8.22	8.33	41.3
High Adults	**P5**	0.02	0.20	0.13	0.09	0.11	0.14	0.11	0.80
	Median	0.04	0.84	0.54	0.58	0.19	0.60	0.54	3.33
	P95	0.08	1.54	1.22	1.14	0.26	1.41	1.43	7.08
Toddler	**P5**	0.48	4.64	3.08	2.15	2.51	3.21	2.50	18.5
	Median	0.91	19.5	12.5	13.4	4.38	14.0	12.5	77.3
	P95	1.98	35.8	28.4	26.7	6.09	32.8	33.3	165
HBLV*		**24,000**	**80,000**	**22,000**	**15,000**	**-**	**70,000**	**13,000**	

*HBLVs (Health based limit values) are those cited by Brommer et al., 2015.

The highest exposures in this study were in the USA and Mexico for TCIPP with these countries generally displaying the highest exposures to all our target PFRs. Comparison of our data with those from elsewhere, reveals that our exposures to TCEP are lower than those reported previously for China; (He et al., 2015).

Indeed, exposures to TCEP reported by He et al., (2015) were similar to those reported here for TDCIPP. Note our exposure estimates are below the HBLV (health based limit values) for all target PFRs (Table III.7).

However, as highlighted by Brommer et al., 2015 dust ingestion is only one potential exposure pathway; thus, other exposure sources have to be considered.

CHAPTER IV. WITHIN-ROOM AND WITHIN-HOME SPATIAL AND TEMPORAL VARIABILITY IN CONCENTRATIONS OF PFRS IN INDOOR DUST.

4.1 Synopsis

A substantial body of evidence exists that flame retardants (FRs) used in everyday products undergo transfer into indoor dust and that contact with this dust is an important pathway of human exposure. To date, the overwhelming majority of assessments of human exposure to FRs via contact with indoor dust relies on measurements of FRs in samples of dust taken from a single point within a room and at a single point in time. Recent studies suggest that for brominated FRs (BFRs), there can be substantial spatial and temporal variability in BFR concentrations in dust samples. However, no studies of such variability have been conducted to date for PFRs. In this chapter, the concentrations of seven PFRs measured in house dust samples from a number of rooms within different homes to examine spatial and temporal variability in PFR concentrations both between different rooms (R) in the same home (H) and between different floors (F) areas in the same rooms (R).

4.2 Sampling strategy

Within-room and within-home spatial and temporal variability in concentrations of PFR in indoor dust were studied in three different rooms (R) within three homes (H) (three R for each of H1, H2 and H3) in Birmingham, UK under normal room use conditions to reflect actual human activity and exposure. Table IV.1 shows the sampling period, F type and R sampled.

H2 was an apartment where the bedroom, living room and kitchen were located on the same floor. In all living rooms and bedrooms, the floors were carpeted, with three 1 m^2 floor (F) areas sampled (each referred to as H#R#F1, F2 and F3).

By comparison, the kitchen floor areas were all bare and thus only a single 4 m^2 area was sampled in each kitchen. In house 3, two samples were lost. Sampling was conducted using a TESCO VC207 1400 W vacuum cleaner according to a previously reported protocol (Harrad et al., 2008b).

Table IV-1 Period of sampling, areas of House sampling and Floor type.

House	Sampling period	Room 1	Room 2	Room 3
House 1	**Nov 2013 Oct 2014**	Living room Carpeted floor	1 Bedroom Carpeted floor	Kitchen Bare floor
House 2	**Feb 2014 March 2015**	Living room Carpeted floor	1 Bedroom Carpeted floor	Kitchen Bare floor
House 3	**May 2014 Apr 2015**	Parents' bedroom Wood floor	Child's bedroom Wood floor	Kitchen Bare floor

In addition to F dust, elevated surfaces (ES) dust was collected from ES such as sofas, tables, chairs, shelves and large items of furniture. Dust was not sampled from highly ES (from the top of wardrobes for example) with which human contact is unusual nor from under furniture for the same reason.

Following sample collection, the low dust loading for the ES dust samples led us to combine three monthly samples into one sample to provide sufficient dust for analysis.

To facilitate study of spatial variability, the samples were taken carefully to avoid overlap of each sampling area, with study of temporal variation facilitated by ensuring that the same areas were sampled each month. Section 2.1.1.1 shows the sampling distribution of each house and room.

4.3 Results and discussion

4.3.1 Within-room spatial differences between PFRs in Floor (F) and Elevated Surface (ES) Dust.

Variations in dust concentration were analysed to elucidate within-room spatial differences between PFRs in F and ES dust sampled from H1, H2 & H3 every month for one year. Tables IV.2, 4.3 and 4.4 provide statistical summaries of concentrations found in floor dust from H1, H2, and H3 respectively.

Tables IV.5, IV.6 and IV.7 provide statistical summaries of concentrations found in elevated surface dust from H1, H2 and H3 respectively, while Figures IV.1, IV.2 and IV.3 illustrate the average contribution of each PFR in each room studied. To illustrate, figure IV.? depicts average ± standard deviation concentrations of PFRs in floor dust and elevated surface dust in each room of each house.

Table IV-2 Concentrations (μg/g) of PFRs in indoor floor dust from H1.

Location	Statistical parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
Bedroom	**Average**	0.14	51.2	1.00	1.31	1.25	24.1	79.1
F1	**Min**	0.07	26.1	0.72	0.90	0.62	2.37	30.8
	Max	0.27	100	1.92	1.71	2.70	91.2	198
	Median	0.13	44.4	0.95	1.36	0.87	10.3	58.1
	% RSD	41.0	47.5	31.9	19.1	60.5	112	67.0
F 2	**Average**	0.15	47.4	1.13	4.63	1.80	16.8	72.0
	Min	0.07	25.5	0.72	1.41	0.62	3.98	32.3
	Max	0.23	96.0	1.74	18.4	9.04	49.4	174
	Median	0.14	40.0	1.14	1.85	0.99	11.88	56.0
	% RSD	33.3	44.6	25.3	124	131	78.29	59.5

Location	**Statistical parameter**	**TnBP**	**TClPP**	**TCEP**	**TDClPP**	**EHDPP**	**TPhP**	**ΣPFRs**
F 3	**Average**	0.14	56.4	1.04	3.38	2.07	42.89	105
	Min	0.08	31.5	0.71	1.98	0.91	3.54	38.7
	Max	0.24	132	1.46	5.81	7.99	141	289
	Median	0.11	48.6	1.02	3.35	1.26	16.3	70.7
	% RSD	39.7	46.3	22.4	31.0	97.0	110	72.5
Living room	**Average**	0.20	34.3	3.16	4.23	1.71	7.51	51.2
F1	**Min**	0.08	11.8	1.65	2.70	1.01	2.01	19.3
	Max	0.41	79.2	5.50	6.70	2.79	15.9	110
	Median	0.21	22.4	3.00	3.93	1.56	5.01	36.2
	% RSD	50.4	70.6	33.9	28.5	33.5	65.6	62.8
F 2	**Average**	0.30	38.7	2.90	8.51	1.36	10.1	61.9
	Min	0.09	16.7	1.28	3.07	0.67	1.10	22.9
	Max	0.71	78.2	5.37	19.1	1.81	33.1	138
	Median	0.30	31.6	2.36	6.14	1.63	4.55	46.6
	% RSD	52.6	45.5	50.6	65.6	33.9	108	58.6
F 3	**Average**	0.65	28.1	2.64	3.94	1.43	2.88	39.6
	Min	0.26	8.42	0.46	2.07	0.86	0.70	12.7
	Max	1.00	119	21.6	17.7	2.14	13.3	175
	Median	0.68	19.3	0.96	2.66	1.30	1.67	26.5
	% RSD	36.2	107	227	111	28.6	121	112
Kitchen	**Average**	0.14	20.1	1.52	0.64	0.36	2.20	24.9
F1	**Min**	0.02	2.82	0.55	0.13	0.18	0.27	3.97
	Max	0.72	54.0	4.34	3.27	0.57	12.8	75.8
	Median	0.07	11.7	1.00	0.33	0.35	0.65	14.1
	% RSD	30.1	67.0	48.2	22.2	9.1	126	62.9

Table IV-3 Concentrations (μg/g) of PFRs in indoor floor dust in H2.

	Statistical parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
Bedroom	**Average**	0.16	34.8	0.72	0.52	6.81	0.69	43.7
F1	**Min**	0.08	17.2	0.44	0.26	3.48	0.29	21.7
	Max	0.31	87.9	1.10	1.09	13.9	1.91	106
	Median	0.14	25.7	0.71	0.42	6.05	0.54	33.5
	% RSD	48.5	55.5	29.2	52.8	42.0	68.6	53.1
F 2	**Average**	0.29	35.7	1.14	2.38	7.96	2.18	49.7
	Min	0.08	17.5	0.55	0.33	3.51	0.56	22.5
	Max	1.72	85.7	5.29	14.4	12.0	9.17	128
	Median	0.14	31.8	0.69	0.98	7.92	1.35	42.9
	% RSD	155	50.3	115	170	28.7	111	57.4
F 3	**Average**	0.16	31.6	0.67	0.93	6.20	0.72	40.3
	Min	0.08	17.9	0.46	0.23	4.25	0.34	23.3
	Max	0.32	50.2	1.09	6.14	9.17	1.94	68.9
	Median	0.08	10.5	0.18	1.67	1.36	0.42	14.2
	% RSD	46.3	33.3	27.0	178	21.9	58.8	35.3
Living room	**Average**	0.23	98.9	0.87	1.96	28.6	1.39	131
F1	**Min**	0.11	37.11	0.59	0.83	19.0	0.62	58.3
	Max	0.42	236	1.81	6.43	51.7	2.30	299
	Median	0.19	83.8	0.76	1.15	27.0	1.42	114
	% RSD	47.8	60.4	39.3	87.7	29.3	41.4	53.7
F 2	**Average**	0.20	153	0.73	1.30	39.6	3.03	198
	Min	0.10	29.2	0.25	0.18	24.9	1.44	56.1
	Max	0.47	384	1.09	3.05	60.0	7.52	456
	Median	0.14	136	0.72	1.15	37.5	2.39	178
	% RSD	63.9	69.7	30.9	53.5	27.2	63.3	60.5
F 3	**Average**	0.23	57.2	1.06	1.76	16.2	4.83	81.2
	Min	0.09	30.5	0.55	0.67	9.55	1.38	42.7
	Max	0.41	108	3.07	4.14	20.7	17.5	154
	Median	0.22	49.1	0.84	1.17	16.4	2.14	69.9
	% RSD	43.7	41.5	63.7	67.4	21.2	109	42.3
Kitchen	**Average**	0.36	65.3	1.40	0.83	13.1	1.61	82.7
F1	**Min**	0.16	25.3	0.70	0.23	4.81	0.51	31.7
	Max	1.13	218	2.65	3.11	33.1	4.47	263
	Median	0.26	44.9	1.22	0.47	11.0	1.51	59.4
	% RSD	74.7	81.7	37.3	100	56.1	64.0	76.7

Table IV-4 Concentration (μg/g) of PFRs in indoor floor dust from H3.

Location	Statistical parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
Bedroom	**Average**	0.08	20.6	1.43	6.99	2.26	0.86	32.2
F1	**Min**	0.04	8.60	0.69	0.87	0.32	0.26	10.7
	Max	0.14	45.1	4.32	44.4	14.0	1.48	109
	Median	0.07	18.8	1.08	1.87	0.91	0.97	23.7
	% RSD	42.2	52.2	69.0	174	170	43.8	87.6
Kids Bedroom	**Average**	0.09	29.3	1.43	8.38	1.37	2.19	42.7
F1	**Min**	0.04	12.4	0.79	1.49	0.53	0.47	15.8
	Max	0.20	53.9	2.59	43.2	3.56	15.1	118
	Median	0.09	26.6	1.34	2.55	1.18	0.74	32.5
	% RSD	56.3	44.2	41.2	148	56.4	190	72.4
Kitchen	**Average**	0.08	19.1	1.29	3.24	4.47	0.46	28.6
F1	**Min**	0.03	5.97	0.56	1.09	0.47	0.25	8.37
	Max	0.18	49.2	2.86	4.89	31.9	0.81	90.0
	Median	0.07	9.99	0.96	3.20	1.18	0.38	15.8
	% RSD	52.6	89.7	59.1	31.8	217	44.1	100

Table IV-5 Concentrations (μg/g) of PFRs in indoor dust from ES in H1.

Location	Statistical parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
Bedroom	**Average**	0.62	65.1	3.42	6.56	2.96	3.96	82.6
ES1	**Min**	0.06	37.2	2.33	1.02	2.52	1.39	44.5
	Max	1.92	94.1	4.11	15.6	4.19	6.67	126
	Median	0.26	64.5	3.61	4.78	2.58	3.88	79.6
	% RSD	139	39.3	22.5	103	27.5	58.0	44.9

Table IV-6 Continuation concentrations (μg/g) of PFRs in indoor dust from ES in H1.

Location	Statistical parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
ES 2	**Average**	0.81	71.8	5.65	11.7	5.22	6.27	101
	Min	0.06	31.33	2.39	1.61	1.05	3.77	40.2
	Max	2.87	107	13.5	27.9	8.37	10.4	170
	Median	0.16	74.4	3.35	8.78	5.73	5.43	97.8
	% RSD	169	54.4	93.3	101	59.2	46.8	62.7
ES 3	**Average**	11.1	77.2	4.60	24.4	2.44	7.88	127
	Min	0.07	56.8	1.56	11.3	1.14	4.24	75.1
	Max	44.1	109	13.0	61.9	4.23	18.1	251
	Median	0.18	71.1	1.91	12.1	2.20	4.57	92.2
	% RSD	197	32.9	122	102	53.4	86.8	67.5
Living room	**Average**	3.46	43.0	9.11	6.10	1.41	2.70	65.8
ES1	**Min**	0.08	17.5	7.48	2.08	0.44	1.90	29.5
	Max	12.9	75.2	10.9	11.2	1.75	3.97	116
	Median	0.43	39.6	9.01	5.56	1.73	2.45	58.8
	% RSD	181	55.7	15.7	65.6	45.9	34.9	56.6
ES 2	**Average**	2.65	48.9	16.7	7.33	0.49	8.19	84.5
	Min	0.11	33.0	6.67	1.99	0.27	2.97	45.0
	Max	9.97	65.6	42.1	12.1	0.70	15.7	146
	Median	0.27	48.4	9.59	7.59	0.49	7.00	73.4
	% RSD	183	30.5	99.0	67.2	38.0	76.9	56.8
ES 3	**Average**	1.64	54.2	10.3	40.9	2.70	9.77	119
	Min	0.25	27.1	4.04	3.06	1.11	2.62	38.2
	Max	5.34	79.9	24.1	140	5.48	23.5	279
	Median	0.48	54.9	6.58	10.0	2.12	6.46	80.5
	% RSD	151	41.0	89.7	162	73.6	96.4	93.7
Kitchen	**Average**	0.59	22.4	2.28	0.92	1.35	5.58	33.15
ES1	**Min**	0.05	3.25	0.79	0.11	0.30	0.42	4.92
	Max	1.74	63.1	5.29	2.98	2.73	19.6	95.5
	Median	0.29	11.6	1.52	0.30	1.19	1.13	16.0
	% RSD	132	123	89.9	149	75.5	168	127
ES 2	**Average**	0.26	31.5	3.88	0.62	1.06	0.46	37.8
	Min	0.04	5.00	1.51	0.17	0.61	0.25	7.59
	Max	0.74	97.1	10.1	1.09	1.48	0.63	111
	Median	0.13	12.06	1.94	0.61	1.08	0.48	16.3
	% RSD	122	138	107	64.2	40.0	38.6	130

Table IV-7 Concentrations (μg/g) of PFRs in indoor dust from ES in H2.

Location	Statistical Parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
Bedroom	**Average**	0.61	89.0	3.53	1.81	19.6	1.95	116
ES1	**Min**	0.35	70.9	2.86	0.41	16.0	1.45	92.1
	Max	1.28	100	5.15	5.72	22.9	2.77	137
	Median	0.40	92.3	3.06	0.55	20.0	1.79	118
	% RSD	73.8	15.5	30.8	144	13.7	31.0	18.2
ES 2	**Average**	0.80	95.0	4.03	2.62	15.5	2.10	120
	Min	0.18	63.0	1.73	0.19	6.26	0.76	72.1
	Max	2.17	130	6.89	7.79	29.9	4.57	181
	Median	0.42	93.4	3.76	1.25	12.9	1.53	113
	% RSD	117	37.8	52.8	134	66.6	83.7	45.5
ES 3	**Average**	0.91	97.3	4.50	3.69	17.4	3.00	126
	Min	0.37	69.3	3.59	0.65	10.6	1.57	86.1
	Max	1.79	136	5.85	9.94	27.7	5.18	187
	Median	0.74	91.5	4.27	2.08	15.7	2.63	116
	% RSD	71.4	30.0	23.3	114	42.1	52.9	34.7
Living room	**Average**	0.45	52.4	2.37	1.83	8.84	3.89	69.8
ES1	**Min**	0.27	22.3	1.80	1.10	6.97	0.75	33.2
	Max	0.68	74.9	2.82	3.34	12.2	7.51	101
	Median	0.42	56.2	2.42	1.45	8.09	3.65	72.2
	% RSD	42.2	41.7	21.0	56.1	27.1	90.0	42.2
ES 2	**Average**	0.40	48.3	2.28	3.79	10.2	4.07	69.0
	Min	0.24	36.4	1.23	2.86	8.26	1.42	50.4
	Max	0.74	59.3	3.49	4.76	12.3	6.76	87.4
	Median	0.31	48.7	2.21	3.77	10.0	4.05	69.1
	% RSD	57.2	19.3	40.6	20.9	20.1	65.5	23.2
ES 3	**Average**	0.50	60.6	2.46	3.63	11.6	4.26	83.1
	Min	0.21	54.6	1.61	3.23	7.05	1.82	68.5
	Max	1.30	72.1	3.49	4.29	18.9	10.9	111
	Median	0.24	57.9	2.36	3.51	10.2	2.15	76.4
	% RSD	108	13.1	33.9	12.5	44.0	104	23.2

Table IV-8 Continuation concentrations (μg/g) of PFRs in indoor dust from ES in H2.

Location	Statistical Parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
Kitchen	**Average**	0.31	57.2	3.98	2.55	11.1	1.64	76.9
ES1	**Min**	0.17	35.6	1.52	0.36	7.19	0.89	45.7
	Max	0.57	76.1	9.07	6.94	13.5	3.04	109
	Median	0.25	58.7	2.66	1.45	11.9	1.31	76.3
	% RSD	58.2	31.9	87.3	120	25.3	58.5	37.4
ES 2	**Average**	0.59	61.5	4.99	3.65	8.43	0.98	80.1
	Min	0.17	34.3	2.33	0.57	5.92	0.79	44.1
	Max	1.65	101	11.8	8.17	12.4	1.50	137
	Median	0.28	55.1	2.88	2.93	7.71	0.82	69.7
	% RSD	119	50.5	92.1	93.6	36.0	35.2	53.8

Table IV-9 Concentrations (μg/g) of PFRs in indoor dust from ES in H3.

Location	Statistical parameter	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP	ΣPFRs
Bedroom	**Average**	0.05	23.4	2.29	0.94	0.52	1.15	28.4
ES1	**Min**	0.03	7.53	1.15	0.79	0.16	0.30	9.96
	Max	0.08	50.5	3.99	1.15	1.11	1.87	58.7
	Median	0.21	69.5	3.48	6.78	4.15	4.65	88.7
	% RSD	41.2	87.2	53.2	16.4	82.1	60.8	80.8
ES 2	**Average**	0.09	27.9	2.39	1.36	1.04	1.24	34.0
	Min	0.03	11.8	0.92	0.45	0.28	0.37	13.9
	Max	0.18	37.9	3.44	2.04	1.33	1.94	46.8
	Median	0.07	31.0	2.59	1.48	1.27	1.32	37.7
	% RSD	72.8	41.7	50.6	50.7	49.0	52.6	43.4
Kids Bedroom	**Average**	0.06	50.4	2.09	4.38	0.89	0.77	58.6
ES1	**Min**	0.04	12.7	1.24	0.58	0.28	0.25	15.1
	Max	0.09	102	2.80	7.91	1.23	1.05	115
	Median	0.05	43.4	2.16	4.51	1.03	0.90	52.1
	% RSD	40.3	75.8	30.9	84.5	47.0	46.2	74.0
ES 2	**Average**	0.29	32.5	2.71	2.69	0.88	1.09	40.1
	Min	0.09	5.96	1.29	1.23	0.37	0.21	9.15
	Max	0.66	57.6	3.80	6.06	1.29	2.56	72.0
	Median	0.21	33.2	2.87	1.73	0.94	0.79	39.7
	% RSD	88.3	67.1	39.9	84.4	45.0	93.8	66.8
Kitchen	**Average**	0.09	23.7	3.35	4.54	0.69	0.58	33.0
ES1	**Min**	0.03	203	0.98	2.39	0.49	0.29	24.4
	Max	0.18	29.4	8.68	9.66	0.80	1.22	49.9
	Median	0.08	22.6	1.87	3.05	0.72	0.40	28.8
	% RSD	66.4	16.6	107	75.5	21.0	75.3	35.1
ES 2	**Average**	0.15	34.3	4.00	2.25	0.57	0.57	41.9
	Min	0.11	6.84	1.48	1.34	0.32	0.24	10.3
	Max	0.20	95.2	10.4	3.15	0.89	1.23	111
	Median	0.15	17.7	2.06	2.25	0.53	0.40	23.0
	% RSD	25.6	119	106	37.6	51.6	79.0	112

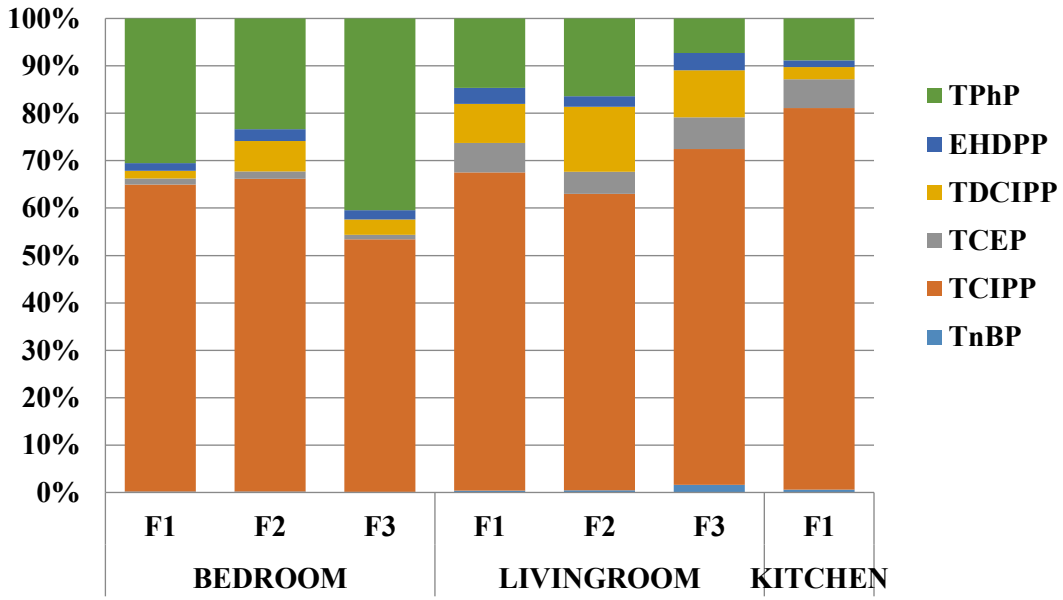


Figure IV-1 Average contributions (%) of individual PFRs in Floor Dust from different rooms in H1.

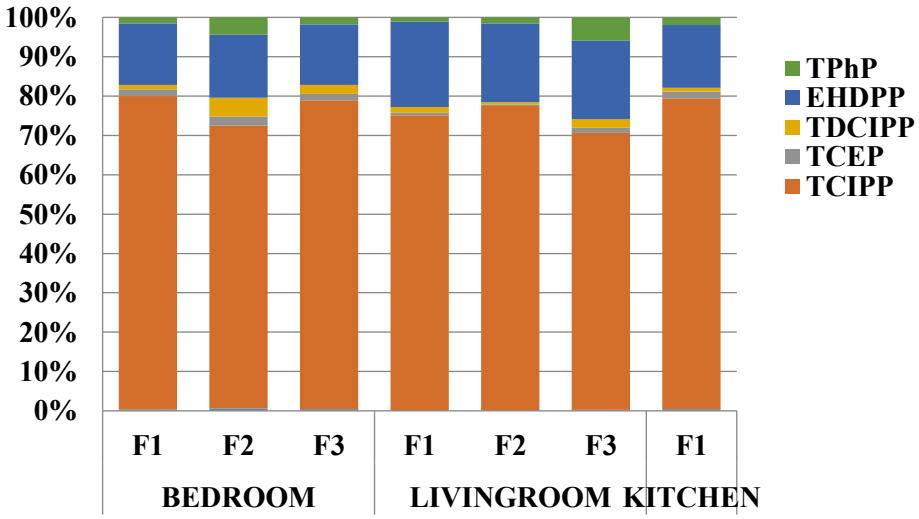


Figure IV-2 Average contributions (%) of individual PFRs in Floor Dust from different rooms in H2.

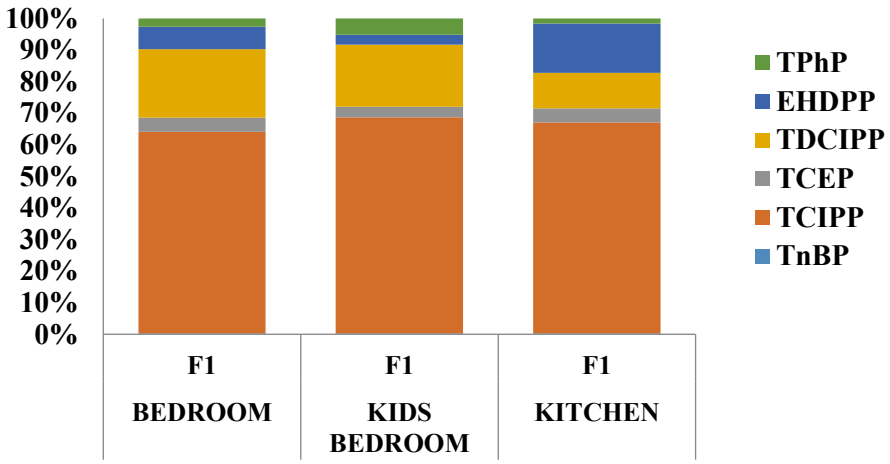


Figure IV-3 Average contributions (%) of individual PFRs in Floor Dust from different rooms in H3.

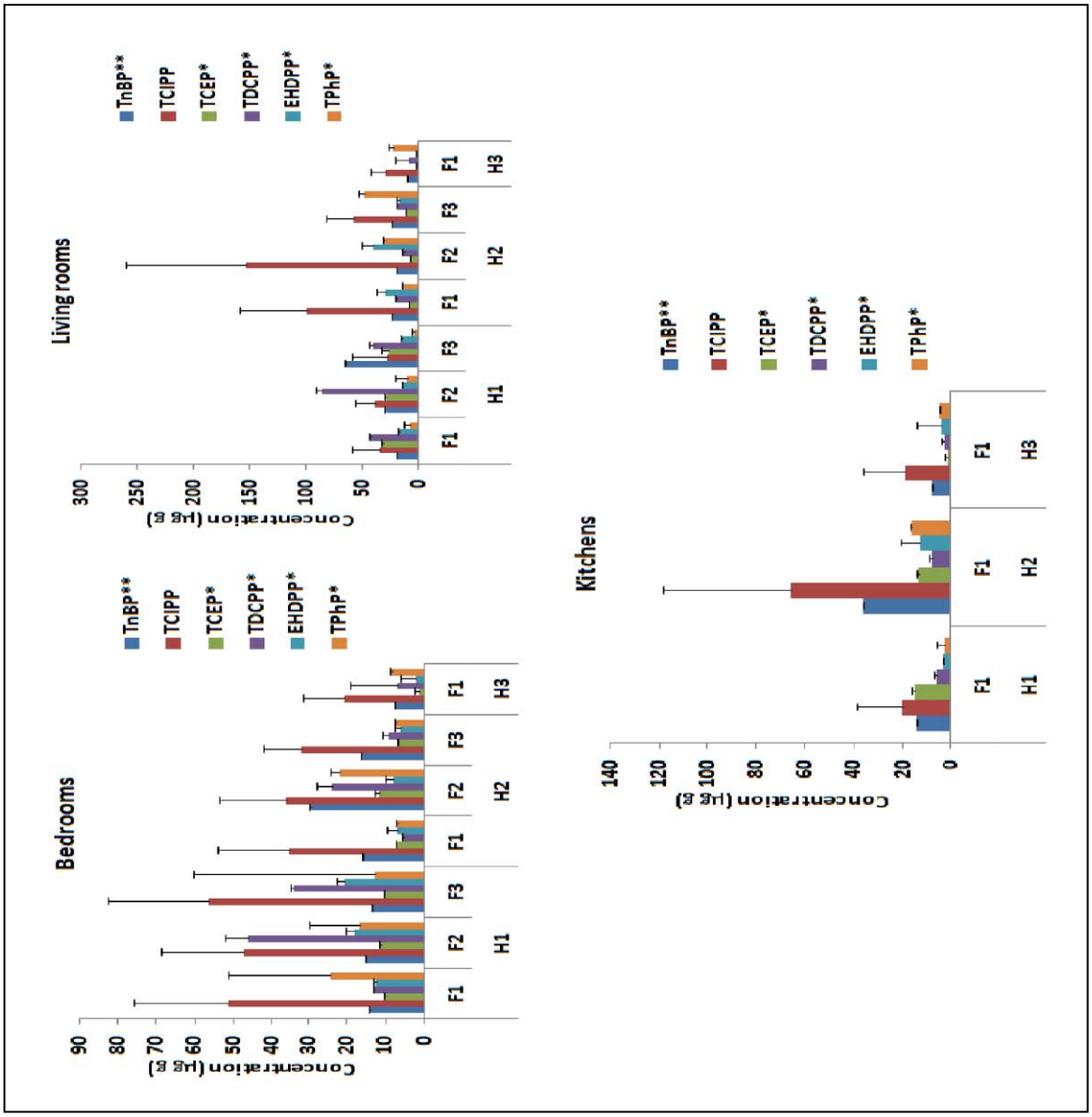


Figure IV-4 Within- home spatial variation in concentrations (µg/g) of PFRs of interest in different floor areas (F1, F2 and F3) in different rooms from H1, H2 and H3.

Due to low concentration *10^1 and **10^2

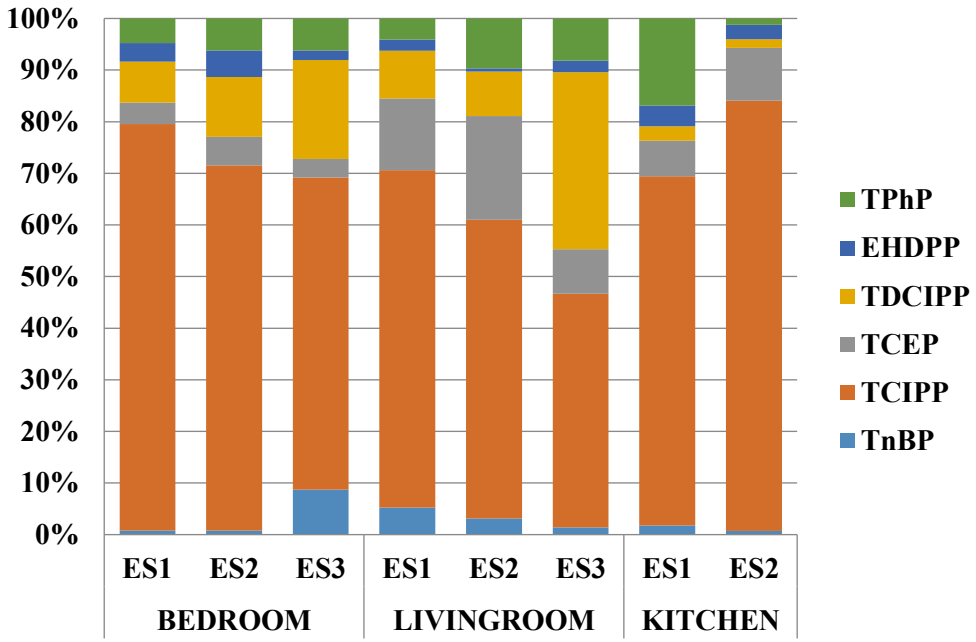


Figure IV-5 Average contributions (%) of individual PFRs in Elevated Surface dust from different rooms in H1.

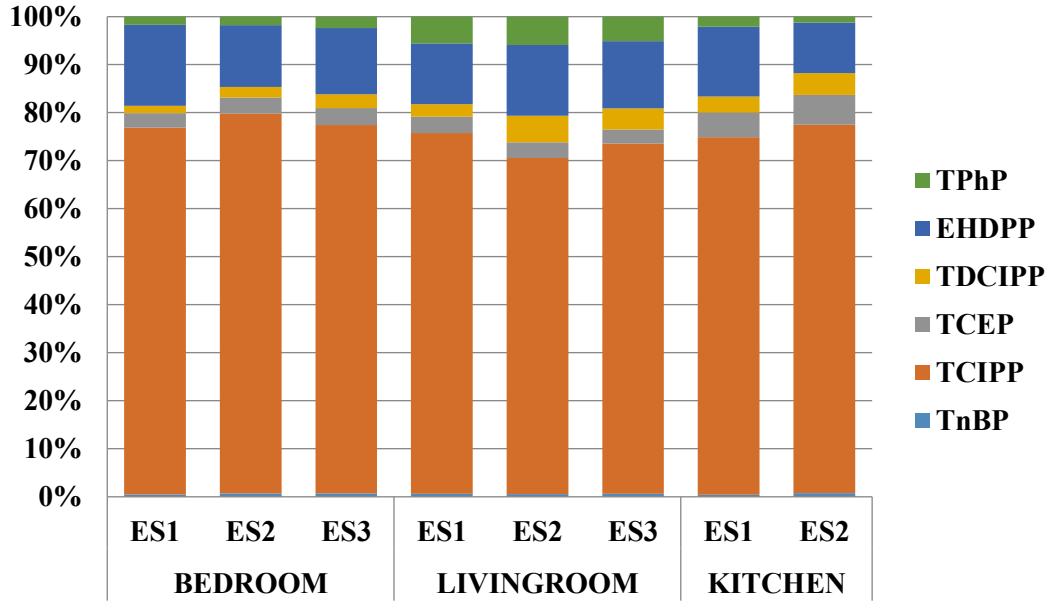


Figure IV-6 Average contributions (%) of individual PFRs in Elevated Surface Dust from different rooms in H2.

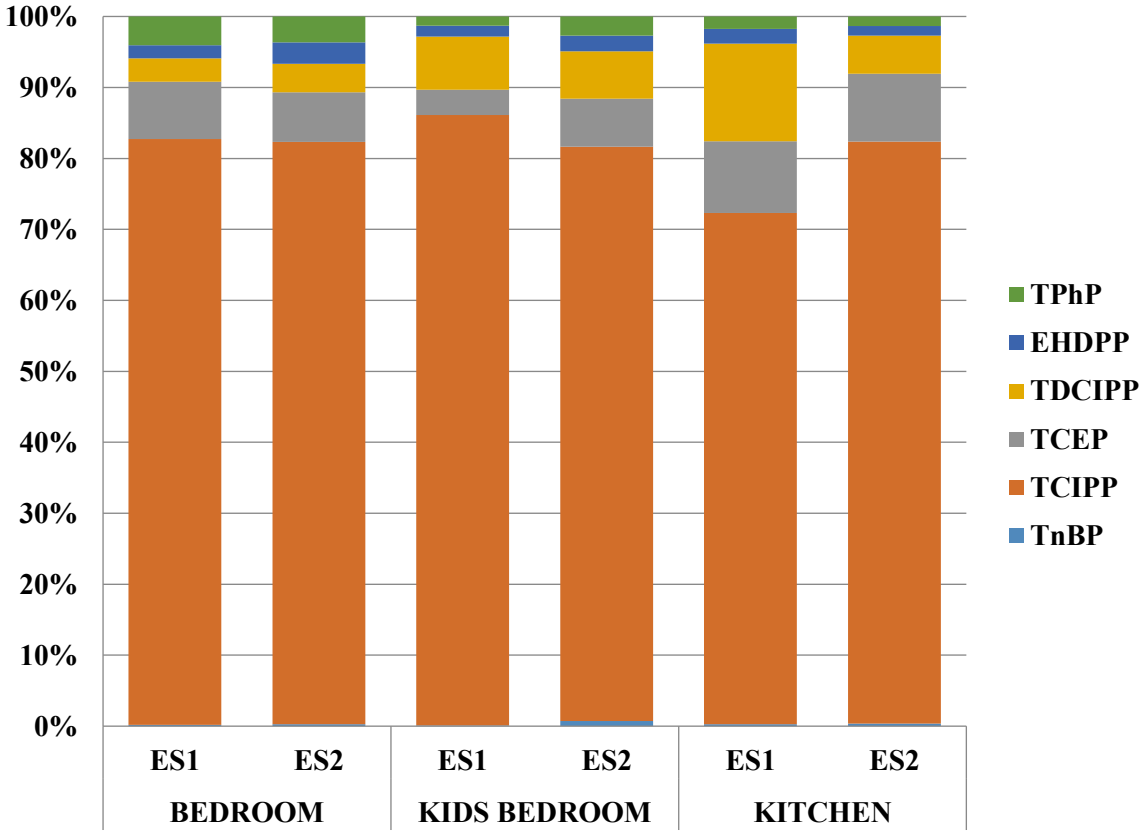


Figure IV-7 Average contributions (%) of individual PFRs in Elevated Surface Dust from different rooms in H3.

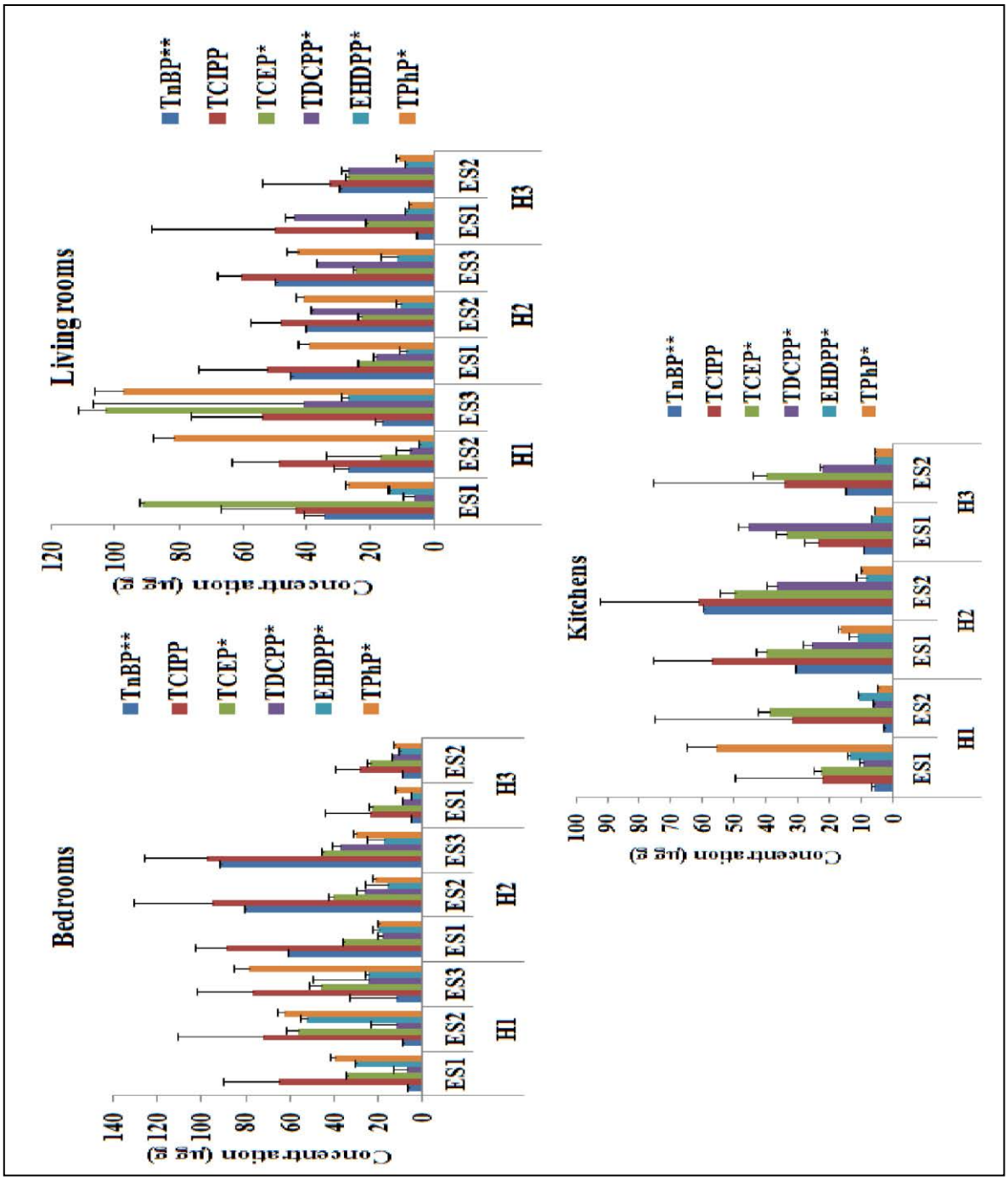


Figure IV-8 Within- home spatial variation in concentrations (µg/g) of PFRs of interest.
in ES1 and ES2 in different rooms of H1, H2 and H3.
Due to low concentrations *10^1 and **10^2

Table IV.8 shows *t*-test was performed to investigate significant differences between ES and F samples within the same room.

House	Area	TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPhP
H1	**R1/F123/ES123**	0.14	**0.02**	**0.01**	**0.02**	**0.02**	**0.00**
	R2/F123/ES123	0.06	**0.01**	**0.01**	0.14	0.47	0.50
	R3/F123/ES123	0.19	0.32	0.16	0.42	**0.04**	0.41
H2	**R1/F123/ES123**	**0.01**	**0.00**	**0.00**	0.07	**0.00**	**0.02**
	R2/F123/ES123	**0.03**	**0.02**	**0.00**	**0.00**	**0.00**	0.17
	R3/F123/ES123	0.38	0.41	0.12	0.13	0.15	0.16
H3	**R1/F123/ES123**	0.12	0.18	0.07	**0.04**	**0.06**	**0.20**
	R2/F123/ES123	0.35	0.37	0.19	**0.00**	0.15	**0.01**
	R3/F123/ES123	0.09	0.23	0.06	0.21	0.11	**0.02**

Significant differences were found between rooms in H1R1 TCEPP, TCEP, TDCIPP, EHDPP and TPhP; H1R2 significant differences between TCIPP and TCEP; H1R3 significant differences just to EHDPP. H2R1 significant differences reported to TnBP, TCIPP, TCEP, EHDPP, and TPhP; H2R2 significant differences to TnBP, TCIPP, TCEP, TDCIPP and EHDPP. H3R1 report a difference between TDCIPP, EHDPP and TPhP. H3R2 significant differences to TDCIPP and TPhP. H3R3 significant differences to TPhP.

Table IV-10 Resume t-test within-room spatial differences between PFRs in Floor (F) and Elevated Surface (ES) Dust.

4.3.2 Within-room spatial differences between PFR concentrations for: (1) Floor (F) and (2) Elevated Surface (ES) Dust.

Within-room spatial differences in concentrations may exist between dust samples taken at the same time from different locations in the same room (Harrad et al., 2008). In this study, within-room spatial differences in concentrations of PFRs from F and ES dust were analysed. To do so, an ANOVA was performed comparing PFR concentrations in elevated surface dust from 3 areas in R1H1, R2H1, R1H2, R2H2, as well as in floor dust from 3 areas in R1H1, R2H1, R1H2, and R2H2. The results of this are shown in Table IV.9. Table IV.10 shows the results of a paired *t*-test comparison of PFR concentrations in elevated surface dust from R3 H1, R3H2 and R3H3 since in each of these R3s just two elevated surface areas were sampled.

Table IV-11 ANOVA comparison of within-room variation in PFR concentrations in floor dust from room #s 1, 2, and 3 in homes 1 and 2.

H1	
R1ES123	NSD
R1F123	TDCIPP F2>F1 (0.040)
R2ES123	EHDPP ES3> ES2 (0.015)
R2F123	TnBP F3> F1 (0.001)
H2	
R1ES123	NSD
R1F123	TPhP F2>F1>F3 (0.015) (0.020)
R2ES123	TDCIPP ES2>ES3>ES1 (0.013) (0.017)
R2F123	EHDPP F2>F1>F3 (0.019) (0.001) TPhP F1>F3 (0.026)

NSD (not significant difference)

Table IV-12 Results of Paired *t*-test comparison of within-room variation of PFR concentrations in elevated surface dust from room #3s in homes 1, 2, and 3.

House	
H1R3ES12	NSD
H2R3ES12	TPhP (0.020)
H3R1ES12	TnBP (0.040)
H3R2ES12	NSD
H3R3ES12	NSD

NSD (not significant difference)

Clearly, our data indicate some within-room spatial differences in PFR concentrations in both floor and elevated surface dust. As suggested for BFRs by Harrad et al., 2008, such within-room variations in contamination may imply a more biologically-relevant measure of exposure may require collecting dust from the most frequented part of a room.

4.3.3 Within-home spatial differences between PFR concentrations in Floor (F) and Elevated Surface (ES) Dust from different rooms.

In this section, we examine our data for the existence of significant differences in concentrations of PFRs in: (a) floor dust from different rooms in the same houses, and (b) elevated surface dust from different rooms in the same houses. To do so, we compared using ANOVA, the average concentration in floor dust in the single area sampled in the kitchen in each house, with the average of the three floor areas sampled in the other two rooms (R1 and R2) in H1 and repeated the same process for H2 and H3.

For ES, we used a similar approach, whereby the average concentrations in ES1, ES2 and ES3 from R1 were compared using ANOVA with the average concentrations of PFRs in elevated surface dust from R2 and R3 in the same house. Table IV.11 shows the results of these analyses.

Table IV-13 Results of ANOVA test of within-home spatial differences in PFR concentrations (μg/g) in Floor and Elevated Surface Dust.

House/Dust Type	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP
H1/ES	NSD	R1>R3 (p<0.037)	R2>R3 (p<0.018)	R1>R3 (p<0.006)	R1>R3 (p<0.042)	NSD
H1/F	R2>R3 (p<0.028)	R1>R3 (p<0.036)	NSD	R2>R3 (p<0.004)	R1>R3 (p<0.001	R1>R3 (p<0.003)
H2/ES	NSD					
H2/F	NSD	R2>R3 (p<0.016)	R3>R1 (p<0.036)	NSD	R2>R3 (p<0.000)	R2>R3 (p<0.008)
H3/ES	NSD					
H3/F	NSD					R2>R1 (p<0.042)

NSD (not significant difference)

In all 3 houses studied, at least 1 significant difference was detected, with the greatest within-house variation present in H1, where room 3 displayed concentrations of several PFRs that were exceeded significantly by those in the other rooms. Overall, while some significant differences were observed for elevated surface dust, these were observed on fewer occasions. This may be attributed to less frequent cleaning of elevated surfaces than floors (Tajima, et al., 2014).

4.3.4 Seasonal variation in PFR concentrations in F and ES Dust.

Although it is difficult to distinguish seasonal variability from month-to-month, it is plausible that seasonal variation in PFR concentrations in dust may occur.

To evaluate its existence, we used a *t*-test to compare concentrations of PFRs in colder (September, October, November, December, January and February) and warmer (March, April, May, June, July and August) seasons. Figures IV.13-IV.18 depict the seasonal differences for floor dust and elevated surface dust for each house, while Table IV.12 and IV.13 summarise the results of the t-tests conducted.

PFR concentration were higher from later winter and early spring; but they were the lowest in autumn to early winter. PFR concentrations change in contrast whit the trend of temperature. The PFR variation pattern was attributable to seasonality.

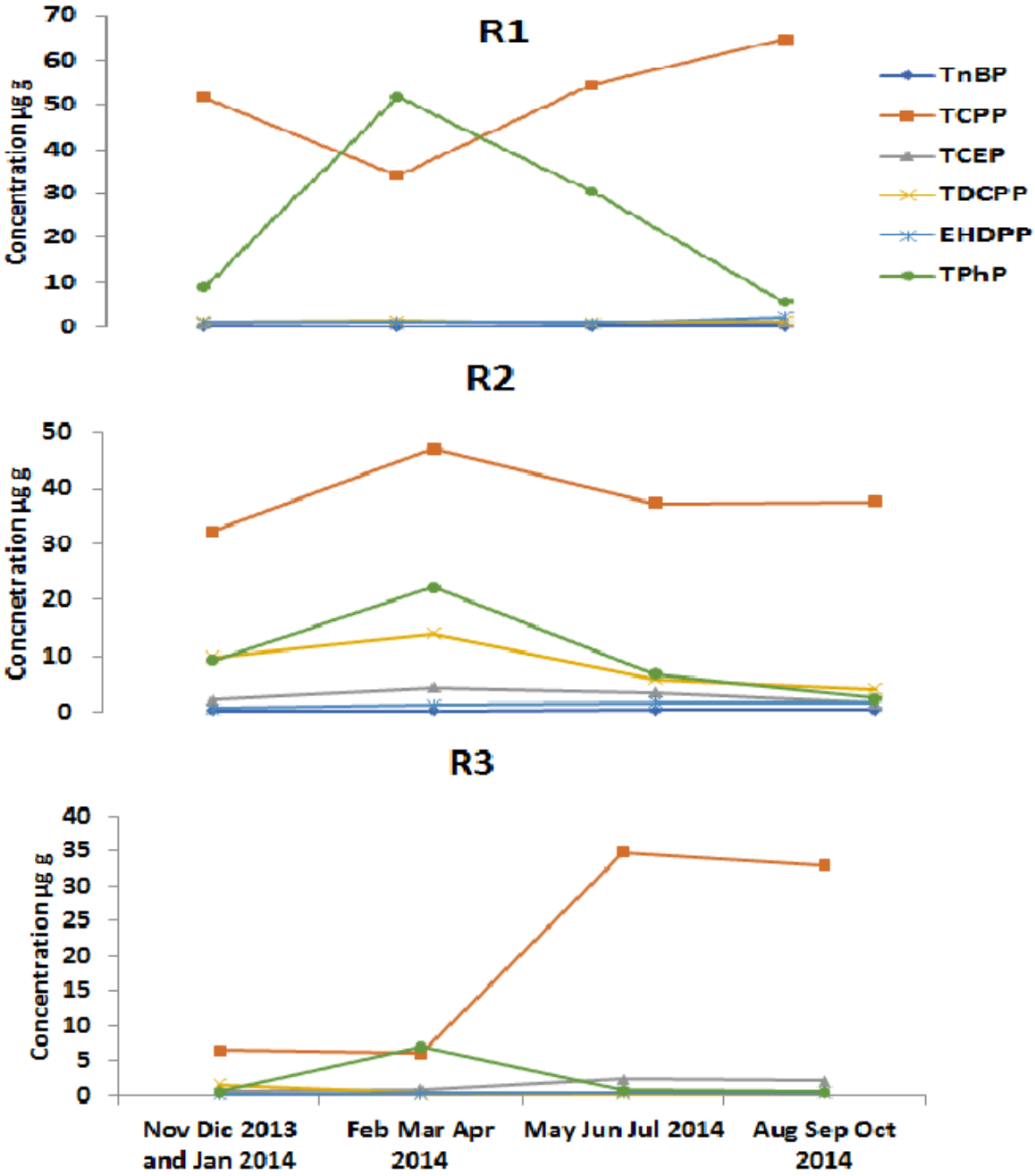


Figure IV-9 House (H) 1 average concentrations (µg/g) of PFRs in floor (F) dust samples from room (R) 1, 2 and 3.

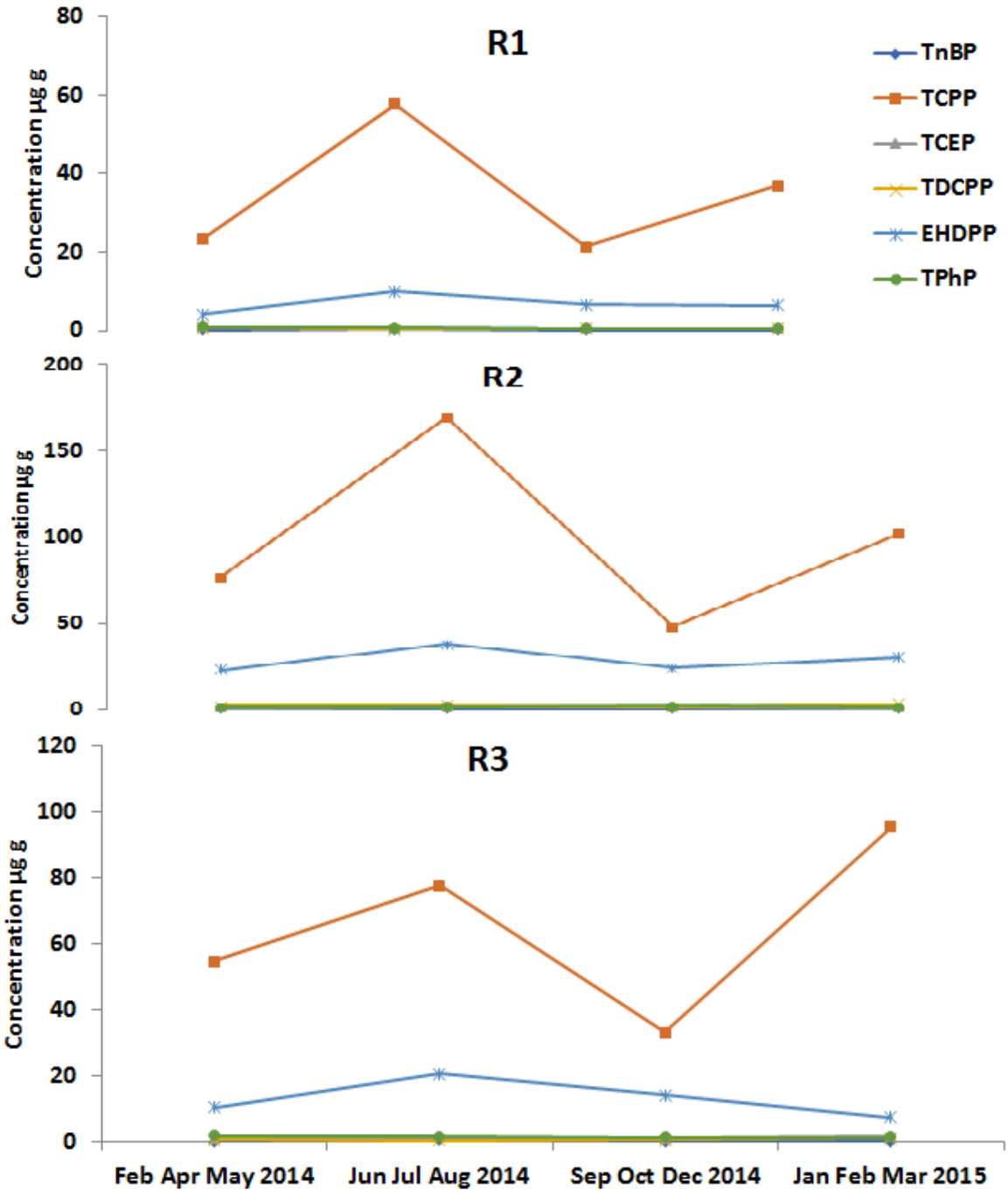


Figure IV-10 H2 average concentrations (µg/g) of PFRs in F dust samples from R 1, 2 and 3.

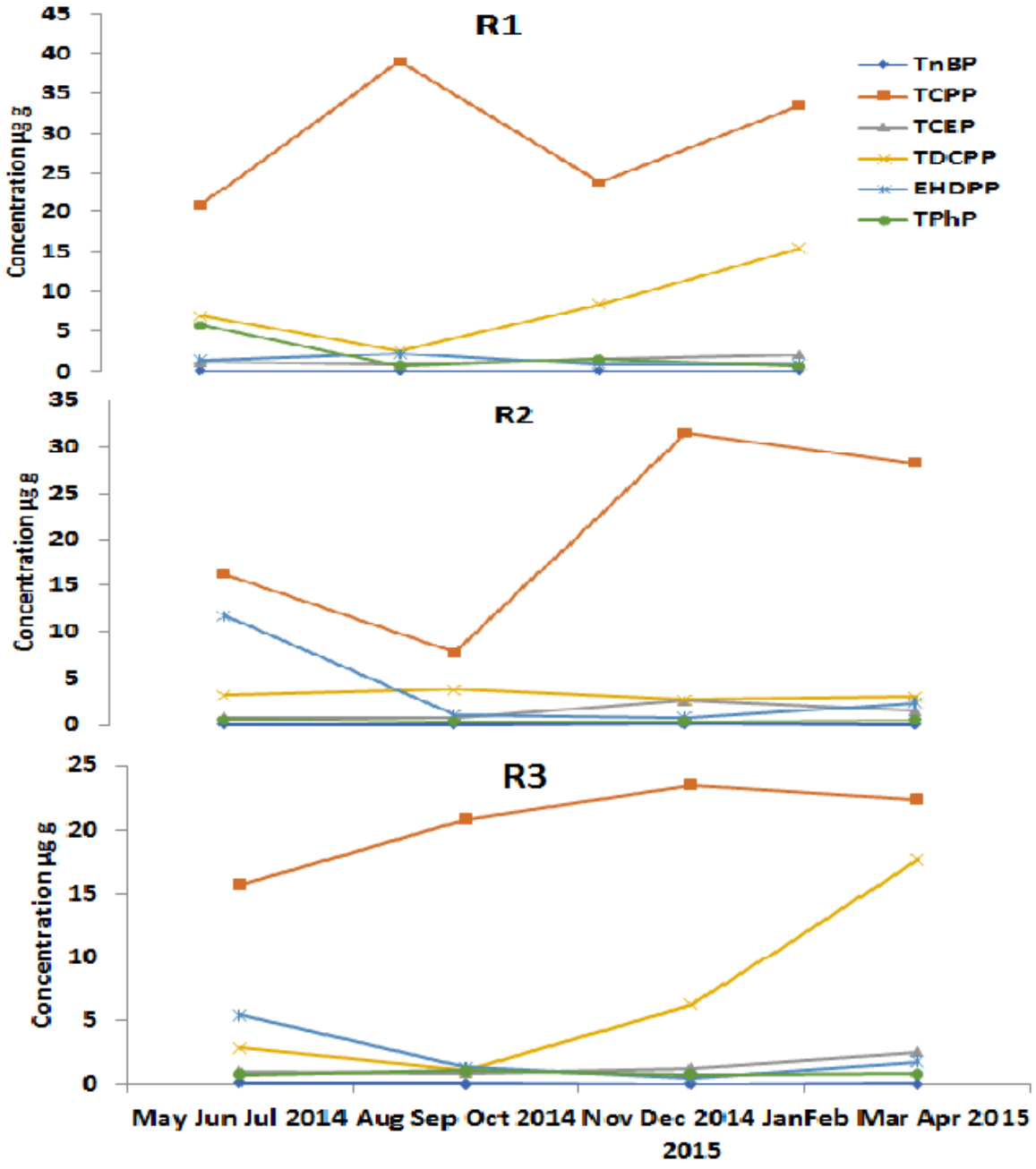


Figure IV-11 H3 average concentrations (µg/g) of PFRs in in floor dust samples from R 1, 2 and 3.

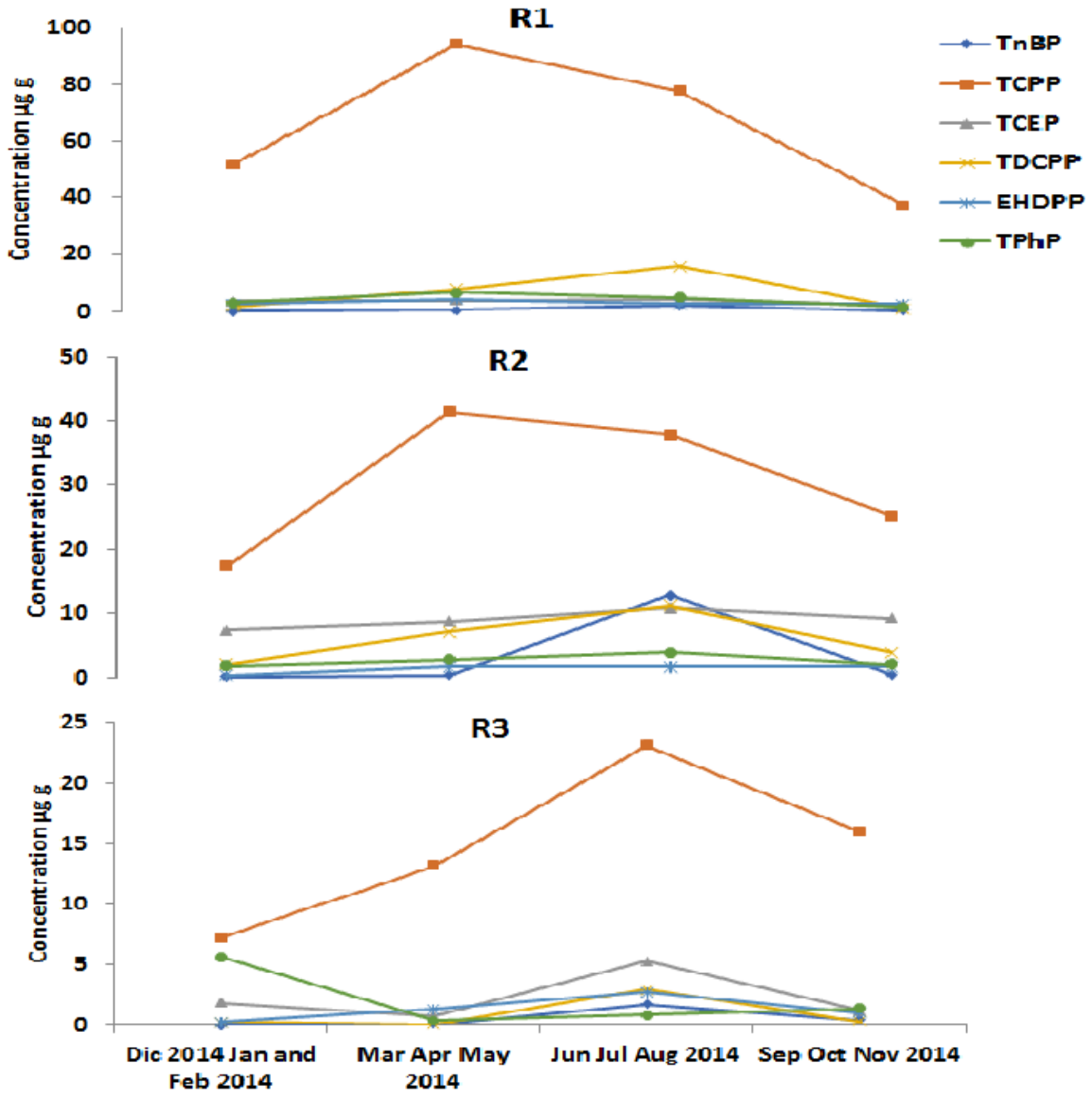


Figure IV-12 Seasonal variation in PFR concentrations (µg/g) in elevated surface (ES) dust from house (H) 1 in room (R) 1, 2 and 3

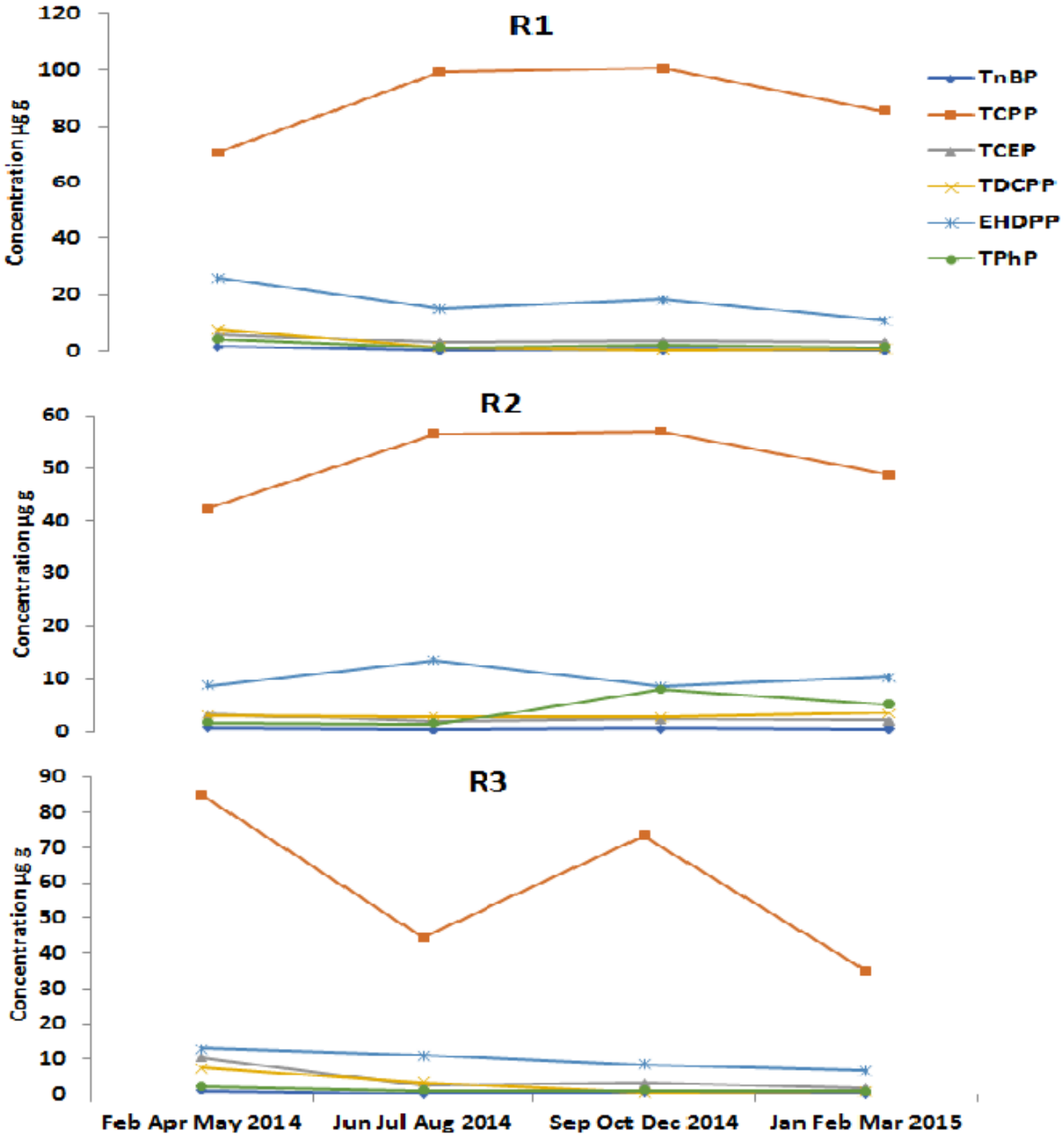


Figure IV-13 Seasonal variation in PFR concentrations (µg/g) in ES dust from H2 in R 1, 2 and 3.

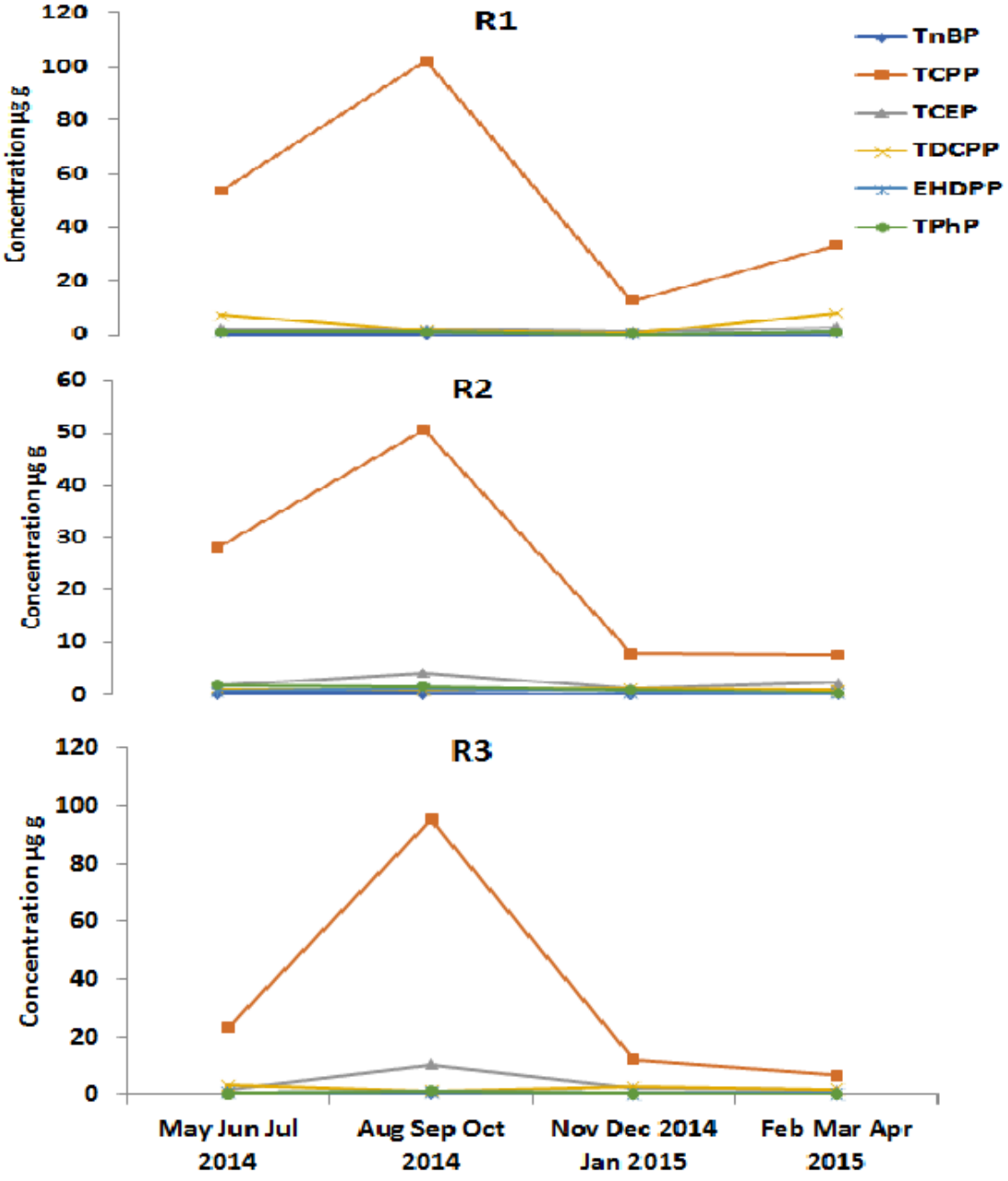


Figure IV-14 Seasonal variation in PFR concentrations (µg/g) in ES dust from H3 in R 1, 2 and 3.

Table IV-14 *t*-test results evaluating seasonal variation in PFR concentrations in floor dust from H1, H2 and H3.

F	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP
H1 R1	**0.03**	**0.00**	**0.04**	0.08	**0.01**	**0.00**
R2	0.23	0.32	**0.04**	0.10	0.10	0.12
R3	0.24	0.32	0.10	0.20	0.46	0.24
H2 R1	0.10	**0.03**	0.09	0.05	0.40	0.11
R2	0.08	0.09	0.30	0.47	0.49	0.23
R3	0.21	0.47	**0.03**	0.28	0.34	0.07
H3 R1	0.14	0.40	0.17	0.21	0.13	0.24
R2	0.44	0.45	0.37	0.41	0.21	**0.03**
R3	0.31	0.31	0.29	0.31	0.22	0.29

Table IV-15 *t*-test results evaluating seasonal variation in PFR concentrations in Elevated Surface dust from H1, H2 and H3.

ES	TnBP	TClPP	TCEP	TDClPP	EHDPP	TPhP
H1 R1	0.15	0.17	0.09	0.06	0.12	0.05
R2	0.05	0.40	0.12	0.14	0.17	0.19
R3	0.09	0.10	0.13	0.16	**0.01**	0.20
H2 R1	0.06	0.17	0.05	**0.03**	**0.03**	**0.04**
R2	0.49	0.21	0.20	0.37	0.24	**0.01**
R3	0.14	0.14	0.08	**0.02**	**0.01**	0.07
H3 R1	0.23	0.33	0.24	**0.02**	0.30	0.10
R2	0.12	0.47	0.49	0.14	0.44	0.28
R3	0.24	0.25	0.48	0.26	0.49	0.46

4.3.5 *Temporal variation in PFR concentrations in Floor and Elevated Surface Dust.*

Clear evidence was found of temporal variability in PFR concentrations in both F and ES dust, with table IV.14 to IV.19 showing the results. The large ratios between the maximum and minimum concentrations and the relative standard deviations in these tables provide evidence that estimates of exposure based on a single dust sample (either floor or elevated surface) taken at a single point in time, will be subject to considerable uncertainty of typically an order of magnitude. This is consistent with similar studies that showed concentrations of BDE 209 in floor dust sampled from three rooms sampled monthly over 10 months could vary by up to 400-fold, dependent on month-to-month changes in room contents, such as an introduction or removal of specific product, ventilation, and occupant life style (Harrad et al., 2008).

Moreover, it has been suggested that two or four replicate dust samples from one sampling site over a full calendar year are not sufficient to represent temporal trends of FRs (Cao et al., 2014).

CHAPTER V. ORGANOPHOSPHATE FLAME RETARDANTS IN INDOOR AIR AND DUST FROM OFFICES AND HOMES IN BIRMINGHAM, UK.

5.1 Synopsis

Indoor air contamination represents a potentially important route of exposure via inhalation since we spend typically at least 85 % of our time in indoor environments in contact with different indoor contaminants with resultant exposure (Liagkouridis et al., 2014). Moreover, as well as inhalation, exposure via ingestion of dust has been shown to be an important contributor to exposure to contaminants such as phosphate flame retardants (Schreder et al., 2015). Hence in this chapter, concentrations of PFRs are measured in samples of indoor air and settled dust from a range of different indoor microenvironments in Birmingham, UK, specifically: living rooms, bedrooms and offices. The relationship between these flame retardants in the analysed air and dust samples will be studied and compared in this chapter.

5.2 Sampling strategy

5.2.1 Air

Passive air samplers possess various advantages over active air samplers such as: cost-effectiveness, less researcher involvement (just deploy and harvest), no requirement for electricity, and silent operation, which is a distinct advantage to study participants.

Indoor passive air samples were collected between January and May 2016 from the following microenvironment categories: 23 bedrooms and 23 living rooms from the same houses within the West Midlands conurbation, UK, 20 offices from the

University of Birmingham, and 7 outdoor air samples taken from the Elms Road Observatory Site (EROS) on the same University campus.

Table V-1 Numbers of passive air samples taken.

Microenvironment	Number of samples
Living rooms	23
Bedrooms	23
Offices	20
Outdoor	7

At the end of each indoor air sampling period (methodology followed in section 2.1.2 to passive air sampling) floor dust was collected from each microenvironment, in accordance with the methodology explained in 2.1.1.1. All samples (air and dust) were collected under normal room use conditions to reflect actual human exposure.

5.2.2 Dust

In order to study the relationship between PFR concentrations in indoor air and dust collected from the same rooms over the same period dust samples were collected at the end of each air sampling period in accordance with the protocol described in 2.1.1.1. In total, air and dust samples were collected from 21 living rooms, 21 bedrooms from the same houses as the living rooms, and 20 offices in the same period of time and the same places and areas as for the air samples collected.

5.3 Concentrations of PFRs in air from different microenvironments

Passive air sampling rates for PAS have been shown to differ depending on whether they are deployed indoors or outdoors for semi-volatile organic compounds (Newton, et al., 2016), (Zhang, et. al., 2012). Indoor sampling rates were obtained by dividing

the outdoor rates by two, to allow for factors such as the lower air flow and the part-sheltered sampler configuration used indoors. The rates used are from Abdollahi et al., (2017) and are listed in Table V.2. These sampling rates for PFRs are not dissimilar to those reported elsewhere for PBDEs e.g. 2.5 m^3 d^{-1} (Wilford, et al 2004) and other POPs for which a default sampling rate of 4 m^3 d^{-1} has been used (Pozo, et al. 2008).

Table V-2 Passive air sampling rates used in this study.

Compound	**Outdoor rate (m^3 day^{-1})**	**Indoor rate (m^3 day^{-1})**
TnBP	3.7	1.8
TCIPP	3.2	1.6
TCEP	3.2	1.6
TDCIPP	5.3	2.7
EHDPP	3.8	1.9
TPhP	2.5	1.3
TCP	3.7	1.8

As shown in figure V.2 and V.3, indoor air concentrations are higher than those detected in outdoor air in this study, except for TDCIPP, EHDPP and TPhP for which the outdoor air average concentration is (0.17, 0.62 and 1.99 ng m^3) respectively, compared to those in living rooms, (0.25, 0.68 and 1.73 ng m^{-3}) respectively; bedrooms, (0.19, 0.43 and 1.39 ng m^{-3}) respectively and average concentrations in offices of TDCIPP, EHDPP and TPhP (0.23, 0.75 and 1.40 ng m^{-3}) respectively. Low concentrations of TDCIPP were reported in previous studies consistent with low concentrations found in our study and its low vapor pressure. TPhP was the

predominant PFR in Toronto semi-urban outdoor air (average 1.06 ng m^3) (Abdollahi et al., 2017).

Moreover, the average outdoor air concentration of TPhP in a remote area from Finland was 12 ng m^3 which the authors attributed to traffic emissions (Marklund et al. 2005c), consistent with the study of Green et al., (2008) who also reported a significant proportion of airborne TPhP to arise from traffic emissions.

In our study, outdoor sampling was conducted near a main road and this may provide at least a partial explanation for the observed higher outdoor compared to indoor concentrations of TPhP.

Our concentrations of TPhP in outdoor air are also consistent with those reported for China and Norway (2.92 and 1.0 ng m^{-3} respectively, Liu et al., (2016)). However, our concentrations exceed those reported for Chicago and Cleveland (0.10 and 0.18 ng m^{-3} respectively) (Salamova et al., 2013). Additionally, our outdoor air samples were collected in May and June, which – given observations of higher concentrations of ΣPFRs in summer than winter (Takeshi et al, 2006) may provide a rationale for the higher outdoor compared to indoor concentrations in our study. The presence of PFRs in outdoor air might be due to the wide use of these compounds in applications such as polyurethane foam (both rigid and flexible), plastics, resins, acrylic, latexes, for back coating and binding of non-woven fabrics (WHO, 1998). Although TPhP was present at higher concentrations in higher outdoor than indoor air, the predominant PFR in outdoor air was TCIPP followed by TCEP with average concentrations of 60 and 12.5 ng m^{-3} respectively, TCIPP concentrations were higher than TCEP might due recent restrictions on the uses of TCEP and the rising usage of TCIPP.

These concentrations compare with previous reports of those for TCIPP in China of 4.92 ng m^{-3}, Finland 0.81 ng m^{-3} and Norway 0.49 ng m^{-3}; and those for TCEP in Toronto of 0.76 ng m^{-3}, China 2.99 ng m^{-3}, Norway 1.45 ng m^{-3} and Japan 14.3 ng m^{-3} (Abdollahi et al., 2017; Salamova et al., 2013 and Liu et al., 2016).

Indoor air concentrations of TCIPP are on average two orders of magnitude higher than those detected in outdoor with indoor average concentrations of 883 ng m^{-3} (living rooms), 632 ng m^{-3} (bedrooms) and 641 ng m^{-3} (offices). Our data are consistent with those reported for concentrations on inhalable particles in US indoor air (average 371 ng m^{-3}, Schreder et al., 2015). Concentrations in bedroom, living room and office air all exceeded significantly those in outdoor air ($p<0.01$ for each). The second most abundant PFR we detected in indoor air was TCEP followed by TnBP, for which the average concentrations were for TCEP and TnBP respectively: living rooms (44.0 and 4.5 ng m^{-3}), bedrooms (33.0 and 4.2 ng m^{-3}) and offices (41.0 and 2.8 ng m^{-3}).

Concentrations of TCEP exceeded significantly those outdoors ($p<0.021$, <0.00 and <0.01 for bedrooms, living rooms, and offices respectively) with those of TnBP significantly higher than outdoors for bedrooms and living rooms only ($p<0.03$, <0.01 respectively). Within the 3 indoor microenvironment categories we studied, the highest concentrations were present in living rooms and bedrooms rather than offices, but no significant statistical differences were observed.

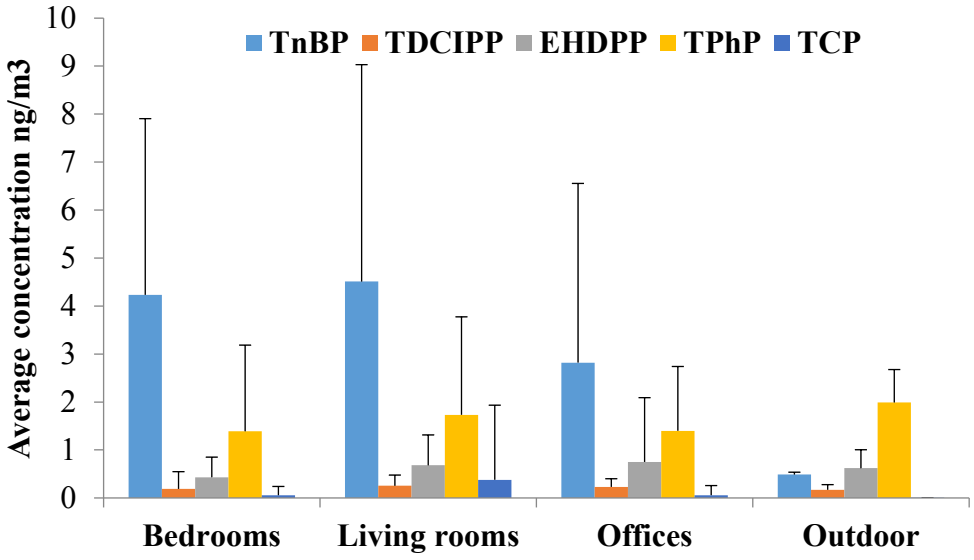


Figure V-1 Average air concentration (ng m^{-3}) of TnBP, TDCIPP, EHDPP, TPhP and TCP for all microenvironments.

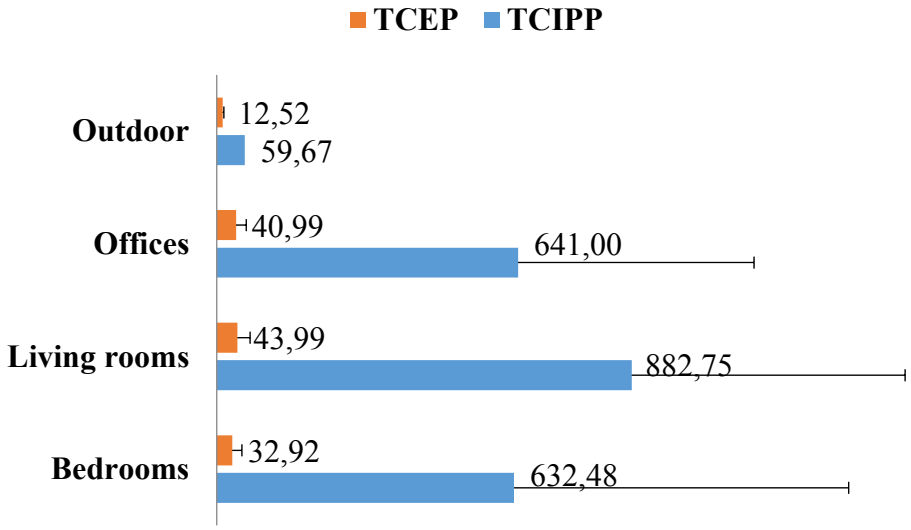


Figure V-2 Average concentrations (ng m^{-3}) of TCIPP and TCEP in air for all microenvironments.

Table V.3 gives an overview of previously reported data on PFR concentrations in outdoor and indoor air. These data provide context to those reported in this study, which are summarised in Table V.4.

Table V-3 Summary of previously reported PFR concentrations (ng m^{-3}) in air samples from outdoor and indoor microenvironments.

OUTDOOR AIR								
Reference	**Microenvironment**	**TnBP**	**TClPP**	**TCEP**	**TDClPP**	**EHDPP**	**TPhP**	**TCP**
Marklund, et al. 2005	Average Finland Air traffic	0.28	0.81	0.10	0.02	N.D.	12.0	N.D.
Saito, et al. 2007	Maximum Japan n=8	1.7	3.1	N.D.	N.D.	N.D.	N.D.	N.D.
Möller et al. 2012	Arctic Mean	N.D.	0.29	0.28	N.D.	N.D.	0.02	N.D.
Salamova et al., 2014	Average Chicago (27) Cleveland	0.25 0.15	0.53 0.85	0.18 0.12	0.12 0.52	N.D.	0.14 0.20	0.09
Shoeib et al., 2015	Mean Toronto	N.D.	0.70	0.58	0.18	N.D.	0.83	N.D.
Rauert et al 2016	Mean Brazil Mexico	N.D.	0.69 1.28	0.36 0.15	0.05 0.02	N.D.	0.11 0.13	N.D.

Table V-4 Continuation summary of previously reported PFR concentrations (ng m^{-3}) in air samples from outdoor and indoor microenvironments.

INDOOR AIR								
Reference	**Microenvironment**	**TnBP**	**TClPP**	**TCEP**	**TDClPP**	**EHDPP**	**TPhP**	**TCP**
Carlsoon, et al., 1997	Mean Sweden Offices	 18	 N.D.	 N.D.	 N.D.	 N.D.	 0.7	 N.D.
Staaf et al., 2005	Homes Offices ranging	7-80 3-7	5-330 41-120	4-115 6-780	N.D.	N.D.	N.D.	N.D.
Saito, et al., 2007	Median Japan House (18) Office (14)	 4.0 6.6	 1.9 6.0	 1.3 3.3	 N.D.	 N.D.	 N.D.	 N.D.
Bergh et al., 2011	Median Sweden Houses (10) Offices (10)	 9.1 2.3	 64 100	 4.8 10	 17 28	 N.D.	 0.08 2.7	 1.0
Takeuchi, et al. 2014	Average Japan Living rooms (6) Bedrooms (6)	 N.D.	 N.D.	 36200 22400	 18000	 3000	 19800 51200	 N.D.
Schreder et al., 2015	Mean Washington Indoor air	N.D.	371	19.1	19.1	N.D.	N.D.	N.D.

Table V-5 Summary of PFR concentrations (ng m^{-3}) in air samples from this study in different microenvironments.

Area	Statistical parameter	TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPhP	TCP
Living Room n=23	**Average**	4.51	883	43.99	0.25	0.68	1.73	0.38
	SD	4.52	582	26.94	0.22	0.38	2.04	1.56
	Median	3.21	847	38.45	0.19	0.55	0.95	0.002
	Minimum	0.41	139	12.69	0.004	0.09	0.51	<0.002
	Maximum	19.97	1961	116	0.82	3.02	8.21	7.49
Bedroom n=23	**Average**	4.23	632	32.92	0.19	0.43	1.39	0.06
	SD	3.67	712	20.74	0.36	0.42	1.80	0.18
	Median	3.58	489	27.51	0.11	0.24	0.65	<0.002
	Minimum	0.15	113	2.38	0.004	0.02	0.10	<0.002
	Maximum	13.14	3308	82.72	1.81	1.56	9.09	0.88
Offices n=20	**Average**	2.82	641	40.99	0.23	0.75	1.40	0.06
	SD	3.73	502	21.82	0.11	1.34	1.34	0.20
	Median	1.29	499	33.48	0.22	0.28	1.05	<0.002
	Minimum	0.53	62	15.60	0.04	0.09	0.27	<0.002
	Maximum	15.39	1964	93.51	0.73	5.34	6.21	0.89
Outdoor n=7	**Average**	0.49	60	12.52	0.17	0.62	1.99	<0.0022
	SD	0.05	9	2.69	0.17	0.63	0.25	<0.0020
	Median	0.48	56	11.46	0.0.9	0.43	1.96	<0.0021
	Minimum	0.42	52	9.47	0.15	0.40	1.63	<0.0021
	Maximum	0.55	78	16.44	0.47	1.51	2.28	<0.0021

5.4 Concentrations of PFRs in dust from different microenvironments.

A statistical summary of the concentrations of our target PFRs in floor dust samples from different microenvironments (living rooms, bedrooms and offices) is provided in table V.5 and illustrated in figure V.4. PFRs were detected in all samples, with TCIPP the most abundant PFR in all three microenvironments. Visual analysis and Kolmogorov-Smirnov test revealed the data were not normally distributed, and thus concentrations were log-transformed prior to ANOVA with Tukey post-hoc testing.

For TCIPP, no statistically significant differences were observed between concentrations in different microenvironments ($p>0.05$). This is consistent with the findings of Brommer et al (2015) for Birmingham, UK who reported TCIPP median concentrations to be: living rooms (29 μg/g), classrooms (16 μg/g) and offices (33 μg/g). These compare closely with those we detected – i.e. median concentrations of TCIPP were: living rooms (30.0 μg/g), bedrooms (32.8 μg/g) and offices (54.8 μg/g) respectively.

Elsewhere, median concentrations of TCIPP similar to those reported here for the UK have been reported – i.e. 39.54 μg/g in offices in China (Cao et al 2014), 18.7 μg/g in living rooms in Japan (Kanazawa et al., 2010), and 33 μg/g in Kuwaiti homes (Ali et al., 2013). On the other hand, Abdallah et al., (2014) and He et al., (2015) reported lower concentrations of TCIPP (0.02 and 0.75 μg/g) from houses in Egypt and China respectively. Abdallah et al., (2014) also report a lower TCIPP median concentration in Egyptian offices (0.08 μg/g).

As well as TCIPP, TnBP, TCEP, TDCIPP, EHDPP and TPhP also feature strongly in one or more microenvironments. Concentrations on our study of these compounds are broadly similar in concentrations to those reported in previous studies, albeit with some differences in the relative abundance of the different PFRs. In living rooms in this study, median concentrations of EHDPP (2.32 μg/g), TCEP (1.98 μg/g), TDCIPP (1.61 μg/g), TPhP (1.44 μg/g) and TnBP (0.09 μg/g) were detected, with median concentrations in bedroom dust being: TPhP (3.48 μg/g), EHDPP (2.86 μg/g), TCEP (1.76 μg/g), TDCIPP (1.52 μg/g) and TnBP (0.08 μg/g). Our data compare quite closely with those of Brommer et al., (2015) who reported concentrations in living rooms from Birmingham, UK to be: TPhP (3.3 μg/g), EHDPP (1.6 μg/g), TCEP (0.81 μg/g) and TDCIPP (0.71 μg/g). Median concentrations in office dust in this study were: TPhP (4.54 μg/g), EHDPP (2.61 μg/g), TDCIPP (1.44 μg/g), TCEP (1.41 μg/g), and TnBP (0.08 μg/g). By comparison, median concentrations in office dust from Japan and the USA have been reported as: TCEP (5.8 and 2.7 μg/g), TPhP (4.5 and 2.8 μg/g) and TDCIPP (2.8 and 2.1 μg/g) respectively. Moreover, in offices median concentrations of EHDPP (0.56 μg g) and TnBP (0.08 μg g) have been reported in dust from US (Araki et al., 2014), (Dodson et al., 2012).

Concentrations of TCIPP and TPhP in offices were significantly higher ($p<0.00$) than those in living rooms. Our lack of significant differences between TDCIPP contamination in different indoor microenvironments contrasts with the findings in the USA of Carignan et. al., (2013), who reported significantly higher TDCIPP concentrations in dust from offices (geometric mean 6.06 μg/g) than in dust from living rooms (geometric mean 4.21 μg/g) and bedrooms (geometric mean 1.40 μg/g).

Our observation that the TPhP concentrations were highest in office dust may be attributable to the greater abundance of computers in offices. This is because TPhP has been detected in dust from computer housing and displays at concentrations of 3.3-4 μg/g (Marklund et. al., 2003).

Table V-6 Summary of PFR concentrations (μg g^{-1}) in UK dust samples from different microenvironment categories.

Location	Statistical Parameter	TnBP	TCIPP	TCEP	TDCIPP	EHDPP	TPhP	TCP
Living rooms n=21	**Average**	0.09	40.7	1.89	7.24	4.76	6.08	0.00
	SD	0.04	23.6	0.93	17.1	7.42	9.62	0.02
	Median	0.09	30.0	1.98	1.61	2.32	1.44	0.00
	Min	0.01	2.73	0.09	0.10	0.63	0.75	0.00
	Max	0.15	95.8	4.60	75.6	27.6	39.6	0.10
Bedrooms n=21	**Average**	0.10	41.5	1.92	1.57	3.76	5.83	0.45
	SD	0.05	21.5	0.68	0.74	2.74	5.99	2.06
	Median	0.09	32.8	1.76	1.52	2.86	3.48	0.00
	Min	0.03	16.5	0.99	0.00	0.50	0.77	0.00
	Max	0.20	104	3.66	2.74	10.7	21.9	9.46
Offices n=20	**Average**	0.10	76.4	1.70	1.66	3.87	8.00	0.00
	SD	0.06	35.5	0.64	0.58	2.05	4.67	0.00
	Median	0.08	54.7	1.41	1.44	2.61	4.54	0.00
	Min	0.04	24.3	0.60	0.57	0.62	0.83	0.00
	Max	0.28	117	2.72	2.82	8.36	17.5	0.00

Table V-7Comparison of median concentrations (μg g^{-1}) of PFRs detected in indoor floor dust from this study and others.

Reference	Country	TNBP	TCIPP	TCEPP	TDCIPP	EHDPP	TPhP
Living rooms							
Kanazawa et al., 2010	**Japan (n=41)**	1.4	18.7	7.5	4.0	N.D	5.4
Araki et al., 2014	**Japan (n=148)**	1.0	8.7	5.8	2.8	N.D	4.5
Abdallah et al., 2014	**Egypt (n=20)**	0.01	0.02	0.02	0.07	0.04	0.06
Luongo et al., 2015	**Sweden (n=62)**	5.6	11	4.0	2.0	2.7	4.3
He et al., 2015	**China (n=11)**	0.08	0.75	3.48	0.13	0.36	0.15
Brommer et al., 2015	**UK (32)**	<0.03	21	0.81	0.71	1.6	3.3
Harrad, S. et al., 2016	**Germany (n=22)**	<0.03	1.00	0.21	0.08	0.14	0.23
Harrad, S. et al., 2016	**Kazakhstan (n=9)**	0.11	1.00	1.40	0.11	0.27	3.80
Harrad, S. et al., 2016	**Australia (n=11)**	0.06	1.80	0.60	0.32	0.38	1.20
Harrad, S. et al., 2016	**Canada (n=14)**	0.13	1.20	0.69	1.10	0.39	1.60
This study	**UK (n=21)**	0.09	30.01	1.98	1.61	2.32	1.44
Bedrooms							
This study	**UK (n=21)**	0.09	32.79	1.76	1.52	2.86	3.48

Table V-8 Continuation comparison of median concentrations (μg g^{-1}) of PFRs detected in indoor floor dust from this study and others.

Reference	Country	TNBP	TCIPP	TCEPP	TDCIPP	EHDPP	TPhP
Offices							
Bergh et al., 2011	**Sweden (n=10)**	0.2	19	6.7	17	1.0	5.3
Brommer et al., 2012	**Germany (n=10)**	0.22	3.0	0.12	0.15	N.D	2.5
Cao, Z., et al., 2014	**China (56)**	0.44	39.54	3.25	1.8	1.02	2.24
Abdallah et al., 2014	**Egypt (n=20)**	0.02	0.08	0.03	0.04	0.04	0.07
Brommer et al., 2015	**UK (n=61)**	<0.03	33	0.87	0.48	5.3	4.3
Min, W., et al., 2016	**China (n=23)**	N.D	11.29	10.59	0.91	N.D	2.00
Harrad, S. et al., 2016	**Germany (n=22)**	N.D	1.60	N.D	0.14	0.36	1.50
Harrad, S. et al., 2016	**Kazakhstan (n=9)**	N.D	2.20	N.D	0.91	0.26	5.30
This study	**UK (n=20)**	0.08	54.77	1.41	1.44	2.61	4.54

N.D. not determinated

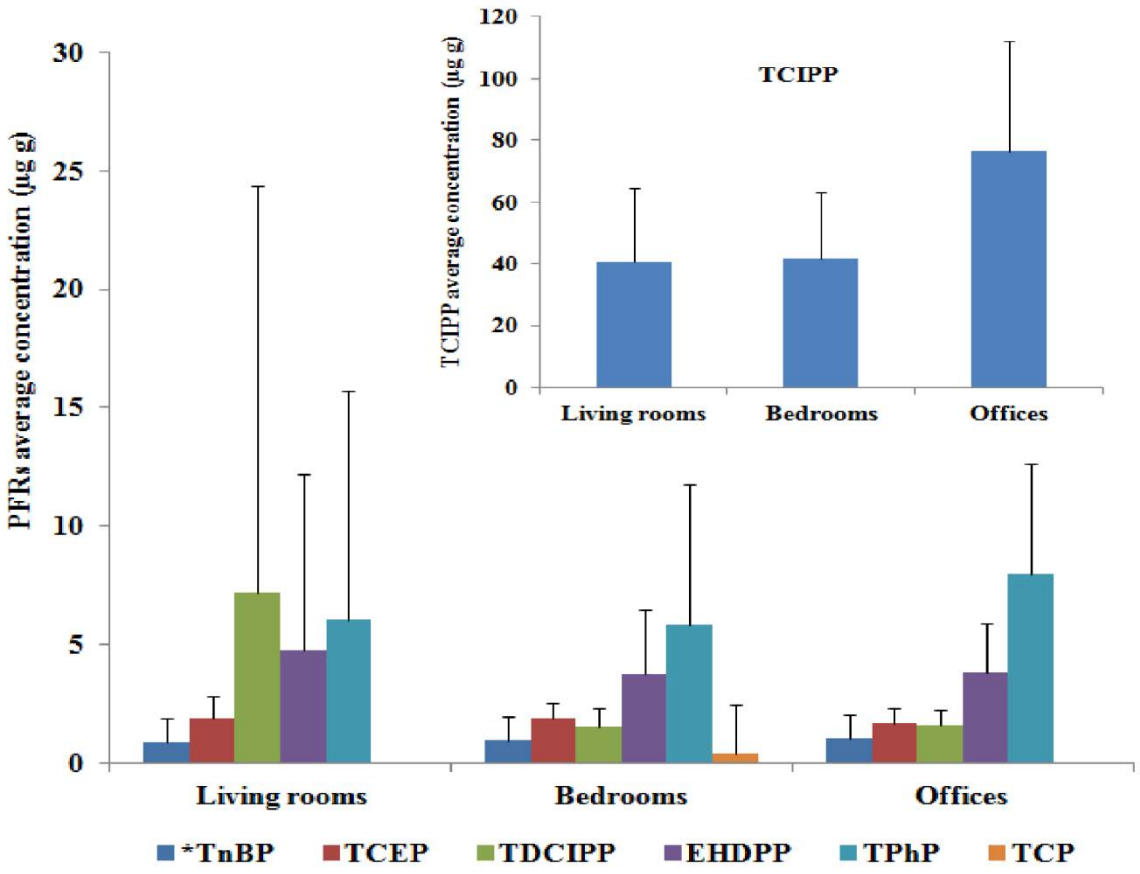


Figure V-3 Median concentrations (ng/g) of PFR of interest in dust from different indoor microenvironment. * Due to the lower concentrations of TnBP, values are multiplied by 10 on the figure.

5.5 Correlations between PFRs concentrations in air and dust.

Pearson rank analyses revealed positive correlations between air and dust concentrations in the three sampled microenvironments with a significant linear regression correlation especially for the more volatile compounds. Table V.7 shows the results of the correlation analyses.

Table V-9 Correlation analyses between air and dust concentrations.

Compound	Correlation coefficient	R^2
TnBP	0.988	0.976
TCIPP	0.990	0.985
TCEP	0.847	0.718
TDCIPP	0.770	0.592
EHDPP	0.962	0.924
TPhP	0.949	0.901

The good correlation between dust and air concentrations might be practically due to the fact that the passive air samplers retain some dust particles as well as vapour. On the other hand, elevated R^2 values suggest that equilibrium conditions were reached between dust and air for the majority of the PFRs studied. Cequier et al., (2014) report a similar correlation between PFR concentrations in dust and air in Norwegian houses and classrooms. In Stockholm, Sweden three different environment categories were analysed (houses, daycare centres and workplaces). PFRs were detected in both in air and dust, with significant correlation reported between dust and air concentrations for TnBP, TCEP, and TCIPP. The authors took this as evidence that dust: air equilibrium was reached for these PFRs, concluding also that high molecular weight PFRs were more abundant in dust than air because of their lower vapour pressures (Bergh et al., 2011).

5.6 Exposure estimates via inhalation and dust ingestion.

Dairy intake is the principal exposure pathway from many FRs, but recent studies have concluded that ingestion of indoor dust can be significant exposure pathway to FRs (Mercier et al., 2011). The total daily intake of PFRs via indoor dust ingestion and inhalation was calculated using the following equation used by another author (Harrad et al., 2006) with some modifications:

$$\sum \text{exposure(ng/kgbw/day)} = \text{dust intake (mg/day)} \{(C_L)x(S_L)+(C_B)x(S_B)+(C_O)x(S_O)\}/bw$$

Where C_L, C_B and C_O are the dust concentrations from living room, bedroom and office respectively and S_L, S_B and S_O are the time spend in different microenvironments.

We assumed an average body weight (bw) of 70 kg for adults and 12 kg for toddlers (http:www.disable-world.com). To make a preliminary assessment of the likely magnitude of human exposure via indoor dust ingestion, a calculation method described by Harrad et al. (2008) was adopted. In absence of evidence, 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 toddler, respectively. We assumed that an average adult person spend 23.8% in office, 33.3% in bedroom and 42.9% in living rooms, and toddlers spend 41.7% in bedroom and 58.3% in living rooms (Harrad and Abdallah, 2011). We assume for inhalation that dults spend 38.4% of their time in living room, 33.3% in bedroom, 23.8 in office and 4.5% outdoor and toddlers spend 53.8% in living rooms, 41.7 in bedrooms and 4.5% outdoor. Air inhalation rate figures for adults and toddlers were assumed to be on average 20 and 3.8 m3/day respectively (Currado et al., 1998) and

(Wilford et al., 2004). Different exposure scenarios were calculated using 5th percentile, media, mean and 95th percentile concentrations from house and office dust and house, office and outdoor air. However, it is stressed that the range exposure estimated in only an indication of the likely range for toddlers and adults within the population. This is partly due to the small number of dust sample analyse, the substantial inter-individual variation depending on the time spend in different microenvironments and the quantity of dust ingest and air inhaled.

Calculated intake of intake dust and inhalation PFR with different exposure scenarios for adults and toddlers is showed in table V-8 and V-9 For both groups, the estimate exposure levels of ∑PFRs were several orders of magnitude lower than their reference dose (RfD) values.

Table V-10 Estimated exposure to PFRs (ng/ (kg bw)/d) via dust ingestion assuming mean and high dust ingestion rates.

		Adults			Toddlers		
		P5	**Median**	**P95**	**P5**	**Median**	**P95**
TnBP	**Mean**	0.01	0.03	0.05	0.17	0.38	0.64
	High	0.03	0.06	0.12	0.67	1.50	2.54
TClPP	**Mean**	5.06	13.1	22.8	64.2	130	289
	High	12.7	32.8	57.0	257	520	1158
TCEP	**Mean**	0.26	0.53	0.84	4.00	7.87	12.7
	High	0.65	1.32	2.10	16.0	31.5	50.8
TDClPP	**Mean**	0.12	0.45	4.05	1.16	6.55	76.4
	High	0.30	1.12	10.1	4.64	26.2	306
EHDPP	**Mean**	0.25	1.10	4.41	3.35	10.6	76.1
	High	0.62	2.74	11.0	13.39	42.4	304
TPhP	**Mean**	0.34	1.07	5.41	3.81	9.53	83.7
	High	0.86	2.68	13.5	15.25	38.1	335

Table V-11 Estimated inhalation exposure to PFRs ng/ (kg bw)/day.

	Adults			Toddlers		
	P5	**Median**	**P95**	**P5**	**Median**	**P95**
TnBP	0.12	0.79	2.86	0.13	1.03	3.32
TCIPP	4.18	9.25	22.2	4.11	10.3	24.5
TCEP	38.3	174	482	48.9	210	561
TDCIPP	0.01	0.04	0.13	0.01	0.05	0.16
EHDPP	0.04	0.09	0.55	0.04	0.11	0.43
TPhP	0.15	0.29	1.25	0.17	0.31	1.52

RfD (ng/ (kg bw)/d): TnBP 24,000; TCEP 22,000; TCIPP 80,000; TDCIPP 15,000; TPhP 70,000; TCP 13,000 (Ali et al., 2012).

For each of the studied compounds, estimated exposure via dust ingestion exceeded estimated exposure from inhalation except for TnBP and TCEP. To illustrate, in our study average adult intake of TCIPP via dust ingestion was an estimated 5.06 ng/ (kg bw)/d; with the high end estimated intake of TCIPP for adults an estimated 12.7 ng/ (kg bw)/d. By comparison, estimated inhalation exposure to TCIPP of adults was 4.18 ng/ (kg bw)/d.

Our UK estimates are lower than previous estimates of exposure via dust ingestion for e.g. California which found that 51 % of children in a study of daycare centres were exposed to TDCIPP levels exceeding a child-specific “No significant risk level” based on California proposition number 65 carcinogen guideline (Bradman et al., 2014).

By comparison, in our study, exposure estimates for both adults and toddlers were several orders of magnitude lower than their corresponding reference dose (RfD)

values (ng/ (kg bw)/ d) derived by dividing the relevant chronic NOAEL values by a factor of 1000 (Ali et al., 2012). However, it is important to note that due to the relatively small number of samples in our study, coupled with the uncertainties introduced to our estimates associated with our assumed dust ingestion and air inhalation rates; our exposure estimates are indicative only; and larger studies may lead to different estimates.

CHAPTER VI. TRANSFER OF PFRS TO DUST VIA DIRECT CONTACT BETWEEN A FABRIC SOURCE AND DUST

6.1 Synopsis

The everyday use of PFRs results in redistribution from the original source into particles. Despite their presence at elevated concentrations in indoor dust, relatively little is known about PFR transfer to dust from goods which are in direct contact. In this chapter, the transfer of PFRs via direct contact from fabric to dust is investigated via a series of controlled test chamber experiments. Additional information about the experimental set up employed can be found in chapter 2.1.3, with details of the extraction and clean-up procedures provided in chapter 2.2.2.

6.2 Sampling strategy

The major material content in many indoor environments is fabrics (Molander et al., 2012). Many such fabrics are treated with flame retardants; however, these chemicals are not bound to fabric, they accumulate in dust with resulting potential adverse health impacts for human contact/exposure – e.g. for toddlers who spend large periods of time playing and crawling over surfaces and display frequent hand-to-mouth contact (Jones-Otazo et al., 2005). Figure VI.1 some of the most commonly used FRs in upholstered furniture are halogenated and/or contain phosphorus (Cooper et al., 2014).

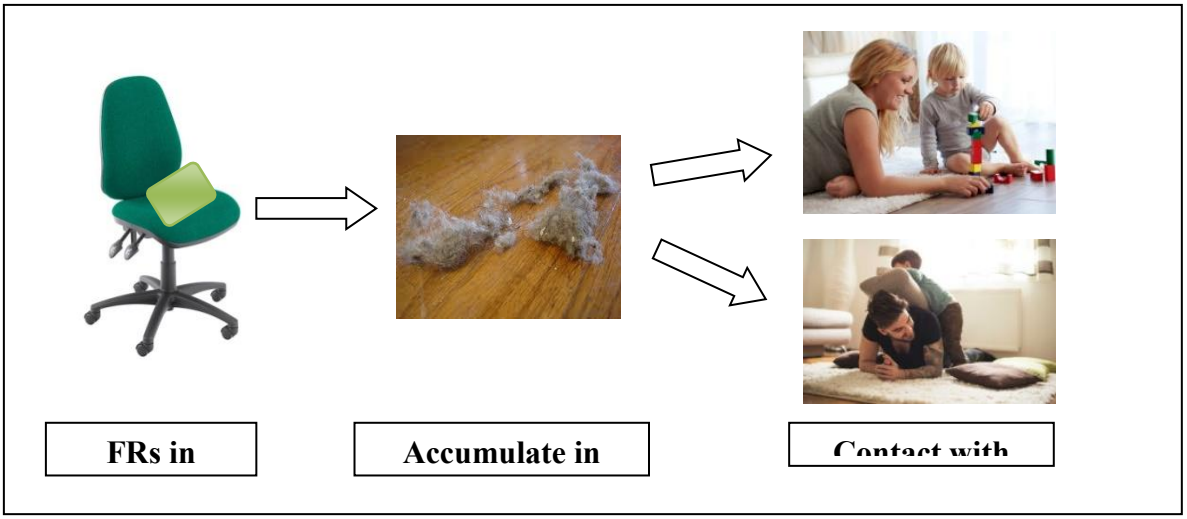


Figure VI-1 Pathways via which PFRs in fabrics transfer to dust in indoor environments.

The majority of PFRs are incorporated into products via an additive process where the PFR is blended into the material, but remains unbound. This may lead to possible migration from treated fabrics to indoor dust via pathways such as: volatilization with subsequent partitioning to dust; by abrasion of an FR-containing fabric resulting in direct transfer of FR-laden fibers to dust; and transfer via direct contact between treated fabric and dust (Suzuki et al., 2009; Webster et al., 2009; Wagner et al., 2013; Cao et al., 2014; Rauert et al., 2016).

In the US, the California legislature recently approved a law (SB1019) requiring labels in furniture to indicate if a product contains FR or not. TDCIPP is more commonly used as flame retardant in US furniture, as evidenced by Stapleton et al. (2012), who report the presence of TDICPP in 50 % of residential furniture PUF samples analysed.

In a recent study, 40 samples of furniture (foam, fabric covers, synthetic fibers and beads) were analysed, finding the following concentrations of PFRs: cover fabrics (TCIPP 6.26 µg/g, TCEP 5 µg/g, and TPhP 4.6 µg/g), synthetic cover pad and batting (TCIPP <6.25 µg/g, TCEP 4.6 µg/g), foam material (TCIPP 6.3 µg/g, TCEP <4.6 µg/g, TDCIPP 3.8 µg/g). The study observed that products manufactured before 2013 displayed the highest concentrations of these compounds (Petreas et al., 2016).

A series of chamber experiments were conducted to investigate the migration of BFRs to dust as a result of direct source: dust contact. After 1 week with plastic containing PBDEs, substantial transfer of BDE-209 to dust was observed, with the greater transfer after 1 week compared to 24 hr. contact suggesting that dust: source equilibrium was not attained within 24 hours (Rauert et al., 2015).

In this chapter, we use the same experimental chamber configuration to study the transfer of PFRs from a treated fabric to dust via direct fabric: dust contract. The fabric used was characterised as wool which is used commonly due to advantages such as: lower rate of flame spread, no melt or drip; ability to form a char when combusted which is insulating and self-extinguishing, and lower emissions of toxic gases and smoke than synthetic materials.

Wool carpets are specified for environments with high fire safety requirements, such as trains and aircraft. Wool is usually specified for garments worn by firefighters, soldiers, and others in occupations where they are exposed to the likelihood of fire.

In addition to clothing, wool has been used for blankets, horse rugs, saddle cloths, carpeting, felt, and upholstery. It is resistant to static electricity, because the moisture retained within the fabric conducts electricity. The use of wool car seat covers or carpets reduces the risk of a shock when a person touches a grounded object. Wool fiber exteriors are hydrophobic and the interior of the wool fiber is hygroscopic. Moreover, wool possesses good abrasion resistance, is comfortable, resists dirt, and is water repellent and as specified above is fire resistant, etc. (Sedlak, 2011).

The fabric segment (30 cm x 20 cm) used for the experiment was kept refrigerated at 4 °C before use. The fabric was originally from a chair obtained for analysis in another project (Stubbings et al., 2016) examining concentrations of BFRs and PFRs in waste soft furnishings. The characteristics of the fabric were: green wool covering the seat cushion of a desk chair sampled in June 2012 in the University of Birmingham. The year of manufacture and purchase was unknown. Details of the extraction and clean-up procedures are provided in chapter 2.2.2.

To examine the transfer of PFRs from the fabric to dust via direct dust: fabric contact, a controlled chamber experiment was conducted, whereby a known amount of dust containing known concentrations of target PFRs was placed on the surface of the fabric. Aliquots of the dust were removed at various time points and analysed for their PFR content. To avoid volatilisation and atmospheric inputs during the experiment, the chamber used was sealed to the air and was and operated at room temperature (22 ± 1 °C). Fig 6.2 shows the chamber set up.

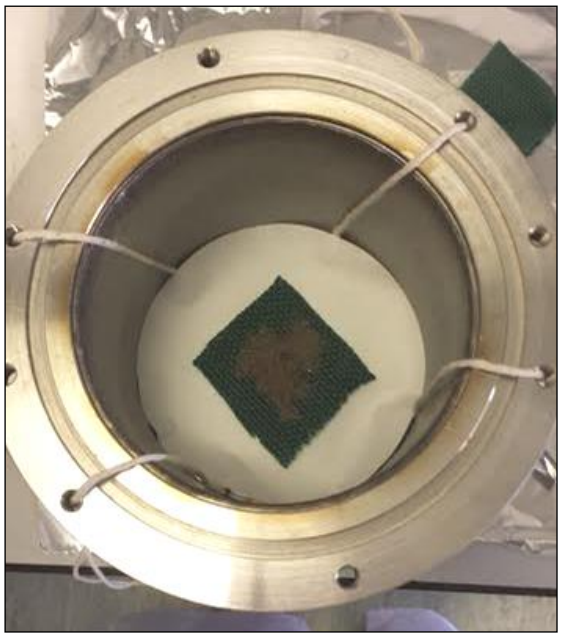


Figure VI-2 Chamber configuration for experiments examining PFR transfer due to direct fabric: dust contact.

A 5 x 5 cm square of fabric was weighed accurately and placed on a clean filter paper into the chamber with a known mass of dust (~0.3 g, accurately weighed) spread as gently and evenly as possible over the fabric surface, before the chamber was sealed (Rauert et. al., 2016). Five different contact times were studied, 1, 2, 4, 7 and 10 days, with each studied in triplicate. After each contact time, the dust was collected very carefully with a soft brush avoiding the removal of fabric fibres with the dust.

The use of the soft brush stemmed from the findings of Clausen et al. (2004), who when studying the direct transfer of the phthalate plasticiser DEHP to dust from a treated PVC material, found that vacuuming the dust from the PVC material resulted in artificially elevated DEHP concentrations in dust which they presumed arose as a result of removal of abraded source material during vacuuming. After removal of our

dust sample and homogenisation, two subsamples were weighed accurately, extracted and analysed for PFR concentrations.

6.3 Initial PFR concentrations in dust and fabric

The dust used in these direct fabric: dust contact experiments was a mixture of five living room dust samples collected from Ciudad Victoria, Mexico between December 2013 and January 2014. These samples were selected for this purpose, as TCIPP concentrations in Mexican dust are substantially lower compared with the UK, with a median concentration in Mexico of 6.86 μg/g versus a median concentration in the UK of 40 μg/g (this study - see table V.5 for details). TCIPP is the primary FR used in the UK for treatment of soft furnishings to meet flammability standards. The initial concentrations of PFRs determined in the dust and fabric used in this experiment is shown in table VI.1. Both the dust and the fabric were analysed for TCEP, TCIPP and TDCIPP, as the literature suggests these are the PFRs used in fabrics.

Table VI-1 Initial concentrations of PFRs of interest in fabric and dust used in this study.

Analysis #	TCEP	TCIPP	TDCIPP
Dust (μg/g) (n=5)			
1	1.70	7.60	5.30
2	1.90	8.00	5.30
3	2.00	6.10	4.70
4	1.90	6.20	4.80
5	2.10	6.40	5.20
Average	1.92	6.86	5.06
SD	0.15	0.88	0.29
Fabric (mg/g) (n=3)			
1	0.011	11.82	0.042
2	0.011	11.55	0.041
3	0.011	11.89	0.041
Average	0.011	11.75	0.041

Each piece of fabric used in these experiments was cut fresh from the main bulk fabric. Hence, PFR concentrations in the fabric at the start of each individual experiment may vary in concentration (due to the heterogeneity of distribution of PFRs across the fabric).

6.4 Influence of fabric: dust contact time

6.4.1 Concentrations in fabric

Concentrations of PFRs in the fabric both pre- and post- experiment are given table VI.2. The average TCIPP concentration present in the fabric at five different exposure durations reveal greater mass transfer, as the average fabric concentration after 1 day contact 44.6 mg/g exceeds that after 10 days contact 22.7 mg/g. Similar observations were made for TCEP and TDCIPP where, after 1 day contact, the average concentrations in fabric were 0.11 mg/g and 0.28 mg/g respectively, while after 10 days, contact fabric concentrations were 0.03 mg/g and 0.19 mg/g respectively. These data suggest that, after 1 day contact, our PFRs of interest had not reached fabric: dust equilibrium maybe due to the heterogeneous distribution of the TCIPP concentration in the fabric.

Table VI-2 Concentrations (mg/g) in fabric after different fabric: dust contact times.

Fabric contact time	**TCEP**	**TCIPP**	**TDCIPP**
Initial concentration (no contact)			
1	0.12	51.65	0.41
2	0.19	48.60	0.31
3	0.19	51.72	0.32
Average	0.17	50.66	0.35
SD	0.04	1.78	0.02

Fabric contact time	TCEP	TCIPP	TDCIPP
1 day contact			
1A	0.114	47.21	0.292
1B	0.094	48.31	0.293
2A	0.090	45.08	0.290
2B	0.117	44.03	0.286
3A	0.111	41.31	0.286
3B	0.140	41.72	0.282
Average	0.11	44.61	0.29
SD	0.02	2.84	0.004
2 days contact			
1A	0.070	47.73	0.283
1B	0.067	47.16	0.262
2A	0.076	43.55	0.277
2B	0.070	51.26	0.287
3B	0.080	33.92	0.301
3C	0.098	39.46	0.282
Average	0.08	43.85	0.28
SD	0.01	6.31	0.01
4 days contact			
1A	0.045	41.73	0.265
1B	0.051	28.56	0.286
2A	0.042	29.88	0.231
2B	0.063	44.95	0.249
3A	0.073	44.92	0.261
3B	0.075	29.91	0.271
Average	0.06	36.66	0.26
SD	0.01	8.00	0.02
7 days contact			
1A	0.038	23.16	0.212
1B	0.036	30.03	0.216
2A	0.039	29.25	0.215
2B	0.046	17.67	0.219
3A	0.041	27.60	0.218
3B	0.049	29.80	0.215
Average	0.04	26.25	0.22
SD	0.01	4.92	0.01
10 days contact			
1A	0.024	15.02	0.180
1B	0.027	18.25	0.179
2A	0.031	19.05	0.182
2B	0.035	27.41	0.210
3A	0.039	27.34	0.195
3B	0.035	29.32	0.198
Average	0.03	22.73	0.19
SD	0.01	5.99	0.01

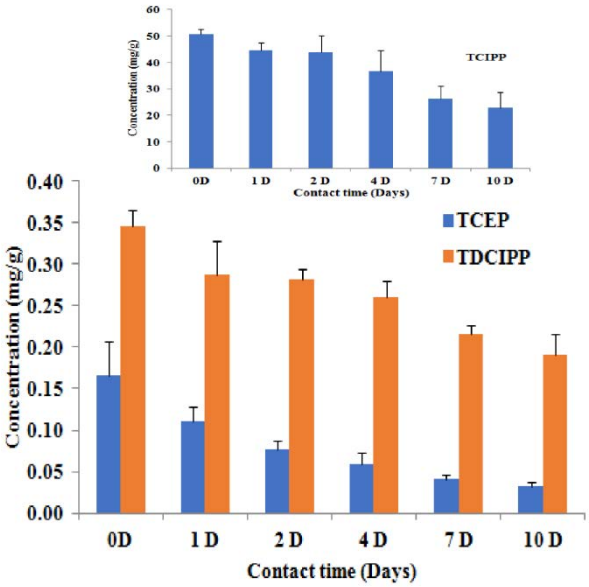


Figure VI-3 Average concentrations (mg/g) of PFRs in fabric over contact time.

Statistical analysis via ANOVA with a post-hoc Tukey test reveals concentrations of PFRs of interest in the fabric to vary significantly ($p<0.05$) between different contact times.

Table VI-3 Results of one-way analysis of variance test with post-hoc Tukey test comparing concentrations of TCEP, TCIPP and TDCIPP in fabric determined in experiment examining the effects of dust: fabric contact time.

Compounds	D1	D2	D4	D7	D10
TCEP	**D1**	**.000**	**.000**	**.000**	**.000**
	D2		.081	**.000**	**.000**
	D4			.143	**.006**
	D7				.631
TCIPP	**D1**	.999	.163	**.000**	**.000**
	D2		.242	**.000**	**.000**
	D4			**.037**	**.003**
	D7				.837
TDCIPP	**D1**	.892	**.004**	**.000**	**.000**
	D2		**.031**	**.000**	**.000**
	D4			**.000**	**.000**
	D7				**.009**

6.4.2 Influence of fabric: dust contact time on PFR concentrations in dust

Concentrations of PFRs in the dust both pre- and post- experiment are given in table VI.3. The average concentration of TCIPP in dust increases from day 1 (86.3 μg/g) to 194.5 μg/g after 10 days of contact. Similar observations were made for TCEP and TDCIPP where, after 1 day contact with fabric, the average concentrations in dust were 2.16 μg/g and 9.32 μg/g respectively and after 10 days contact were 4.10 μg/g and 11.81 μg/g respectively. While transfer to dust occurs in the early stages of contact, it continues to increase (most markedly for TCIPP due to its far greater starting concentration in the fabric) throughout the experiments, suggesting that fabric: dust equilibrium takes longer than 10 days to be attained.

Table VI-4 Concentrations (μg/g) in dust after different fabric: dust contact times.

Fabric contact time	TCEP	TCIPP	TDCIPP
Initial concentration contact			
1	1.70	7.60	5.30
2	1.90	8.00	5.30
3	2.00	6.10	4.70
4	1.90	6.20	4.80
5	2.10	6.40	5.20
Average	1.92	6.86	5.06
1 day contact			
1A	2.02	57.47	9.02
1B	2.06	65.63	9.19
2A	2.21	74.23	9.28
2B	2.21	104.86	9.41
3A	2.24	107.99	9.30
3B	2.24	108.02	9.74
Average	2.16	86.37	9.32
SD	2.02	57.47	9.02
2 days contact			
1A	2.24	110.60	9.59
1B	2.20	111.91	9.97
2A	2.30	114.19	9.98
2B	2.48	129.15	10.01
3B	2.59	144.06	10.54
3C	2.59	149.39	10.66
Average	2.40	126.55	10.12
SD	0.17	17.07	0.40
4 days contact			
1A	2.59	146.32	10.60
1B	2.69	154.23	10.88
2A	2.72	153.18	10.87
2B	2.70	160.61	10.87
3A	2.70	162.46	10.58
3B	2.73	167.74	10.78
Average	2.69	157.42	10.76
SD	0.05	7.66	0.14

Table VI-5 Continuation concentrations (μg/g) in dust after different fabric: dust contact times.

Fabric contact time	TCEP	TCIPP	TDCIPP
7 days contact			
1A	2.72	173.68	11.08
1B	2.75	171.02	11.18
2A	2.76	180.01	11.20
2B	2.88	176.50	11.42
3A	2.85	172.33	11.50
3B	2.87	167.01	11.07
Average	2.80	173.43	11.24
SD	0.07	4.49	0.18
10 days contact			
1A	3.59	207.02	11.49
1B	3.86	209.31	12.54
2A	3.39	190.68	12.72
2B	3.98	188.00	11.04
3A	4.83	184.01	11.76
3B	4.96	188.27	11.33
Average	4.10	194.55	11.81
SD	0.65	10.79	0.68

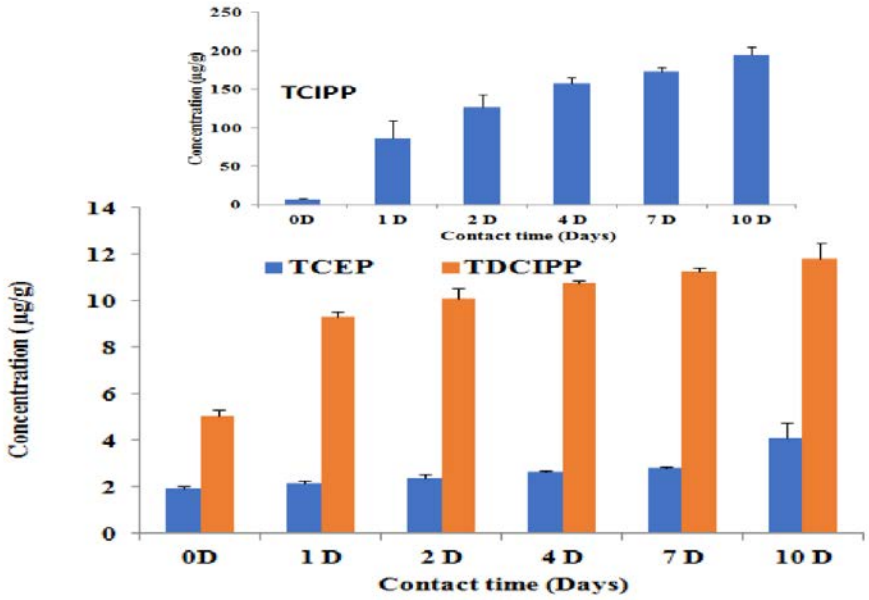


Figure VI-4 Average concentrations (μg/g) of PFRs in dust over contact time.

Statistical analysis via ANOVA with a post-hoc Tukey test reveals concentrations of PFRs of interest in the analysed dust all significantly ($p<0.05$) increase with increasing contact time. The transfer seen in our experiments is likely due to the PFR concentration gradients between the fabric and the dust, which may be expressed in terms of the fugacity of the compounds as stated by Rauert et al. (2016). The fugacity potential of a chemical can be defined as the escape potential of that chemical in a given phase (air, water, solid, dust, fabric). When the fugacity of the chemical in two phases are equal the chemical is in equilibrium between the two phases and no net chemical transfer between the phases (e.g. fabric and dust) occurs; however when chemical fugacity in the phases are different there is net transfer of the chemical from the phase in which its fugacity (concentration) is higher into the other phase. This net transfer will continue until equilibrium is reached – i.e. fugacity of the chemical in the two phases are equal (Rauert et al., 2016). The exact mechanisms governing the migration of SVOCs from source to dust via direct contact are not completely understood; however, Schripp et al. (2010) suggested that transfer occurs as a result of contact between dust and gas phase FRs present in the boundary layer directly above the source (e.g. fabric). According to this theory, compounds with low vapour pressures will be less abundant in this layer and thus are less efficiently transferred. Alternatively, Clausen et al. (2004) suggested that source-dust transfer may occur as a consequence of direct contact between the source and dust particles that replace the boundary layer. In such a scenario, the influence of vapour pressure on the efficiency of transfer is negligible.

Unfortunately, our experiments could not provide insights into which of these mechanisms govern the PFR transfer from the fabric to dust, owing to the very different concentrations of the 3 target PFRs in the fabric. Experiments to generate evidence to better understand the mechanisms of source-dust transfer of PFRs and related compounds are thus a research priority.

Table VI-6 Results of one-way ANOVA analysis of variance test with post hoc Tukey test comparing concentrations of TCEP, TCIPP and TDCIPP in dust samples resulting from different fabric: dust contact times

Compounds	**D1**	**D2**	**D4**	**D7**	**D10**
TCEP	**D1**	.671	**.047**	**.010**	**.000**
	D2		.493	.182	**.000**
	D4			.963	**.000**
	D7				**.000**
TCIPP	**D1**	.061	**.000**	**.000**	**.000**
	D2		.218	**.000**	**.000**
	D4			**.005**	**.000**
	D7				**.001**
TDCIPP	**D1**	.407	**.028**	**.001**	**.000**
	D2		.623	.056	**.000**
	D4			.591	**.000**
	D7				**.003**

CHAPTER VII. SUMMARY AND CONCLUSIONS

Organophosphate flame retardants are compounds used in a wide range of consumer products such as textiles, fabrics and polyurethane foams, car interiors, carpets and construction material (EFRA 2010 a, b). The extensive application and use of these compounds has led to growing scientific interest into their potential effects on the environment and humans. Many studies reveal that PFRs undergo release from products to the indoor environment (air, dust) and outdoor environment as evidenced by their presence in e.g. soil, water, and snow. As a result, PFRs have been reported in fish, birds, and marine mammals in addition to humans (Brommer et al., 2012, Abdallah et al., 2014, Luongo et al., 2015; He et al., 2015). The concerns associated with these FRs are potential health effects such as endocrine disruption, neurotoxic effects, reproductive problems, immunotoxicity and carcinogenicity (WHO 1998, Andersen et al., 2004, Meerker et al., 2010). Such concerns have led to regulations on their use and applications (Nightwear Safety legislation revised in 1985, The Furniture and Furnishings (Fire Safety) Regulations 1988).

Given the above, the main aim of this work was to investigate the pathways and magnitude of human exposure of seven widely used PFRs (TnBP, TCEP, TCIPP, TDCIPP, EHDPP, TPhP and TCP) via indoor environments. Within this, we examined variations between different countries, as well as evaluating within-room and within-house spatial and temporal variability in dust contamination, and the relative significance of air inhalation and dust ingestion as pathways of exposure to PFRs, and how this is influenced by the physicochemical properties of the contaminant.

In an additional strand of research, experiments were conducted to develop understanding of the extent to which PFRs transfer from fabrics into dust via direct fabric: dust contact.

The principal findings of this project were as follows:

- Concentrations of PFRs in dust from living room floors from seven countries were compared to test the hypothesis that PFR contamination of indoor dust will be influenced by international differences in flame retardant use. Concentrations in North America were highest (US>Mexico), exceeding significantly those in the other (mainly European) countries studied.
- Within-room and within-home spatial and temporal variability in concentrations of seven PFRs in floor and elevated surface dust from a number of homes in Birmingham, UK was evaluated. This tested the hypothesis that such variability can exert an appreciable influence on human exposure assessments. Within-room differences were observed principally in living rooms and kitchens, while within-home differences were observed depending on between-room differences in the content of putative sources like furniture and electronic equipment. To illustrate, house 3 had no sofa, no TV or other electronic equipment and thus reported the lowest PFR concentrations. Temporal variability was influence by the movement of the house contents as well as the introduction of new products; the seasonal variability reported the highest concentrations in warmer months, likely due to enhanced volatilization of PFRs from sources.

- Concentrations of seven PFRs were measured in both indoor air and dust from offices and homes in Birmingham, UK. These data were used *inter alia* to test the hypothesis that the relative significance of inhalation and dust ingestion as pathways of human exposure will vary according to the physicochemical properties of the PFR. Our data show that inhalation represents a more important pathway of exposure than dust ingestion.

- Test chamber experiments designed to test the hypothesis that direct fabric-dust contact is an important pathway via which TCEP, TCIPP and TDCIPP may transfer from *a treated* fabric to dust were conducted. These experiments revealed the hypothesis to be valid.

7.1 *Research gaps and future perspectives*

Given the widespread use of PFRs and the evidence for their potential harmful effects, future research is required to:

- Measure concentrations of PFRs in both indoor air and dust from other environments such as nursery and school classrooms, or furniture stores.
- Conduct further test chamber experiments to quantify direct source-dust transfer of PFRs from a variety of treated fabrics and hard polymers such as housing for electrical articles.
- Evaluate within-room and within-home spatial and temporal variability in concentrations of PFRs in floor and elevated surface dust from other microenvironments.
- Use ‘personal’ air samplers to evaluate inhalation exposure versus dust ingestion for PFRs.

- Conduct further chamber experiments to investigate other pathways of PFR migration from sources into indoor dust – such as volatilisation and abrasion.
- Investigate the influence of other factors on PFR concentrations in dust such as human and pet activities, as well as cleaning frequency.

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