CHARACTERISING HUMAN EXPOSURE TO ORGANOPHOSPHATE ESTER FLAME RETARDANTS

by

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ABSTRACT

Concentrations of selected PFRs were determined in indoor dust from cars, couches, living rooms, offices, and school classrooms in Australia, Canada, Germany, Kazakhstan, and the UK. Greater TCIPP use in the UK, is implied by the significantly higher concentrations found in UK living rooms and offices compared to those in other countries; while the significantly lower PFR concentrations in Germany suggest German use of PFRs is low. Significant differences were found between concentrations of PFRs in dust from different microenvironment categories in the same country. For example, TDCIPP was the predominant PFR detected in car dust samples analysed from Australia, Germany and the UK, TCIPP and TPHP were dominant in living rooms and offices from all countries, and EHDPP was significantly higher in Australian and UK classrooms than in other microenvironments. Elevated TCIPP concentrations in both Australian and UK couch dust samples suggests that couches are a potential source of PFRs. Consistent with the hypothesis that PFRs are amongst the chemicals replacing PBDEs, concentrations of ΣPFRs in Australian and UK classrooms exceeded significantly those of ΣPBDEs in the same samples. Assessment of human exposure via dust ingestion, revealed the majority of exposure to most PFRs occurs in the domestic environment. However, exposure to TDCIPP occurs primarily in cars, and a substantial proportion of the exposure of young children to EHDPP occurs in classrooms. Reassuringly, the exposure estimates in this study are at least 2 orders of magnitude below health based limit values reported in the literature. However, continued monitoring of PFRs in the environment is recommended, as greater understanding of their toxicity and additional exposure via other pathways may erode this apparent margin of safety. In particular, improved characterisation of exposure to TCIPP via inhalation is identified as a research priority. To address the substantial uncertainty in existing values reported for PFR vapour pressures, they were determined experimentally via the GC-RT method. For most target PFRs, results showed good overall agreement with the mean of experimental and *in silico* literature values. However, values for the chlorinated PFRs exceeded the average of literature values.

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Organohalogen Compounds, 74: 1502-1505 “Dioxin 2012”, 32nd International Symposium on Halogenated Persistent Organic Pollutants, 26. – 31st August 2012, Cairns/Australia

ABBREVIATIONS

%RSD	Relative Standard Deviation (%)
%IS Rec	Internal standard recovery
BBEP	Bis(2- butoxyethyl)phosphate
BCPP	Bis (2- chloropropyl)phosphate
BDCPP	Bis(1,3-dichloro-2-propyl)phosphate
BFRs	Brominated flame retardants
bw	Bodyweight
DBP	Di-n-butylphosphate
DPP	Diphenyl phosphate
EHDPP	2-Ethylhexyl diphenyl phosphate
FAV	Final adjusted value
FPD	Flame photometric detection
GC	Gas chromatography
GC-RT	GC-retention time
HBLV	Health based limit value
H_c	Henry's constant
ISTD	Internal Standard
J-P	Junge-Pankow
K_{oa}	octanol: air partition coefficient
K_{ow}	octanol - water partition coefficient
LC	Liquid chromatography
LOD	Instrument limit of detection
LOQ	Sample limit of quantification
MRV	Minimum reported value
MS	Mass spectrometry
NAT	Native compound
nd	Not detected
NPD	Nitrogen-phosphorus detection
OSHA	Occupational Safety and Health Administration
p_{298}	Vapour pressures at 298 K/ 25°C
PBDEs	Polybrominated diphenyl ethers
PC	Principal Component Score

PCA	Principal Component Analysis
PFRs	Organophosphate ester flame retardants/plasticiser
PICI	Positive-ion chemical ionisation
RRFs	Relative response factors
RRTs	Relative retention times
stdev	Standard deviation
T	Temperature
$t_{1/2}$	Half life
TAP	Triamylphosphate
TBEOP	Tris(2- butoxyethyl) phosphate
TCEP	Tris(2-chloroethyl) phosphate
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate
TEHP	Tris(2-ethylhexyl) phosphate
TMPP	Tri-cresyl phosphate
TnBP	Tri-n-butyl-phosphate
TPHP	Triphenyl phosphate
Vp	vapour pressure
$\Delta^{l}{}_{g}H$	Enthalpie of vaporisation

1 INTRODUCTION

Every year fires kill thousands of people and the estimated cost of fire losses in the UK alone was estimated at £1800 million in 2009 (The Geneva Association, 2012). More than 80% of fires start in the domestic environment (European Flame Retardants Association, 2012a) and over three-quarters of all fire-related deaths occur in the home. Dwelling fires also result in more fire-related deaths per 1000 fires than fires in vehicles or other buildings. To illustrate, in 2010/11 there were 6.8 deaths per 1000 domestic fires compared to 1.4 deaths per 1000 road vehicle fires and less than 1 death per 1000 fires in other buildings (Department for Communities and Local Government UK, 2011). Reassuringly, there has been a significant reduction in fire-related fatalities over the last 30 years, from a peak of 865 dwelling fire-related deaths in the UK in 1979, to 388 fire-related deaths overall in the UK in 2010-11. This decrease in fatal fire incidences has been attributed by some authors to the fact that fire prevention regulations require the presence of flame retardants in common used industrial products (Birnbaum and Staskal, 2004).

Recent restrictions on the use and manufacture of polybrominated diphenyl ethers (PBDEs), which have been used as flame retardant additives in e.g. furniture, building materials, electronics, and vehicles for many years has led the industry to search for alternatives. One of those alternatives are organophosphate ester flame retardants (PFRs) (Reemtsma et al., 2008; USEPA, 2005; Stapleton et al., 2009; European Flame Retardants Association, 2008).

PFRs have a wide range of applications. They are mainly used as flame retardants; for example tris(1,3-dichloro-2-propyl)phosphate (TDCIPP) and triphenyl phosphate (TPHP) are used in polyurethane foams deployed in car upholstery, sofas, chairs, and related products (Reemtsma et al., 2008; Stapleton et al., 2009; Marklund et al., 2003). By comparison, non-chlorinated organophosphates like tri-n-butyl-phosphate (TnBP) and tris(2-butoxyethyl)phosphate (TBOEP) are mainly used as plasticisers and antifoaming agents (Marklund et al., 2003, 2005b), while TnBP is employed in aircraft hydraulic fluids (Marklund et al., 2003).

Following the introduction in the UK of the Furniture and Furnishings (Fire) (Safety) Regulations 1988, the foam industry moved away from ‘standard’ foam to ‘combustion modified’ foam as its default product. A consequence of this is that a number of products are actually made with combustion modified foam even though flame retardancy is not essential in that application (European Union, 2008a; Furniture Industry Research Association (FIRA), 2009). To illustrate, TCIPP can be found for example in the foam contained within padded greeting cards (European Union, 2008a).

Another indication of the increasing use of PFRs is a recent study of 102 US couches. Of the 61 couches purchased after 2005, 16 % contained various mixtures of non-halogenated PFRs, while TDCIPP showed a significant increase from 24% detection in couches purchased prior to 2005 compared to 52 % in couches bought post-2005 (Stapleton et al., 2012).

Another Penta-BDE replacement product named Firemaster 550 contains TPHP as one of its constituents (Stapleton et al., 2008). Likewise, TBOEP is additionally used in rubber stoppers and floor wax (WHO, 2000b), while TnBP, TPHP and tri-cresyl phosphate (TMPP) are used as lubricants in hydraulic fluids (Solbu et al., 2007).

The biggest problem in an environmental context with PFRs in products is that they are usually used as additives (i.e. physically mixed with the product material) rather than being chemically bound to the material. This results in more facile release into the environment from treated products where PFRs are incorporated additively.

Once released into the environment, the detection of TCEP and TCIPP in aquifers in which the residence time of groundwater was between 20 and 45 years, indicates substantial persistence under such conditions (Regnery et al., 2011). Moreover, a very recently published study showed that particulate bound PFRs are highly persistent in the atmosphere and can undergo medium or long-range transport (Liu et al., 2014).

Current knowledge about the toxicity of PFRs remains insufficient. Notwithstanding this, initial indications show interference with liver toxicity and growth during long term exposure in laboratory animal tests studying the effects of long-term exposure (WHO, 2000b, 1991b, 1991a, 1998). Chlorinated alkyl phosphates are suspected carcinogens with observed tumour growth in rat thyroid and kidney for TCEP, as well as in rat liver, brains and testes for TDCIPP. Further reported effects include: reduced thyroid hormone levels for TDCIPP (Meeker and Stapleton, 2010), linkage of TnBP with sick building syndrome (Kanazawa et al., 2010), and contact dermatitis for TPHP (Camarasa and Serra-Baldrich, 1992).

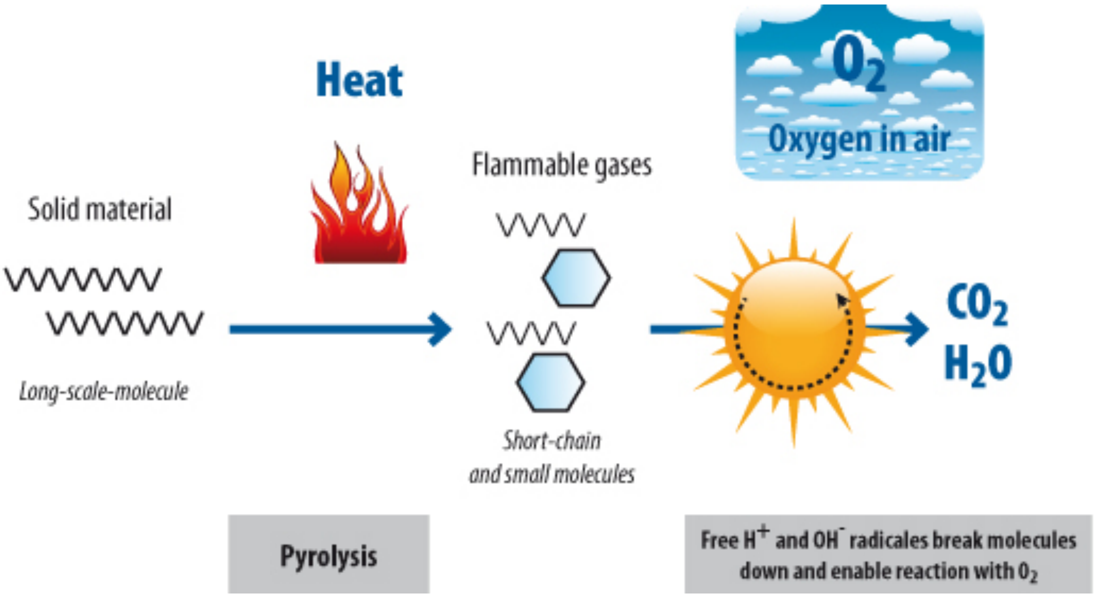
Since contact with indoor dust represents a major pathway of human exposure to PBDEs and other brominated flame retardants (BFRs) (Harrad et al., 2010b), it is plausible to hypothesise that this might also be the case for those chemicals which replace PBDEs. This is especially likely when those replacement chemicals have very similar properties like high K_{oa} (octanol: air equilibrium partitioning coefficient) and low vapour pressure that favour partitioning to solid organic matrices like dust. To date, data on PFR concentrations in indoor dust remain limited, but available studies indicate concentrations in the µg/g range with lower levels in Europe compared to the US and Japan (Stapleton et al., 2009; Van den Eede et al., 2011b; Ali et al., 2012; Takigami et al., 2009). Moreover, PFR levels tend to be at least one order of magnitude higher than PBDE concentrations in the same samples (Dodson et al., 2012; Van den Eede et al., 2011b, 2011a).

A common problem within the literature is that until very recently, there were no guidelines on how to apply systematic acronyms and nomenclature to PFRs, which might hinder searches for older data. Systematic nomenclature guidelines have now been proposed (Bergman et al., 2012) but it will take a while until these are adopted universally.

There remains a huge lack of information about human metabolism and the magnitude of human exposure to PFRs, and the pathways via which they occur. However, recent studies found urinary metabolites of the flame retardants TnBP, di-n-butylphosphate (DBP) and TCIPP, bis (2-chloropropyl)phosphate (BCPP) (Schindler and Förster, 2009) as well as TDCIPP, bis(1,3-dichloro-2-propyl)phosphate (BDCPP) and TPHP, and diphenyl phosphate (DPP) (Cooper et al., 2011). These studies suggest that such metabolites are formed *in vivo*. However, as there is such a sparse knowledge about the actual human metabolism of PFRs, this may mean that metabolites monitored currently, may not be the most appropriate. For example, (Van den Eede et al., 2013a) showed in in vitro studies using human liver fractions, that the diester metabolites BCPP and DPP might actually not be the main metabolites of TCIPP and TPHP respectively.

1.1 Mechanism of Flame-Retardancy Action of PFRs

A solid material will not burn directly. It needs to be decomposed by heat to release flammable gases. When those flammable gases burn with oxygen in air, a flame can be visible. If this decomposition does not happen solid materials will only smoulder slowly and might even self extinguish, especially when a “char” is formed which prevents further access of the flame to the underlying material. High energy radicals (H• and OH•) maintain the gas flame through decomposing molecules to provide carbon that can react with oxygen to produce CO_2 in a highly exothermic reaction (European Flame Retardants Association, 2013).



O_2 CO_2 H_2O

Figure 1.1 *How materials burn (European Flame Retardants Association, 2013)*

It is impossible to describe the reaction of PFRs in one general working mechanism (Schmitt, 2007). The actual mechanism depends on the chemical composition of the PFR involved. Non-halogenated PFRs act in the solid phase of the burning material. When heated, the phosphorus reacts to give a polymeric form of phosphoric acid. Phosphoric acid chars the material, to form a glassy layer that inhibits further pyrolysis. As a result, no further flammable gases needed to feed the flames can be released. Because char rather than combustible gas is formed, the amount of fuel produced is significantly reduced. The formed char acts as a two-way barrier. It hinders the passage of combustible gases and melted polymer towards the flame and also shields the polymer from the heat of the flame (European Flame Retardants Association, 2012b).

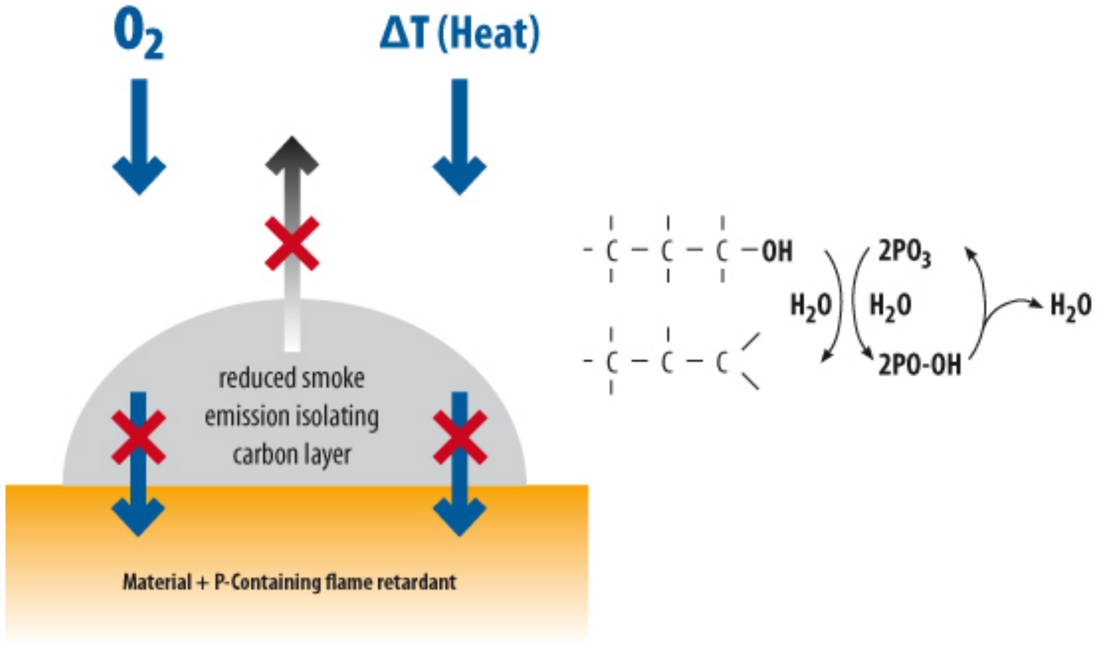


Figure 1.2 *Mode of flame retardancy action for non-halogenated PFRs (European Flame Retardants Association, 2012b)*

For halogenated PFRs, there is an additional mechanism *via* which they act as flame retardants. In addition to the phosphoric acid char, halogenated PFRs act in the gas phase by removing OH• and H• radicals from the flammable gases through a reaction with Cl atoms. This removal results in a slowdown of the burning process which helps limit the spread of the fire. The number of halogen atoms in the molecule influences the effectiveness of this process (van der Veen and de Boer, 2012). An advantage of halogenated PFRs is that halogens and phosphorus both act independently in the polymer system offering additional flame retardancy (WHO, 1997).

1.2 Production volumes of PFRs

Table 1.1 shows a summary of the available data on production volumes of PFRs. Production volumes are in general only available for the last decade or so. Only the Scandinavian countries of Sweden, Norway and Denmark provide *via* their chemical database, a minor insight into the current production volumes of PFRs in Europe. In general, TPHP, TDCIPP and TCIPP are the three most used PFRs.

Table 1.1 *Production volumes of PFRs*

PFR	Production/ use volume (tonnes/year)	Country	Year	Reference
TCEP				
	500 – 1000	Germany	1997	(Bayerisches Landesamt für Umwelt, 2006)
	120	Australia	2011	(NICNAS, 2001)
	1286	Norway	2003	(Green et al., 2008)
TCIPP				
	5000 – 6000	Germany	1997	(Bayerisches Landesamt für Umwelt, 2006)
	>40000	World wide	1997	(Green et al., 2008)
	36000	EU	2000	(European Union, 2008a)
	812.9	Finland	2001	(SPIN Database, 2012)
	704.2	Denmark	2001	(SPIN Database, 2012)
	145.0	Sweden	2001	(SPIN Database, 2012)
	50.5	Norway	2001	(SPIN Database, 2012) (Green et al., 2008)
	290	Australia	2001	(NICNAS, 2001)
	199.5	Denmark	2010	(SPIN Database, 2012)
	84	Sweden	2010	(SPIN Database, 2012)
	43.3	Norway	2010	(SPIN Database, 2012)
TDCIPP				
	>8000	World wide	1997	(Green et al., 2008)
	10000	Total EU	2000	(Green et al., 2008)
TDCIPP				
	132.8	Denmark	2000	(SPIN Database, 2012)
	<10000	EU	2000	(European Union, 2008a)
	134.1	Denmark	2001	(SPIN Database, 2012)
	134.1	Denmark	2002	(SPIN Database, 2012)
	20-40 (predicted)	Australia	2001	(NICNAS, 2001)
TPHP				
	7000- 10500	Asia	2000	(OECD SIDS, 2002)
	5000-7500	West Europe	2000	(OECD SIDS, 2002)
	8000- 12000	USA	2000	(OECD SIDS, 2002)
TPHP				
	55	Norway	2004	(Green et al., 2008)
	6.7	Norway	2005	(Green et al., 2008)
EHDPP				
	2.8	Norway	2002	(Green et al., 2008)
	30.1	Norway	2005	(Green et al., 2008)
TnBP				
	33.8	Norway	2005	(Green et al., 2008)
TEHP				
	1000	Germany	1992	(WHO, 2000b)
	24	Sweden	1999	(SPIN Database, 2012)
	37	Sweden	2000	(SPIN Database, 2012)
	9	Denmark	2000	(SPIN Database, 2012)
	7.1	Norway	2000	(SPIN Database, 2012)
	262.6	Finland	2010	(SPIN Database, 2012)
	25	Sweden	2010	(SPIN Database, 2012)
	7.0	Denmark	2010	(SPIN Database, 2012)
	1000-5000	Worldwide	-	(WHO, 2000b)
TBOEP				
	18	Sweden	2010	(SPIN Database, 2012)
	1.7	Denmark	2010	(SPIN Database, 2012)
	71	Sweden	2006	(SPIN Database, 2012)
	73	Sweden	1999	(SPIN Database, 2012)
	5000-6000	Worldwide	-	(WHO, 2000b)
	<1000	Europe	-	(WHO, 2000b)
	1.3-1.5	Norway	2003-2004	(Green et al., 2008)
	0.6	Norway	2005	(Green et al., 2008)

Use of TPHP in the Penta-BDE replacement product Firemaster 550 (Stapleton et al., 2008) might be an explanation for the high volume used, especially in the US. Even though no current data for TCEP are available, its replacement by TCIPP means that a decrease in production/use volume is expected. PFR production/use volumes for the more widely used PFRs (TPHP, TDCIPP and TCIPP) can be compared to those of PBDEs. As an illustration, estimated European consumption of Deca-BDE was 8,210 tonnes/year in the mid-1990s, rising by 2001 to 56,100 tonnes world-wide and 7,600 tonnes in Europe (Pakalin et al., 2007). Data for Australia reveals comparatively low PFR use, which might be due to the fact that chlorinated PFRs were reported as of 2001 to be not manufactured in Australia (NICNAS, 2001). Moreover, use data for other PFRs are not available for Australia, and it has been reported that the main sources of flame retardants for Australia are Germany, Singapore and the UK (NICNAS, 2001).

1.3 Exposure assessment/Human exposure

Exposure is defined as the contact over space and time between a chemical and the outer part of a person (skin, nostrils or mouth). While this contact could occur with the pure chemical, typically humans are exposed to PFRs through a carrier medium (dust, air, water, soil or food), which contains a certain amount of the chemical (WHO, 2000a).

As with other chemicals like PBDEs and HCBDs, detailed knowledge of the physicochemical properties of PFRs is important for the determination of their environmental behaviour and human exposure potential. Table 1.2 shows the physicochemical properties with most relevance for the environmental behaviour of PFRs.

While it is known that PBDEs are retained in fatty tissues due to their hydrophobicity, a clear understanding on the behaviour of PFRs in the human body is still lacking. Human exposure is indicated by the fact that in the late 1980s, TDCIPP was detected in 31 out of 115 human adipose tissue samples from cadavers in autopsies from two cities in Canada, with concentrations ranging from <1 to 251 ng/g (LeBel and Williams, 1986).

While such biomonitoring data is indisputable evidence that exposure to PFRs is occurring, the pathways via which this occurs and their relative importance is far from well-understood. For example, currently very little is known about the dermal absorption of PFRs, despite early indications that TDCIPP may be absorbed dermally. (Hughes et al., 2001). In an occupational exposure context, TDCIPP and TPHP were detected in hand wipe samples from circuit board factory workers (Mäkinen et al., 2009); implying that the potential for dermal uptake exists under such a scenario.

A significant exposure pathway for the PFRs studied here could be air inhalation, especially in work environments. However, exposure to the target compounds *via* inhalation of indoor air was reported as low in non-occupational indoor living environments (Bergh et al., 2011b) and in outdoor air (Möller et al., 2011). On contrast, a very recent Norwegian study (Cequier et al., 2014) indicates that air contributes significantly to human exposure for PFRs with a higher vapour pressure. Specifically, this study showed that for its subjects, the intake through inhalation for TnBP and TCIPP was respectively 85% and 49% of the total PFR intake respectively. Furthermore PFR concentrations in indoor air were shown to be around 2 orders of magnitude higher than BFRs in the same samples. However that study only analysed living room so no conclusion can be drawn overall relevance of air inhalation versus dust ingestion for the work space environment.

An indication of the relative significance of inhalation as a pathway of human exposure to PFRs may be gleaned by comparison of their vapour pressures with a reference compound – e.g. BDE-47 – for which reliable data exists about the extent of inhalation exposure – e.g. (Harrad et al., 2006) showed inhalation to contribute on average 2.3% of Σtri-hexa-BDEs exposure of UK adults via inhalation, dust ingestion, and diet combined. Such comparison supports the hypothesis that inhalation may be of some importance for the chlorinated PFRs, as even the least volatile of these (TDCIPP) has a vapour pressure 7.36 x 10^{-8} mm Hg (SRC, 2013) only slightly lower than that of BDE-47 (3.5 x 10^{-7} mm Hg) (SRC, 2013), while those of TCIPP and TCEP (6.13 x 10^{-2} mm Hg and 2.02 x 10^{-5} mm Hg (SRC, 2013) respectively) both exceed substantially that of BDE-47. For other PFRs, TnBP with a vapour pressure of 0.00113 mm Hg (SRC, 2013) is not only the most volatile PFR targeted in this study, but is substantially more volatile than BDE-47. As a consequence, it is reasonable to hypothesise that inhalation will be of some importance for TnBP. In contrast, vapour pressures for the other target PFRs are all lower than that of BDE-47 (e.g. TMPP = between 1.46 x 10^{-6} mm Hg and 3.49 x 10^{-9} mm Hg for the different isomers (SRC, 2013)). As a consequence, these less volatile PFRs will partition mainly to the particle phase, and inhalation will likely be insignificant as an exposure pathway.

Even though literature data on PFR concentrations in drinking water is very sparse, a Spanish study (Rodil et al., 2012) of concentrations of PFRs in drinking water showed that the same trend, which is seen in surface water was determined in drinking water. So was TnBP detected at a median concentration of 32 ng/L in all 28 drinking water samples. Even though TCIPP was detected at a slightly higher median concentration of 40 ng/L it was not detected in of all the analysed samples. TCEP was detected at much lower median concentrations of 5 ng/L, while TDCIPP was not detected in any sample (LOQ 13 ng/L). A preliminary ingestion estimate based on a consumption of 2 L/day drinking water and an adult average body weight of 70 kg would result in an exposure of 0.9 ng/day kg/bw and 1.1 ng/day kg/bw of TnBP and TCIPP respectively through drinking water. TnBP exposure in drinking water would be broadly similar to the estimate of Cequier et al. (2014) for exposure through inhalation (0.57 ng/day kg/bw). In contrast, the same authors' estimate of TCIPP exposure via inhalation and dust ingestion were in turn (at 4.1 ng/day kg/bw and 2.1 ng/kg bw/day respectively) four and two times higher than the above estimate for drinking water.

However, the situation may be different in the UK, as TCIPP concentrations in UK river water (Cristale et al., 2012) are up to 7.7 ug/L, at least an order of magnitude higher than those reported in Germany and Spain (Rodil et al., 2012; Andresen et al., 2004) Moreover, it has been suggested that drinking water treatment processes are not wholly effective at removing TCIPP. (Rodil et al., 2012) Also noteworthy is the observation of (Cristale et al., 2012) that PBDE concentrations in the same UK river water samples were all below detection limits, suggesting likely greater exposure to PFRs via drinking water than for PBDEs.

Even though diet is believed to be the major source of human exposure to many POPs (Sjödin et al., 1999), this seems not to be the case for PFRs. The small number of studies of PFR concentrations in food indicate a level of contamination which is frequently around the detection limit with a non-detect frequency >50% in diet samples. Such evidence is not wholly consistent however, with a recent study from the Philippines that indicates TPHP is adsorbed onto aquatic particles, settles to surficial sediments and accumulates though the benthic food web (Kim et al., 2011).

Children are exposed to PFRs in the same way as adults, even though their lower body mass and the fact that they are still developing makes them more sensitive to reverse health effects. Furthermore, EHDPP and TMPP were detected at median concentrations of 6.5 ng/g and 0.8 ng/g lipid weight respectively in Swedish breast milk samples (Sundkvist et al., 2010). Based on this evidence, human milk consumption may be an important exposure pathway for nursing infants.

Dust ingestion has been shown to be a major pathway of exposure to BFRs for both adults, and especially toddlers (Harrad et al., 2010a) That this pathway is likely also important for PFRs, is underlined by recent literature published during the period of this research project, that indicates concentrations of PFRs exceed substantially those of PBDEs in the same indoor dust samples (Dodson et al., 2012; Dirtu et al., 2012; Cequier et al., 2014). In one such study (Cequier et al., 2014), the ingestion of dust was estimated to contribute 54% of total exposure for children for PFRs with lower vapour pressures (e.g. TCDIPP). Notwithstanding this, the PFR daily intake rates in this study were still some orders of magnitude lower than calculated health based limit values.

In terms of human exposure the metabolism of PFRs is still not fully understood, and constitutes an important gap, as it will provide insights into possible urinary metabolites that could act as biomarkers of exposure. A metabolite of TBEP (bis(2-butoxyethul)phosphate – BBEP) was detected in 31% of human adult urine samples (n=59) in Belgium (Van den Eede et al., 2013b). More recently, the same authors reported on the metabolic pathways for TBOEP (Van den Eede et al., 2013a).

Cooper et al. (2011), detected the TDCIPP metabolite BDCPP in each of nine randomly collected urine samples, at concentrations ranging from 46 to 1662 pg/mL with a geometric mean of 147 pg/mL. Likewise, a metabolite of TPHP - diphenyl phosphate (DPhP) - was detected in 93% of samples taken from 59 adult volunteers in Belgium (Van den Eede et al., 2013b). Reassuringly, a very recent study showed that urine samples from aircraft technicians in charge of changing and refilling turbine oil, showed no indication of occupational exposure; as concentrations of TMPP metabolites were below detection limits even immediately post-shift. (Schindler et al., 2014)

Table 1.2 *Physicochemical properties and their environmental relevance*

Parameter	Abbreviation	Environmental relevance
Octanol-air partition coefficient	K_{OA}	Ability of a chemical to partition between air and lipid e.g. between vapour and particle phase/soil/plant lipid
Henry's constant	H_c	Tendency for a chemical to partition between an aqueous solution and air e.g. between a lake and the overlying atmosphere
Vapour pressure	V_p	Ability of a chemical to exist as a vapour
Octanol-water partition coefficient	K_{OW}	Ability of a chemical to partition between water and lipid e.g between water and particle phase/soil/fish lipid
Half-life or residence time	$T_{1/2}$ or τ	Persistence of the chemical - its resistance to degradation via chemical, physical or biological means

1.4 PFR groups and their individual physicochemical properties and environmental behaviour

In general, PFRs are derivatives of phosphoric acid. The various side chains (R) can be for example alkyl, aryl or haloalkyl either alone or in combination. Figure 1.3 represents the basic structure of a PFR.

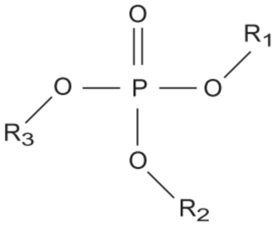


Figure 1.3 *Basic structure of a PFR*

As mentioned previously, the applications of PFRs vary according to their structure owing to the structural influences on their general behaviour. While chlorinated alkyl phosphates are primarily used as flame retardants, triaryl phosphates are used for their combination of flame retardant and plasticising properties.

On this basis, coupled with their different environmental behaviour and relevance as a result of their respective production volumes, PFRs are divided into different groups and discussed individually in the following sections.

1.4.1 Chlorinated alkyl phosphates

As a class, chlorinated alkyl phosphates appear to be the most commonly detected PFRs in the environment and which tend to dominate PFR profiles worldwide (Covaci et al., 2012; van der Veen and de Boer, 2012). TCEP, TCIPP and TDCIPP are the chlorinated PFRs analysed in this thesis.

1.4.1.1 Applications and uses

TCEP

TCEP has found widespread use as a flame retardant plasticiser and viscosity regulator in polyurethanes, polyacrylates, polyester resins and other polymers. It has been mainly used in the building industry, e.g. in roofing insulation material which represents more than 80% of its use in the EU, as well as in the furniture and textile industry where it has been used e.g. as back-coatings for carpets and upholstery. Additional uses reported are in aircrafts, cars and trains, as well as in professional paints, varnishes and lacquers (European Union, 2009; Scientific Committee on Health and Environmental Risks SCHER, 2012).

The production and use of TCEP has declined since the 1980s since when it has been progressively replaced by other flame retardants, e.g. TCIPP (WHO, 1998; Schindler and Förster, 2009). Specifically, global consumption of TCEP peaked at over 9,000 tonnes in 1989, before declining to under 4,000 tonnes in 1997 (WHO, 1998). Registered trade names are Antiblaze 100, Celluflex CEF, Disflamoll TCA, Fyrol CEF, Niax 3CF, Tolgard TCEP, Genomoll P, Hostaflam UP810 and Levagard EP (ATSDR, 2012).

However, TCEP is a known impurity in the commercial 2,2-bis(chloromethyl)-propane-1,3-diyltetrakis(2-chloroethyl) bisphosphate “V6” mixture at concentrations of 4.5 – 7% (European Union, 2007). Consistent with this, concentrations of V6 and TCEP in house and car dust concentrations have been shown to correlate (Fang et al., 2013).

TCIPP

In a global context, TCIPP is used mainly in rigid polyurethane foams, which may be sub-divided into blocks and spray systems for building insulation or refrigerator castings. Registered trade names are Hostaflam OP 820, Antiblaze 80, Amgard TMCP and Fyrol PFC (ATSDR, 2012). However, in the UK and Ireland, TCIPP is mainly used in flexible polyurethane foams for furniture upholstery. An additional minor use is in textile back-coating formulations (WHO, 1998). Moreover, TCIPP is normally used for seat cushions where these are flame retarded (Lassen, 1999), and it has been reported that 80% of UK produced foam is flame treated with TCIPP (European Union, 2008a). TCIPP has also been reported to be used in PVC wallpaper (Ni et al., 2007).

In summary, following its first commercialisation in the mid-1960s, the production of TCIPP grew at an average of 4% per year through to the late 1990s (WHO, 1998). As noted above, TCIPP has been used as the main substitute for TCEP (Schindler and Förster, 2009). Furthermore, in 2006 more than a third of all PFRs used, and at least 80 % of chlorinated PFR production was TCIPP, highlighting its status as the most important PFR in Europe (Bayerisches Landesamt für Umwelt, 2006).

TDCIPP

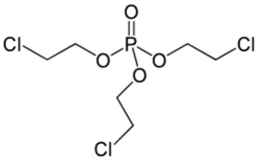
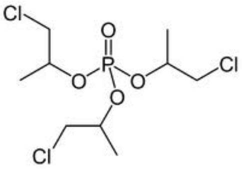
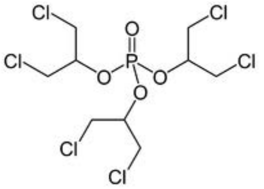
TDCIPP is used as a flame retardant in rigid and flexible polyurethane foam, other plastics and resins and acrylic latexes for back coating and binding of non-woven fabrics (WHO, 1998; Andresen et al., 2004). TDCIPP has in general similar applications to those for TCIPP but because of its higher price is only used in applications requiring a particularly high degree of flame retardancy (European Union, 2008a). Registered trade names are Fyrol FR-2 and Antiblaze 195 (ATSDR, 2012).

1.4.1.2 Physicochemical properties

A summary of the physicochemical properties of chlorinated PFRs analysed in this thesis is given in Table 1.3.

TCEP has the highest vapour pressure of the chlorinated PFRs. According to the data cited in Table 1.3, the vapour pressure of TCEP is about 3 orders of magnitude higher than that of TCIPP and six orders of magnitude more volatile than TDCIPP. TDCIPP has a slightly lower vapour pressure compared to BDE-47, which means that chlorinated PFRs are in general more volatile than the Penta-BDE mixture. As a result, binding of TDCIPP to soil and dust, particles is much more likely than for TCEP and TCIPP. Moreover, TDCIPP has the lowest water solubility within this group, implying that drinking water is unlikely to be a significant source of human exposure.

Table 1.3 *Physicochemical Properties of Chlorinated PFRs (SRC, 2013)*

	PFR		
Parameter	Tris(2-chloroethyl) phosphate	Tris(2-chloroisopropyl) phosphate	Tris(1,3-dichloroisopropyl) phosphate
Abbreviation	TCEP	TCIPP	TDCIPP
Chemical formula	$C_6H_{12}Cl_3O_4P$	$C_9H_{18}Cl_3O_4P$	$C_9H_{15}Cl_6O_4P$
Structure			
CAS-number	115-96-8	13674-84-5	13674-87-8
Molecular weight	285.49	327.57	430.91
Boiling point	330 °C	>270 °C	236-237 °C at 5 mm Hg
Melting point	-35 °C	-40 °C	27 °C
Vapour pressure (25°C)	6.13×10^{-2} mm Hg	2.02×10^{-5} mm Hg	7.36×10^{-8} mm Hg
Water solubility	7000 mg/L (20 °C)	1200 mg/L (25 °C)	7 mg/L (24 °C)
Log K_{OW}	1.44	2.59	3.65
Henry's Law constant (25 °C)	3.29×10^{-6} atm-m^3/mole	5.96×10^{-8} atm-m^3/mole	2.61×10^{-9} atm-m^3/mole

1.4.1.3 Environmental levels and behaviour

Table 1.4 summarises the available literature data on TCEP, TCIPP and TDCIPP in dust samples. So far only one study (Dodson et al., 2012) has studied temporal variations in concentrations of PFRs in dust. It indicates that TCEP levels in US house dust have decreased slightly between 2006 and 2011, while TCIPP levels appear stable. TCEP/TCIPP average/median levels appear higher in car dust than house dust (Ali et al., 2013). Studies (Van den Eede et al., 2011b; Dirtu et al., 2012; García et al., 2007a) indicate that TCEP levels in Europe (Spain, Belgium, Romania) are lower than those in the US (Dodson et al., 2012) and Japan (Kanazawa et al., 2010). Substantial international variation is apparent in the relative abundance of TDCIPP compared to other PFRs. While TDCIPP is the most abundant chlorinated PFR in US house dust (Dodson et al., 2012), concentrations in Europe (Van den Eede et al., 2011b; García et al., 2007a) are much lower with TDCIPP not the most abundant PFR. Interestingly, the highest median value of TDCIPP in all dust samples in a recent study was for car dust samples from Kuwait (Ali et al., 2013).

Air

Table 1.5 summarises the available literature data on TCEP, TCIPP and TDCIPP concentrations in indoor and outdoor air samples. Average TCEP and TCIPP indoor air levels are higher in Sweden (Bergh et al., 2011a) than Japan (Saito et al., 2007). One gym in the US (Carignan et al., 2013a) had similar airborne concentrations of TCIPP and TDCIPP, while in Japan (Saito et al., 2007) concentrations were below detection limits in indoor air. With respect to outdoor air, all three chlorinated PFRs were detected in air samples from various remote oceanic locations, thereby indicating a propensity for long range transport (Möller et al., 2011, 2012). Furthermore urban air samples from Chicago and Cleveland showed higher concentrations compared to rural sampling locations (Sturgeon Point, Sleeping Bear Dunes and Eagle Harbor) in the US (Salamova et al., 2014).

Precipitation, River water and bank filtrate

Table 1.6 summarises the available literature data on concentrations of chlorinated PFRs in samples of precipitation, river water and bank filtrate (i.e. water sampled at the inlet of water treatment plants). To our knowledge, only one study is available about concentrations of TCEP, TCIPP, and TDCIPP in precipitation, for a statistically significant number of samples (Regnery et al., 2011). As predicted from their respective use data and water solubility, TCIPP was the most abundant PFR detected in rural and urban precipitation samples, with TDCIPP the least. (Bacaloni et al., 2008) analysed three rain water samples, concluding that urban precipitation samples appear more contaminated than the rural sample.

TCEP was detected both in the East Arctic ice sheet (Cheng et al., 2013) and snow samples from Sweden (Marklund et al., 2005b).

Some preliminary data are also available on PFR concentrations in river water that indicate TCIPP levels to be much higher in the UK (Cristale et al., 2013a) than Italy (Bacaloni and Cavaliere, 2007; Bacaloni et al., 2008). TCEP was detected in comparable levels to surface water in bank filtrate (Knepper et al., 1999), feeding into a drinking water plant. However, the limited sample numbers and the year of sampling (1999), suggests that contemporary TCEP concentrations are likely lower.

Lake Sediment

Only one study is available on concentrations in lake sediment (Table 1.7) where it seems that TCEP, TCIPP and TDCIPP in China are present at more or less identical average concentrations. However, as only mean concentrations were reported, this may mask some element of variability (Cao et al., 2012).

Animals

A very recently published study showed that TCEP and TCIPP are most likely the most bioaccumulative PFRs. Specifically, concentrations of these PFRs within plasma from White-tailed eagles were similar to those of BDE-47 in the same samples (Eulaers et al., 2014). Elsewhere, analysis of herring gull eggs (n=11) from the Channel-Shelter Island (Lake Huron, Canada) colony showed TCIPP concentrations to range from <LOQ to 4.1 ng/g wet weight (ww), with those of TCEP falling between <LOQ and 0.6 ng/g ww (Chen et al., 2012)

Table 1.4 *Literature data on concentrations of TCEP, TCIPP and TDCIPP in indoor dust*

	n	Country	Year	Median (µg/g)	Mean (µg/g)	Range (µg/g)	Environment	Reference
TCEP								
	16	US	2006	5.1	N/A	0.61-160	Home	(Dodson et al., 2012)
	40	Japan	2006	7.5	N/A	<1.3-308	Home floor	(Kanazawa et al., 2010)
	41	Japan	2006	9.8	N/A	1.3-70.7	Home multisurface	(Kanazawa et al., 2010)
	8	Spain	2007	N/A	1.7	0.25-9.8	Home	(García et al., 2007a)
	47	Romania	2010	0.10	0.18	<0.02 – 1.16	House/apartment	(Dirtu et al., 2012)
	15	Belgium	2010	N/A	0.59	<0.08-5.46	Store	(Van den Eede et al., 2011b)
	33	Belgium	2010	N/A	0.23	<0.08-2.65	Home	(Van den Eede et al., 2011b)
	15	Kuwait	2011	0.71	0.76	0.28-1.8	Home	(Ali et al., 2013)
	16	US	2011	2.7	N/A	0.33-110	Home	(Dodson et al., 2012)
	15	Kuwait	2011	1.77	3.48	<0.01-13.65	Car	(Ali et al., 2013)
	15	Pakistan	2011	0.15	0.38	<0.01-0.18	Home	(Ali et al., 2013)
	15	Pakistan	2011	0.26	0.75	<0.01-1.52	Car	(Ali et al., 2013)
	34	New Zealand	2012	0.11	0.15	0.02 – 7.6	Home	(Ali et al., 2012)
	16	New Zealand	2012	0.04	0.06	<0.02 – 0.48	Mattress	(Ali et al., 2012)
	17	Philippines	2008	0.034	N/A	<0.00044-1.2	House dust, residential area	(Kim et al., 2013)
	20	Philippines	2008	0.016	N/A	<0.000044-0.14	House dust, municipal dumping area	(Kim et al., 2013)
	10	Sweden	N/A	2.1	7.6	nd-33	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	30	51	2.5-150	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	6.7	36	1.3-260	Work	(Bergh et al., 2011b)

	n	Country	Year	Median (μg/g)	Mean (μg/g)	Range (μg/g)	Environment	Reference
TCIPP								
	16	US	2006	2.1	N/A	0.34-120	Home	(Dodson et al., 2012)
	40	Japan	2006	18.7	N/A	5.4-291	Home floor	(Kanazawa et al., 2010)
	41	Japan	2006	50.9	N/A	10.3-462	Home multisurface	(Kanazawa et al., 2010)
	8	Spain	2007	N/A	3.9	0.35-10.3	Home	(García et al., 2007a)
	47	Romania	2010	0.86	2.5	<0.02 -16.4	House/apartment	(Dirtu et al., 2012)
	15	Belgium	2010	N/A	2.94	0.58-24.4	Store	(Van den Eede et al., 2011b)
	33	Belgium	2010	N/A	1.38	0.19-7.37	Home	(Van den Eede et al., 2011b)
	15	Kuwait	2011	1.46	1.95	0.12-7.07	Home	(Ali et al., 2013)
	16	US	2011	2.2	N/A	0.49-140	Home	(Dodson et al., 2012)
	15	Kuwait	2011	31	36	2.5 - 134	Car	(Ali et al., 2013)
	15	Pakistan	2011	<0.02	<0.02	<0.02-0.85	Home	(Ali et al., 2013)
	15	Pakistan	2011	0.10	0.59	<0.02-2.62	Car	(Ali et al., 2013)
	34	New Zealand	2012	0.35	0.82	0.02 – 7.6	Home	(Ali et al., 2012)
	16	New Zealand	2012	0.25	0.54	0.13 – 1.9	Mattress	(Ali et al., 2012)
	10	Sweden	N/A	1.6	3.1	0.7-11	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	3.1	4.5	0.8-12	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	19	32	3.4-120	Work	(Bergh et al., 2011b)

	n	Country	Year	Median (µg/g)	Mean (µg/g)	Range (µg/g)	Environment	Reference
TDCIPP								
	50	US	2002-2007	N/A	1.88	<0.11-56	Home	(Meeker and Stapleton, 2010)
	40	Japan	2006	4	N/A	<1.2-105	Home floor	(Kanazawa et al., 2010)
	41	Japan	2006	22.3	N/A	5.8-127	Home multisurface	(Kanazawa et al., 2010)
	16	US	2006	2.8	N/A	0.73-24	Home	(Dodson et al., 2012)
	8	Spain	2007	N/A	0.35	<0.05-1.1	Home	(García et al., 2007a)
	47	Romania	2010	0.06	0.095	<0.02 – 0.46	House/apartment	(Dirtu et al., 2012)
	15	Belgium	2010	N/A	0.76	<0.08-56	Store	(Van den Eede et al., 2011b)
	33	Belgium	2010	N/A	0.36	<0.08-6.6	Home	(Van den Eede et al., 2011b)
	15	Kuwait	2011	0.36	0.53	0.060-1.56	Home	(Ali et al., 2013)
	15	Kuwait	2011	7.63	36	0.60-166	Car	(Ali et al., 2013)
	15	Pakistan	2011	<0.005	0.03	<0.005-0.26	Home	(Ali et al., 2013)
	15	Pakistan	2011	0.029	0.13	<0.005-1.24	Car	(Ali et al., 2013)
	16	US	2011	2.1	N/A	0.92-44	Home	(Dodson et al., 2012)
	5	US	2012	N/A	N/A	2.84-23	Gym	(Carignan et al., 2013a)
	3	US	2012	N/A	N/A	3.19-38	Gym	(Carignan et al., 2013a)
	34	New Zealand	2012	0.23	0.47	0.02 – 17	Home	(Ali et al., 2012)
	16	New Zealand	2012	0.11	0.14	0.02 – 6.5	Mattress	(Ali et al., 2012)
	10	Sweden	N/A	10	12	2.2-27	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	9.1	28	3.9-150	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	17	30	3.3-91	Work	(Bergh et al., 2011b)

Table 1.5 *Available literature data on concentrations of chlorinated PFRs in air*

	n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
TCEP								
	169	Sweden	N/A	4	10	nd-230	Apartments	(Bergh et al., 2011a)
	10	Sweden	N/A	4.8	8.3	nd-28	House	(Bergh, et al., 2011b)
	10	Sweden	N/A	25	47	7.8-230	Day care centre	(Bergh, et al., 2011b)
	10	Sweden	N/A	10	21	nd-140	Work place	(Bergh, et al., 2011b)
	8	N/A	2010	N/A	N/A	0.006-0.16	Northern sea outdoor	(Möller et al., 2011)
	a)	N/A	2010/11	0.289	N/A	0.126-0.585	Arctic Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.237/1.96	Sea of Japan	(Möller et al., 2012)
	a)	N/A	2010/11	0.204	N/A	0.159-0.282	Northern Pacific Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	0.077	N/A	0.019-0.156	East Indian Archipelago, Philippine Sea	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.074	Southern Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	0.223	N/A	0.046-0.570	Indian Ocean	(Möller et al., 2012)
	18	Japan	2006	N/A	1.3	<0.67-136	House	(Saito et al., 2007)
	14	Japan	2006	N/A	3.3	<0.67-42.1	Office	(Saito et al., 2007)
	27	US	2012	0.12	0.18	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	0.10	0.12	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	0.15	0.13	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	0.0077	0.011	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	0.0055	0.0055	N/A	Eagle Harbor	(Salamova et al., 2014)

	n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
TCIPP								
	18	Japan	2006	N/A	1.9	<0.94-1260	House	(Saito et al., 2007)
	8	Japan	2006	N/A	<0.94	<0.94-3.1	Outdoor	(Saito et al., 2007)
	14	Japan	2006	N/A	6.0	<0.94-57.6	Office	(Saito et al., 2007)
	169	Sweden	N/A	14	59	<0.5-1200	Apartment	(Bergh et al., 2011a)
	10	Sweden	N/A	5.6	15	2.4-64	House	(Bergh et al., 2010)
	10	Sweden	N/A	8.4	19	1.3-72	Day care centre	(Bergh et al., 2010)
	10	Sweden	N/A	100	110	16-240	Work place	(Bergh et al., 2010)
	1	US	N/A	N/A	15.1	N/A	Gym near loose foam pit	(Carignan et al., 2013a)
	1	US	N/A	N/A	10.9	N/A	Near gym entrance	(Carignan et al., 2013a)
	8	N/A	2010	N/A	N/A	0.038-1.2	Northern sea outdoor	(Möller et al., 2011)
	a)	N/A	2010/11	0.281	N/A	0.085-0.529	Arctic Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.129/0.619	Sea of Japan	(Möller et al., 2012)
	a)	N/A	2010/11	0.160	N/A	0.098-0.269	Northern Pacific Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	0.074	N/A	0.022-0.411	East Indian Archipelago, Philippine Sea	(Möller et al., 2012)
	a)	N/A	2010/11	0.251	N/A	0.037-0.549	Indian Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.055	Southern Ocean	(Möller et al., 2012)
	27	US	2012	0.41	0.53	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	0.32	0.85	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	0.072	0.17	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	0.027	0.025	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	0.029	0.032	N/A	Eagle Harbor	(Salamova et al., 2014)

	n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
TDCIPP								
	18	Japan	2006	N/A	<0.72	<0.72	House	(Saito et al., 2007)
	14	Japan	2006	N/A	<0.72	<0.72-8.7	Office	(Saito et al., 2007)
	1	US	N/A	N/A	11.1	N/A	Gym near loose foam pit	(Carignan et al., 2013a)
	10	Sweden	N/A	nd	3.1	nd-17	House	(Bergh, et al., 2011b)
	10	Sweden	N/A	nd	6.7	nd-30	Day care centre	(Bergh, et al., 2011b)
	10	Sweden	N/A	28	24	nd-73	Work place	(Bergh, et al., 2011b)
	1	US	N/A	N/A	7.3	N/A	Near gym entrance	(Carignan et al., 2013a)
	a)	N/A	2010/11	N/A	N/A	nd-0.005	Arctic Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.016/0.052	Sea of Japan	(Möller et al., 2012)
	a)	N/A	2010/11	0.005	N/A	0.005-0.008	Northern Pacific Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	0.08	N/A	0.049-0.78	East Indian Archipelago, Philippine Sea	(Möller et al., 2012)
	a)	N/A	2010/11	0.053	N/A	nd-0.22	Indian Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.080	Southern Ocean	(Möller et al., 2012)
	27	US	2012	0.079	0.12	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	0.11	0.52	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	0.028	0.028	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	nd	nd	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	0.032	0.055	N/A	Eagle Habor	(Salamova et al., 2014)

Table 1.6 *Literature data on Concentrations of Chlorinated PFRs in Aqueous Samples*

	n	Country	Year	Median (ng/L)	Mean (ng/L)	Range (ng/L)	Reference	Comment
River water								
TCEP	1	Italy	2006	N/A	7	N/A	(Bacaloni and Cavaliere, 2007)	River Tiber winter
TCEP	1	Italy	2006	N/A	<3.9	N/A	(Bacaloni and Cavaliere, 2007)	River Tiber summer
TCEP	13	UK	2011	N/A		119-316	(Cristale et al., 2013b)	River Aire
TCIPP	1	Italy	2006	N/A	54	N/A	(Bacaloni and Cavaliere, 2007)	River Tiber winter
TCIPP	1	Italy	2006	N/A	117	N/A	(Bacaloni and Cavaliere, 2007)	River Tiber summer
TCIPP	13	UK	2011	N/A	6040	113 -26050	(Cristale et al., 2013b)	River Aire
TDCIPP	1	Italy	2006	N/A	<1.8	N/A	(Bacaloni and Cavaliere, 2007)	River Tiber winter
TDCIPP	1	Italy	2006	N/A	<1.8	N/A	(Bacaloni and Cavaliere, 2007)	River Tiber summer
TDCIPP	13	UK	2011	N/A		62-149	(Cristale et al., 2013b)	River Aire
Storm water holding tank								
TCEP	42	Germany	2007-2009	77	N/A	33-275	(Regnery and Püttmann, 2010)	Frankfurt/Main
TCIPP	42	Germany	2007-2009	880	N/A	16-5791	(Regnery and Püttmann, 2010)	Frankfurt/Main
TDCIPP	42	Germany	2007-2009	13	N/A	<1-73	(Regnery and Püttmann, 2010)	Frankfurt/Main
TCEP	10	Germany	2007-2009	78	N/A	23-131	(Regnery and Püttmann, 2010)	Bekond
TCIPP	10	Germany	2007-2009	410	N/A	197-4847	(Regnery and Püttmann, 2010)	Bekond
TDCIPP	10	Germany	2007-2009	11	N/A	<1-36	(Regnery and Püttmann, 2010)	Bekond
Precipitation								
TCEP	90	Germany	2007-2009	71	N/A	10-485	(Regnery and Püttmann, 2010)	Frankfurt/Main
TCEP	48	Germany	2007-2009	12	N/A	<2-127	(Regnery and Püttmann, 2010)	Bekond
TCEP	29	Germany	2007-2009	40	N/A	11-390	(Regnery and Püttmann, 2010)	Kleiner Feldberg
TCIPP	90	Germany	2007-2009	403	N/A	32-3562	(Regnery and Püttmann, 2010)	Frankfurt/Main
TCIPP	48	Germany	2007-2009	134	N/A	5-1214	(Regnery and Püttmann, 2010)	Bekond
TCIPP	29	Germany	2007-2009	57	N/A	<1-1154	(Regnery and Püttmann, 2010)	Kleiner Feldberg
TDCIPP	90	Germany	2007-2009	5	N/A	<1-532	(Regnery and Püttmann, 2010)	Frankfurt/Main
TDCIPP	48	Germany	2007-2009	7	N/A	<1-87	(Regnery and Püttmann, 2010)	Bekond
TDCIPP	29	Germany	2007-2009	16	N/A	<1-497	(Regnery and Püttmann, 2010)	Kleiner Feldberg
Bank filtrate (inlet for drinking water treatment plant)								
TCEP	18	Germany	1999	N/A	50	20-170	(Knepper et al., 1999)	

Table 1.7 *Literature data on concentrations of TCEP, TCIPP and TDCIPP in lake sediment*

	n	Country	Year	Mean (µg/kg)	Reference
TCEP	28	China	2011	1.75	(Cao et al., 2012)
TCIPP	28	China	2011	1.36	(Cao et al., 2012)
TDCIPP	28	China	2011	1.16	(Cao et al., 2012)

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1.4.1.4 Toxicology and health effects

TCEP

TCEP is classed as a carcinogen class 2 (Scientific Committee on Health and Environmental Risks SCHER, 2012). Furthermore, a study in Austria showed a significant relationship between TCEP concentrations in dust/air and the cognitive performance of exposed school children (Umweltbundesamt, 2008). Moreover, TCEP was the proposed cause of the deaths of two dogs following their consumption of car seat material (Lehner et al., 2010).

TCIPP

While there is in general a lack of information about the health impacts of TCIPP (Dodson et al., 2012), it is seen as potentially carcinogenic (van der Veen and de Boer, 2012). Moreover, animal studies demonstrate it can accumulate in kidneys and liver, and that it can cause skin and eye irritation in rats (Leisewitz et al., 2001).

TDCIPP

TDCIPP is considered to irritate the skin and be harmful by inhalation (Sigma Aldrich, 2013), and is considered a potential hazard to consumers by the Consumer Product Safety Commission (CPSP) (Babich, 2006). More specifically, TDCIPP concentrations in US house dust were associated with prolactin hormone and altered thyroid (free T4) levels in men. (Meeker and Stapleton, 2010). Moreover, TDCIPP alters neurodifferentiation and decreases cell numbers, although it is unclear whether such effects are caused by TDCIPP or its metabolite bis(1,3-dichloro-2-propyl)phosphate (BDCPP) (Dishaw et al., 2011).

1.4.1.5 Regulatory aspects

TCEP

In 1998, restrictions were placed on the further use of TCEP as a flame retardant additive in block polyurethane foams and textiles because of the possibility of its decomposition (WHO, 1998; Bayerisches Landesamt für Umwelt, 2006). The production of TCEP was evaluated under the EU existing substances regulation (EEC) 793/93 in 2009, where it was stated that starting from 2001-2002 EU production of TCEP ceased (based on the information provided by industry) (Scientific Committee on Health and Environmental Risks SCHER, 2012). Moreover, the only North American manufacturer of TCEP stopped its production in 2009, but there remain indications that production in Asia continues (Government of Canada, 2012).

The European Standard EN 71-9 (Safety of Toys – Part 9: Organic Chemical Compounds – Requirements) specifies that TCEP should be under the limit of quantification of the test method, for textiles used in of toys and accessible components of toys for use by children under 3 years of age (European Union, 2008a). Further, an amendment to the bills s.4085-A and A. 6195-A in New York, agreed in 2011, states that from 1st December 2013, the sale of any child care products intended to be used by a child under 3 years or younger, that contains more than 0.1 % TCEP is forbidden. Childcare products covered within this bill are toys, baby products, car seats, nursing pillows, strollers and crib mattresses (New York Senate Chapter Amendments to S.4085-A and A. 6195-A, 2011).

TCIPP

So far there are no emission or exposure controls that directly address TCIPP. Unlike TCEP, TCIPP is not specifically mentioned in the European Standard EN 71-9 (Safety of Toys – Part 9: Organic Chemicals Compounds –

Requirements) but is more generally covered by the following statement ‘toys must not contain dangerous substances or preparations within the meaning of Directives 67/548/EEC and 88/379/EEC (repealed by 1999/45/EC) in amounts which may harm the health of children using them (European Union, 2008a).

TDCIPP

TDCIPP was banned for use in children’s pyjamas in the late 1970s (OEHHA, 2011b). A ban on its use in foam products e.g. mattresses and baby products is now underway in California (Betts, 2013) and might lead to a global policy change, given the far-reaching influence of Californian state flame retardancy regulations. At the end of 2012, Israel Chemicals' subsidiary, ICL Industrial Products (ICP-IP), announced the ongoing development of a replacement product for TDCIPP in transport applications, e.g. cars; that they were discontinuing the sale of TDCIPP for upholstery furniture from January 2013, and intended to stop the production of TDCIPP completely by 2015 (Chemicals-technology.com, 2012).

1.4.2 Non-halogenated aryl phosphates

According to production data non-halogenated, aryl phosphates are the second most important group after chlorinated PFRs.

1.4.2.1 Application and uses

TPHP

TPHP is the most commonly used plasticiser for cellulose acetate (Ferro, 2011). About 50% of the overall production of TPHP is for use as a flame retardant plasticiser in PVC. Other uses include: as a flame retardant in polymers (22%), printed circuit boards (11%) and photographic films (7%). Additional minor uses of TPHP include: hydraulic liquids, adhesives, coatings and inks (OECD SIDS, 2002). Registered trade names are Celluflex TPP, Phosplex ® TPP and Disflamoll ® TP, Reomol ® TPP, Reofoss ® TPP (Lassen, 1999; ATSDR, 2012).

Excluding eastern Europe, total worldwide production of TPHP was estimated in 2000 to be between 20000 to 30000 tonnes. About 40 % is estimated to be produced in the USA compared to 35 % in Asia and around 25 % in Western Europe. There are no data available for Eastern European countries (Leonards, 2011). While the usage of TPHP in e.g. Norway declined from 55 tonnes in 2004 to 6.7 tonnes in 2005, it increased subsequently to around 18.4 tonnes in 2008 (Leonards, 2011).

More recently, resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BADP) have been used as a substitute for TPHP as they are considered less likely to be released into the environment due to their lower volatility (Leonards, 2011; Pawlowski and Schartel, 2007).

TMPP

TMPP is used as a flame retardant, a plasticiser in vinyl plastic manufacture, a solvent for nitrocellulose, an additive in extreme pressure lubricants, and as a non-flammable fluid in hydraulic systems (WHO, 1990). Minor uses of TMPP are additives in making synthetic leather (Franchini et al., 1978), polyvinyl acetate products (WHO, 1990), shoes (Pegum, 1966) and as a solvent for acrylate lacquers and varnishes (WHO, 1990). Registered trade names of TMPP are Antiblaze ® TCP, Lindol ®, Londol ® XP Plus, Disflamol ® TKP, Pliabrac ® TCP and Kronitex ® TCP (Lassen, 1999).

EHDPP

The principal use of EHDPP is as a plasticiser/flame retardant in flexible PVC and it has been approved for use in food packaging in the US (Environment Agency, 2009a). European use data for 2001 indicated application in PVC, rubber, polyurethanes, photo films, paints, pigment dispersions, adhesives and textile coatings (Environment Agency, 2009a). Registered trade names are Disflamoll DPO®, Phosflex 362® and Santicizer 141® (Environment Agency, 2009a).

1.4.2.2 Physicochemical properties

A summary of the physicochemical properties of non-halogenated aryl phosphates is given in Table 1.8.

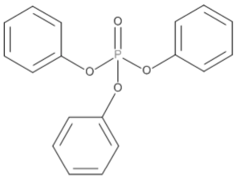
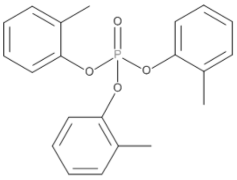
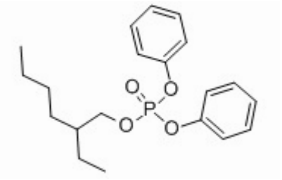
1.4.2.3 Environmental levels and behaviour

Dust

Table 1.9 summarises the available literature data on concentrations of non-halogenated aryl phosphates in dust samples._It was shown in an initial study in Japan (Kanazawa et al., 2010), that TPHP and TMPP levels were significantly higher in multi surface dust compared to floor dust. As seen for the chlorinated PFRs, levels of non-chlorinated aryl phosphates appear much higher in the Japanese study (Kanazawa et al., 2010) compared to all other studies to date. When comparing PFR concentrations in car versus home dust, cars appear to have higher concentrations compared to home dust (Ali et al., 2013). Samples from Belgium (Van den Eede et al., 2011a) and Romania (Dirtu et al., 2012) showed comparable concentration ranges for TPHP while those from Kuwait and Pakistan (Ali et al., 2013) displayed a narrower range. There are tentative indications of rising levels of TPHP in US house dust (Dodson et al., 2012) as maximum concentrations detected in a second sampling round in 2011 exceeded those in samples collected in 2006. The authors suggested this could be indicative of increased usage of Firemaster 550 (which contains TPHP) in recent years (Dodson et al., 2012).

While literature data on EHDPP is sparse, EHDPP concentrations in samples from day care centres and offices exceeded those detected in homes. (Bergh et al., 2011b) Moreover, while concentrations of EHDPP in house dust were of similar magnitude in Sweden (Bergh et al., 2011b) and the US (Dodson et al., 2012), concentrations in both countries exceed those in house dust from the Philippines (Kim et al., 2013).

Table 1.8 *Physicochemical properties of TPHP, TCP and EHDPP* (SRC, 2013)

	PFR		
Parameter	Triphenyl phosphate	Tricresyl phosphate	2-Ethylhexyl diphenyl phosphate
Abbreviation	TPHP	TMPP	EHDPP
Chemical formula	$C_{18}H_{15}O_4P$	$C_{21}H_{21}O_4P$	$C_{20}H_{27}O_4P$
Structure			
CAS Number	115-86-6	* different isomers*	1241-94-7
Molecular weight	326.29	368.37	362.41
Boiling point	245 °C at 11mm Hg	* different isomers*	375°C
Melting point	50.5 °C	* different isomers*	-54°C
Vapour pressure (25 °C)	6.28 x 10^{-6} mm Hg	* different isomers*	5 x 10^{-5} mm Hg
Water solubility (25 °C)	1.9 mg/L	* different isomers*	1.9 mg/L
Log P (octanol-water)	4.59	* different isomers*	5.73
Henry's Law constant (25 °C)	3.31x 10^{-6} atm-m^3/mole	* different isomers*	5.42 x 10^{-5} atm-m^3/mol

Air

Table 1.10 summarises the available literature data on concentrations of non-halogenated aryl phosphates in air samples. TPHP has the highest vapour pressure out of the three non-halogenated aryl phosphates analysed in this study, and has been found in remote outdoor air (Möller et al., 2011, 2012), an indication that it is capable of long-range atmospheric transport.

The available literature data on EHDPP concentrations in air samples are very few. This may be attributable to the fact that it has until very recently been monitored only rarely, likely due to its low vapour pressure (approximately 10-fold lower than TPHP) which makes its presence in air and resultant human exposure via inhalation less likely.

TMPP has been only very rarely monitored in air samples, with the main focus on the airplane industry. While its low vapour pressure (between 1.46 x 10^{-6} mm Hg and 3.49 x 10^{-9} mm Hg for the different isomers (SRC, 2013)) suggests that elevated atmospheric concentrations are unlikely to be due to evaporation from a product; one Japanese study (Takimoto et al., 1999) analysed atmospheric concentrations and concluded that those are the result of engine oils used for cars and motorcycles. Concentrations of o-TMPP and m-TMPP in motorcycle oils were 1.7 – 7.3 mg/g and 1.5 - 6.8 mg/g respectively. Furthermore, a study of concentrations of TMPP in Australian military airplanes, reported them to be below the detection limit of 0.005 ng/m^3 in 48 out of 78 samples; with the highest total TMPP concentration (associated with a smoke event) reported as 51.3 µg/m^3 (Denola et al., 2011). This study also showed airborne TMPP to be present as an oil aerosol rather than in the vapour phase (Denola et al., 2011).

Fish

A study from the Philippines indicates that TPHP is adsorbed onto particles, settles down to the bottom sediment and than accumulates though the benthic food web (Kim et al., 2011). Despite this, PFR concentrations in fish samples collected from Swedish retail markets were below detection limit in all 24 samples (Campone and Piccinelli, 2010)

E-Waste

Even though there is hardly anything known about PFR concentrations in e-waste, recent reports suggest e-waste could be a major source of TPHP to the environment (Roth et al., 2012). Consistent with this, although EHDPP was <0.001% w/w in two printed circuit boards; TPHP was identified at 0.4 % and 0.2 % w/w, and TMPP at 0.06 and 0.001 % w/w (Ballesteros-Gómez et al., 2013). Additionally, a very recently published study showed that TPHP was the most common PFR detected in e-waste and consumer products (Ballesteros-Gómez et al., 2014).

Table 1.9 *Summary of concentrations of non-halogenated aryl phosphates in indoor dust*

	n	Country	Year	Median (µg/g)	Mean (µg/g)	Range (µg/g)	Environment	Reference
TPHP								
	41	Japan	2006	14	N/A	<1.6-180	Home multisurface	(Kanazawa et al., 2010)
	41	Japan	2006	5.4	N/A	<1.6-78	Home floor	(Kanazawa et al., 2010)
	16	US	2006	3	N/A	0.58-14	Home	(Dodson et al., 2012)
	8	Spain	2007	N/A	2.6	0.29-9.5	Home	(García et al., 2007a)
	15	Belgium	2010	N/A	1.97	0.15-34.2	Store	(Van den Eede et al., 2011b)
	33	Belgium	2010	N/A	0.50	0.040-29.8	Home	(Van den Eede et al., 2011b)
	47	Romania	2010	0.50	1.6	<0.02 – 22.6	House/apartment	(Dirtu et al., 2012)
	15	Kuwait	2011	0.43	1.08	0.044-6.89	Home	(Ali et al., 2013)
	15	Kuwait	2011	1.76	2.17	<0.02-7.42	Car	(Ali et al., 2013)
	15	Pakistan	2011	0.16	0.18	<0.02-0.33	Home	(Ali et al., 2013)
	16	US	2011	2.8	N/A	0.79-36	Home	(Dodson et al., 2012)
	15	Pakistan	2011	0.25	0.67	<0.02-4.8	Car	(Ali et al., 2013)
	34	New Zealand	2012	0.6	0.59	0.02 – 7.5	Home	(Ali et al., 2012)
	16	New Zealand	2012	0.24	0.47	0.02 – 35	Mattress	(Ali et al., 2012)
	17	Philippines	2008	0.089	N/A	0.0085-2.1	House dust, residential area	(Kim et al., 2013)
	20	Philippines	2008	0.071	N/A	0.013-0.44	House dust, municipal dumping area	(Kim et al., 2013)
	10	Sweden	N/A	1.2	1.6	0.1-4.2	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	1.9	3.5	0.3-17	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	5.3	8.8	0.9-32	Work	(Bergh et al., 2011b)

	n	Country	Year	Median (µg/g)	Mean (µg/g)	Range (µg/g)	Environment	Reference
TMPP								
	40	Japan	2006	<4	N/A	<4-102	Home multisurface	(Kanazawa et al., 2010)
	16	US	2006	1	N/A	0.33-4.4	Home	(Dodson et al., 2012)
	40	Japan	2006	<4	N/A	<4-13.9	Home floor	(Kanazawa et al., 2010)
	15	Belgium	2010	N/A	0.20	<0.040-12.5	Store	(Van den Eede et al., 2011b)
	33	Belgium	2010	N/A	0.24	<0.040-5.07	Home	(Van den Eede et al., 2011b)
	47	Romania	2010	0.50	1	<0.050 – 5.5	House/apartment	(Dirtu et al., 2012)
	16	US	2011	0.68	N/A	0.18-10	Home	(Dodson et al., 2012)
	15	Kuwait	2011	0.16	0.57	0.028-6.0	Home	(Ali et al., 2013)
	15	Kuwait	2011	0.37	1.58	0.215-14.76	Car	(Ali et al., 2013)
	15	Pakistan	2011	0.036	0.06	0.015-0.20	Home	(Ali et al., 2013)
	15	Pakistan	2011	0.11	0.53	0.024-3.17	Car	(Ali et al., 2013)
	34	New Zealand	2012	0.12	0.20	<0.05 – 3.8	Home	(Ali et al., 2012)
	16	New Zealand	2012	0.16	0.19	<0.05 – 2.2	Mattress	(Ali et al., 2012)
	17	Philippines	2008	0.018	N/A	<0.00027-0.025	House dust, residential area	(Kim et al., 2013)
	20	Philippines	2008	0.077	N/A	<0.000027-0.14	House dust, municipal dumping area	(Kim et al., 2013)
	10	Sweden	N/A	1.0	1.2	nd-3.0	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	0.4	2.0	nd-13	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	0.6	0.8	nd-2.9	Work	(Bergh et al., 2011b)

	n	Country	Year	Median (μg/g)	Mean (μg/g)	Range (μg/g)	Environment	Reference
EHDPP								
	17	Philippines	2008	0.11	N/A	0.08-0.77	House dust, residential area	(Kim et al., 2013)
	20	Philippines	2008	0.034	N/A	0.077-0.56	House dust, municipal dumping area	(Kim et al., 2013)
	10	Sweden	N/A	0.5	0.6	nd-1.8	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	0.8	24	0.2-160	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	1.0	15	nd-73	Work	(Bergh et al., 2011b)
	16	US	2006	0.61	N/A	0.18-3	Home	(Dodson et al., 2012)
	16	US	2011	0.56	N/A	0.14-1.5	Home	(Dodson et al., 2012)
	134	Canada	N/A	0.54	N/A	<MDL-105	“Fresh” house dust	(Fan et al., 2014)
	134	Canada	N/A	1.0	N/A	<MDL-15	Vacuum cleaner bag dust	(Fan et al., 2014)
	15	Kuwait	2011	0.190	0.925	0.075-11	Home	(Ali et al., 2013)
	15	Kuwait	2011	0.520	0.875	0.02-4.2	Car	(Ali et al., 2013)
	15	Pakistan	2011	0.067	0.085	<0.02-0.36	Home	(Ali et al., 2013)
	15	Pakistan	2011	0.037	0.073	0.02-0.44	Car	(Ali et al., 2013)

Table 1.10 *Available literature data on non-halogenated aryl phosphate concentrations in air samples*

	n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
TPHP								
	18	Japan	2002	Nd	N/A	Nd-5.4	House	(Saito et al., 2007)
	14	Japan	2002	Nd	N/A	Nd-0.6	Office	(Saito et al., 2007)
	a)	N/A	2010/11	0.019	N/A	0.010-0.060	Arctic Ocean	(Möller et al., 2012)
	10	Sweden	N/A	nd	0.2	nd-0.8	House	(Bergh, et al., 2011b)
	10	Sweden	N/A	nd	0.1	nd-0.9	Day care centre	(Bergh, et al., 2011b)
	10	Sweden	N/A	nd	0.6	nd-2.7	Work place	(Bergh, et al., 2011b)
	a)	N/A	2010/11	N/A	N/A	0.025/0.097	Sea of Japan	(Möller et al., 2012)
	a)	N/A	2010/11	0.019	N/A	0.009-0.024	Northern Pacific Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	0.017	N/A	nd-0.155	East Indian Archipelago, Philippine Sea	(Möller et al., 2012)
	a)	N/A	2010/11	0.026	N/A	nd-0.074	Indian Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.019	Southern Ocean	(Möller et al., 2012)
	8	N/A	2010	N/A	N/A	0.004-0.290	Northern sea outdoor	(Möller et al., 2011)
	27	US	2012	0.11	0.14	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	0.18	0.20	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	0.034	0.043	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	0.044	0.042	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	0.031	0.055	N/A	Eagle Harbor	(Salamova et al., 2014)
EHDPP								
	10	Sweden	N/A	nd	nd	nd	House	(Bergh, et al., 2011b)
	10	Sweden	N/A	nd	nd	nd-2.2	Day care centre	(Bergh, et al., 2011b)
	10	Sweden	N/A	nd	nd	nd-14	Work place	(Bergh, et al., 2011b)
	169	Sweden	N/A	<5.5	5.6	nd-24	Work place	(Bergh, et al., 2011a)

	n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
***o*-TMPP**								
	10	Japan	1995/96	0.051	0.057	0.038-0.088	Higashi-Hiroshima city	(Takimoto et al., 1999)
	27	US	2012	0.00024	0.00093	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	nd	nd	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	nd	nd	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	nd	nd	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	nd	nd	N/A	Eagle Harbor	(Salamova et al., 2014)
***m*-TMPP**								
	10	Japan	1995/96	0.061	0.061	0.039-0.085	Higashi-Hiroshima city	(Takimoto et al., 1999)
***p*-TMPP**								
	27	US	2012	0.0055	0.013	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	0.0029	0.0054	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	0.0036	0.0036	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	nd	nd	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	nd	nd	N/A	Eagle Harbor	(Salamova et al., 2014)
TMPP								
	78	Australia	N/A			<0.005-513000	Military Airplanes	(Denola et al., 2011)

a) samples were taken on two cruises with a total of 30 samples included in the study

1.4.2.4 Toxicology and health effects

TPHP

Even though a number of studies of the toxicity of TPHP have been conducted, its impacts on human health remain unclear. For example, while on one hand a study did not find any evidence of neurotoxicity in animal experiments (Lassen, 1999), another found some (albeit) low neurotoxicity (Pakalin et al., 2007), and there are other reports of its association with neurotoxicity (Ni et al., 2007; Andresen et al., 2004). Likewise, while one study has claimed TPHP to be a sensitizer for allergies (Hartmann et al., 2004), this is disputed (van der Veen and de Boer, 2012). However, TPHP has been reported to cause contact dermatitis (Björklund et al., 2004) and to affect the human immunologic defence system by inhibiting the blood monocyte carboxylesterase (Saboori et al., 1991). TPHP causes only moderate eye irritation, and is not thought to be mutagenic (Lassen, 1999; US EPA, n.d.), nor to cause skin irritation. (US EPA, n.d.) However, a recent study suggested that exposure to TPHP at the concentrations found in US house dust, may be associated with altered male hormone levels and decreased sperm concentration (Meeker and Stapleton, 2010). With respect to ecotoxicity, TPHP is seen as acutely toxic to water organisms (Leisewitz et al., 2001), and is most acutely toxic to shrimps, fish and daphnia (Lassen, 1999).

TMPP

Substantial concerns exist about the toxicity of TMPP, principally *o*-TMPP (De Nola et al., 2008). The toxicity varies between the 10 possible isomers of TMPP. As a result, the pure *ortho* isomer (*o,o,o*-TMPP) is removed as much as possible from commercial products (Lassen, 1999). Nowadays, the three mono-*o*-isomers (*o,p,p, o,m,p* and *o,m,m*) and the two di-*o* isomers (*o,o,p* and *o,o,m*) are considered 10 times and 5 times respectively more toxic than the pure *ortho* isomer. Moreover, isomers which contain only *para* and *meta* substituents are not considered neurotoxic (De Nola et al., 2008). As stated in

1.4.2.1, TMPP can be used as an additive for turbine oil in the airplane industry. Due to this, concerns have been raised recently that it may be the cause of adverse effects that arise from so called fume-events (Schindler et al., 2014). A fume event occurs when contamination of the cabin air through e.g. hydraulic oil occurs. However, as contemporary commercial turbine oil mixture contains less than 5% of TMPP isomer mixture (BP, 2012) with an o-TMPP content of less than 0.01% (Schindler et al., 2014), the link between TMPP and adverse impacts of fume events does not appear strong. (van Netten, 2009) developed a small personal air monitor and tested it on two flights resulting in exposure to 0.031 ng/m^3 and 0.083 ng/m^3 TMPP respectively. No isomer-specific concentrations were given. Consistent with this, a very recent study showed that urine samples from aircraft technicians in charge of changing and refilling the turbine oil, showed no indication of work related exposure, as concentrations of TMPP metabolites were below detection limits even immediately post-shift. (Schindler et al., 2014)

EHDPP

A preliminary Swedish study of blood donor plasma showed that the collection bags used, led to contamination of the collected plasma with EHDPP at levels of 0.73-1.2 µg/g plasma which is of similar magnitude to the EC20 value for its haemolytic effects (rupture of red blood cells) (Jonsson and Nilsson, 2003). It was concluded that this might have an adverse impact on recipients of donated blood plasma, and it was suggested that plasticiser free donor bag systems be used instead (Jonsson and Nilsson, 2003).

1.4.2.5 Regulatory aspects

Occupational Safety and Health Administration (OSHA) states that the employer must use work and engineering practices, that ensure exposure to TPHP is less than 3 mg/m^3 and to o-TMPP less than 0.1 mg/m^3 at any time (OSHA, 2009). To our knowledge, no specific workplace limits exist for EHDPP.

1.4.3 Non-halogenated alkyl phosphates

1.4.3.1 Applications and uses

TnBP

80% of the overall production of TnBP is used as a flame retardant in aircraft hydraulic fluids and as a solvent for rare earth extraction and purification. Minor uses of TnBP are as an anti-air entrainment additive for floor finishes and coatings, as a solvent in nuclear fuel processing, and a defoamer additive in cement casing for oil wells. Moreover, it has been reported that non-specific plant herbicides contained TnBP until their reformulation in the mid-1980s (OECD SIDS, 2001). TnBP is traded as Disflamoll TB, Celluphos 4, Phosflex 4, and Skydrol LD-4 (ATSDR, 2012).

TEHP

TEHP is used as a flame retardant plasticiser, mainly in PVC in low temperature applications. It is also used in cellulose acetate and as a solvent for certain chemical reactions (e.g. H_2O_2 synthesis) (WHO, 2000b; ECETOC, 1992). Interestingly, in the context of human exposure, TEHP is used as a flame retardant in clothing (OEHHA, 2011a).

1.4.3.2 Physicochemical properties

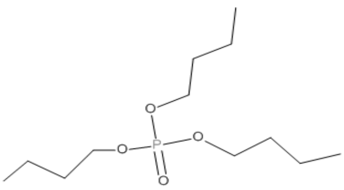
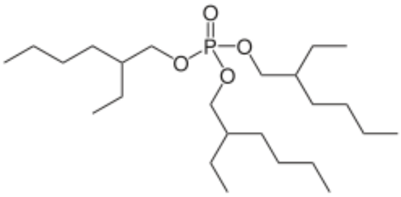
A summary of the physicochemical properties of non-halogenated alkyl phosphates is given in Table 1.11. TnBP is the PFR with the highest vapour pressure analysed in this study. Its high vapour pressure makes it less likely to be present in dust, and air inhalation is expected to be a more important exposure pathway.

1.4.3.3 Environmental levels and behaviour

Dust

Table 1.12 summarises the available literature data on non-halogenated PFRs in dust samples. Average levels of TnBP are much lower than those of the chlorinated PFRs analysed in this study. Furthermore, Japanese homes (Kanazawa et al., 2010) appear to be more highly contaminated with TnBP than those from Romania, Spain, and Belgium (Dirtu et al., 2012; Van den Eede et al., 2011b; García et al., 2007a).

Table 1.11 *Physicochemical properties of TnBP and TEHP* (SRC, 2013)

	PFR	
Parameter	Tri-n-butyl phosphate	Tris(2-ethylhexyl) phosphate
Abbreviation	TnBP	TEHP
Chemical formula	$C_{12}H_{27}O_4P$	$C_{24}H_{51}O_4P$
Structure		
CAS number	126-73-8	78-42-2
Molecular weight	266.32	434.65
Boiling point	289 °C	215 °C at 4 mm Hg
Melting point	-79 °C	-74 °C
Vapour pressure	0.00113 mm Hg	8.25×10^{-8} mm Hg
Water solubility	280 mg/L (25 °C)	0.6 mg/L (24 °C)
Log K_{ow}	4.00	9.49
Henry's Law constant (25°C)	1.41×10^{-6} atm-m^3/mole	7.86×10^{-8} atm-m^3/mole

Air

Table 1.13 summarises the available literature data on non-halogenated PFRs in air samples. TnBP concentrations in air appear lower than those of the chlorinated PFRs analysed in this study. The study of (Bergh et al., 2011b) reported a significant positive correlation between building age and TnBP concentrations in indoor air, while TEHP was below the detection limit in the same Swedish study. Likely due to its low vapour pressure, concentrations of TEHP in air are generally lower than those of the other PFRs studied; suggesting that air is not a significant pathway of human exposure to TEHP.

Table 1.12 *Available literature data on concentrations of non-halogenated alkyl phosphates in dust samples*

	n	Country	Year	Median (µg/g)	Mean (µg/g)	Range (µg/g)	Environment	Reference
TnBP								
	16	US	2006	<0.08	N/A	<0.08-1.8	Home	(Dodson et al., 2012)
	40	Japan	2006	1.1	N/A	<0.73-2.7	Home multisurface	(Kanazawa et al., 2010)
	40	Japan	2006	1.4	N/A	<0.73-16	Home floor	(Kanazawa et al., 2010)
	8	Spain	2007	N/A	0.25	0.09-0.65	Home	(García et al., 2007a)
	47	Romania	2010	0.045	0.07	<0.02 – 0.38	House/apartment	(Dirtu et al., 2012)
	15	Belgium	2010	N/A	0.21	0.05-6.0	Store	(Van den Eede et al., 2011b)
	33	Belgium	2010	N/A	0.13	0.03-2.7	Home	(Van den Eede et al., 2011b)
	15	Kuwait	2011	0.73	1.7	<0.020-9.8	Car	(Ali et al., 2013)
	15	Pakistan	2011	<0.02	<0.02	<0.02-0.02	Home	(Ali et al., 2013)
	15	Pakistan	2011	0.018	0.05	<0.02-0.25	Car	(Ali et al., 2013)
	15	Kuwait	2011	0.058	0.12	0.02-0.80	Home	(Ali et al., 2013)
	16	US	2011	<0.08	N/A	<0.08-1.8	Home	(Dodson et al., 2012)
	34	New Zealand	2012	0.08	0.17	<0.02 – 7.5	Home	(Ali et al., 2012)
	16	New Zealand	2012	0.07	0.09	0.02 – 1.9	Mattress	(Ali et al., 2012)
	17	Philippines	2008	0.19	N/A	<0.00058-0.079	House dust, residential area	(Kim et al., 2013)
	20	Philippines	2008	0.02	N/A	<0.00058-0.28	House dust, municipal dumping area	(Kim et al., 2013)
	10	Sweden	N/A	0.3	0.6	nd-1.7	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	1.2	2.0	0.1-6.2	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	0.2	0.7	nd-3.2	Work	(Bergh et al., 2011b)

	n	Country	Year	Median (μg/g)	Mean (μg/g)	Range (μg/g)	Environment	Reference
TEHP								
	40	Japan	2006	4.3	N/A	1.3-16	Home floor	(Kanazawa et al., 2010)
	40	Japan	2006	2.1	N/A	1.3-6.6	Home multisurface	(Kanazawa et al., 2010)
	17	Philippines	2008	0.14	N/A	0.0041-0.97	House dust, residential area	(Kim et al., 2013)
	20	Philippines	2008	0.041	N/A	<0.000017-0.37	House dust, municipal dumping area	(Kim et al., 2013)
	10	Sweden	N/A	nd	nd	nd-0.2	Home	(Bergh et al., 2011b)
	10	Sweden	N/A	0.1	0.2	nd-0.7	Day Care	(Bergh et al., 2011b)
	10	Sweden	N/A	nd	0.1	nd-0.3	Work	(Bergh et al., 2011b)
	16	US	2006	<0.2	N/A	<0.2-3.7	Home	(Dodson et al., 2012)
	16	US	2011	<0.2	N/A	<0.2-0.34	Home	(Dodson et al., 2012)
	15	Kuwait	2011	0.07	0.12	<0.005-0.34	Home	(Ali et al., 2013)
	15	Kuwait	2011	0.14	0.21	0.005-1.3	Car	(Ali et al., 2013)
	15	Pakistan	2011	0.02	0.02	<0.005-0.05	Home	(Ali et al., 2013)
	15	Pakistan	2011	0.01	0.05	<0.05-0.33	Car	(Ali et al., 2013)

Table 1.13 *Available literature data on atmospheric concentrations of non-halogenated alkyl phosphates*

	n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
TnBP								
	18	Japan	2002	4.0	N/A	<0.04-30.6	House	(Saito et al., 2007)
	14	Japan	2002	6.6	N/A	0.46-21.7	Office	(Saito et al., 2007)
	8	Japan	2002	<0.04	N/A	<0.04-1.7	Outdoor	(Saito et al., 2007)
	169	Sweden	N/A	N/A	11	N/A	Apartments	(Bergh et al., 2011a)
	10	Sweden	N/A	9.1	16	3.5-45	Houses	(Bergh et al., 2011b)
	10	Sweden	N/A	18	61	3.7-320	Day care centre	(Bergh et al., 2011b)
	10	Sweden	N/A	2.3	21	nd-100	Work places	(Bergh et al., 2011b)
	8	N/A	2010	N/A	N/A	Nd – 0.150	Northern sea outdoor	(Möller et al., 2011)
	a)	N/A	2010/11	0.011	N/A	nd-0.036	Arctic Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.010/0.033	Sea of Japan	(Möller et al., 2012)
	a)	N/A	2010/11	0.011	N/A	0.006-0.014	Northern Pacific Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	0.014	N/A	0.010-0.099	East Indian Archipelago, Philippine Sea	(Möller et al., 2012)
	a)	N/A	2010/11	0.027	N/A	0.007-0.075	Indian Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.014	Southern Ocean	(Möller et al., 2012)
	27	US	2012	0.18	0.25	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	0.16	0.15	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	0.032	0.034	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	0.028	0.034	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	0.061	0.18	N/A	Eagle Habor	(Salamova et al., 2014)

	n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
TEHP								
	8	N/A	2010	N/A	N/A	nd-0.031	Northern sea outdoor	(Möller et al., 2011)
	a)	N/A	2010/11	0.001	N/A	nd-0.006	Arctic Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.005/0.038	Sea of Japan	(Möller et al., 2012)
	a)	N/A	2010/11	0.002	N/A	0.001-0.012	Northern Pacific Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	0.012	N/A	0.006-0.092	East Indian Archipelago, Philippine Sea	(Möller et al., 2012)
	a)	N/A	2010/11	0.020	N/A	0.004-0.051	Indian Ocean	(Möller et al., 2012)
	a)	N/A	2010/11	N/A	N/A	0.007	Southern Ocean	(Möller et al., 2012)
	27	US	2012	0.26	0.32	N/A	Chicago	(Salamova et al., 2014)
	22	US	2012	0.057	0.066	N/A	Cleveland	(Salamova et al., 2014)
	16	US	2012	0.0081	0.085	N/A	Sturgeon Point	(Salamova et al., 2014)
	16	US	2012	0.0047	0.0047	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
	26	US	2012	0.0086	0.0087	N/A	Eagle Habor	(Salamova et al., 2014)

a) samples were taken on two cruises with a total of 30 samples included in the study

Precipitation storm water holding tank river water

Table 1.14 summarises the available literature data on TnBP levels in precipitation and storm water holding tank samples. TnBP was the most abundant PFR detected in precipitation collected from a measurement station installed on the German mountain “Kleiner Feldberg” (Regnery and Püttmann, 2010). By comparison, in urban and rural samples collected in the same study, it was the second most abundant PFR after TCIPP. Supporting this high relative abundance of TnBP, levels detected in three rain samples from Italy (Bacaloni et al., 2008) were of the same order of magnitude to those detected in the rural samples from the German study.

Table 1.14 *Available literature data on concentrations of TnBP in precipitation, storm water holding tank and river water samples from Germany taken between 2007 and 2009* (Regnery and Püttmann, 2010)

	n	Median (ng/L)	Range (ng/L)	Comment
Storm water holding tank				
	42	57	4-417	Frankfurt/Main
	10	359	13-347	Bekond
Precipitation				
	90	108	<1-1679	Bekond
	48	16	<1-110	Bekond
	29	64	<1-458	Kleiner Feldberg

1.4.3.4 Toxicology and health effects

There are in general a lack of studies of the human health effects of TnBP and TEHP (Dodson et al., 2012), although TnBP has been linked with sick building syndrome (Kanazawa et al., 2010).

1.4.3.5 Regulatory aspects

The US Occupational Safety and Health Administration (OSHA) states that the employer must use work and engineering practices, that ensure exposure to TnBP remains below 5 mg/m^3 at any time (OSHA, 2009). To our knowledge, there are no specific limits on TEHP levels within the workplace environment.

1.4.4 Alkyl ether phosphates

1.4.4.1 Applications and uses

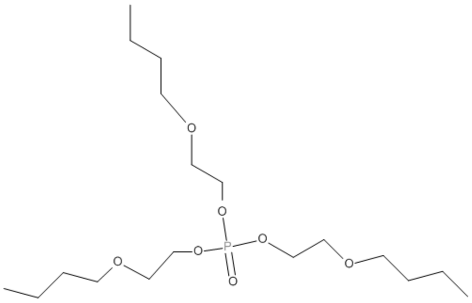
TBOEP

TBOEP is mainly used in floor polishes, a viscosity modifier in plastisols, a solvent in some resins, an antifoam and plasticiser in plastics, synthetic rubber and lacquers. It is also commonly used as a plasticiser in rubber stoppers for vacutainer tubes and plastic ware (WHO, 2000b). Registered trade names for TBOEP include Kronitex KP-140, KP 140 and Phosflex T-bep. (ATSDR, 2012).

1.4.4.2 Physicochemical properties

A summary of the physicochemical properties of TBOEP is given in Table 1.15.

Table 1.15 *Physicochemical properties of TBOEP* (SRC, 2013)

	PFR
Parameter	Tris(2-butoxyethyl) phosphate
Abbreviation	TBOEP
Chemical formula	$C_{18}H_{39}O_7P$
Structure	
CAS Number	78-51-3
Molecular weight	398.48
Boiling point	221°C at 4 mm Hg
Melting point	-70 °C
Vapour pressure (25 °C)	2.5×10^{-8} mm Hg
Water solubility (25 °C)	1100 mg/L
Log K_{ow}	3.75
Henry's Law constant (25 °C)	1.2×10^{-11} atm-m^3/mole

1.4.4.3 Environmental levels and behaviour

Dust

Table 1.16 summarises the available literature data on TBOEP concentrations in dust samples. TBOEP levels in Pakistan (Ali et al., 2013) are the lowest worldwide with Japanese house dust (Kanazawa et al., 2010) displaying the highest median concentrations reported to date. As observed elsewhere for brominated flame retardant concentrations in indoor dust (Harrad et al., 2008a), concentrations in each country display a highly positively skewed distribution.

Air

TBEOP concentrations in air are on average about the same order of magnitude as those of the other PFRs included in this study. In general, concentrations indoors exceed substantially those outdoors, which suggests sources are mainly indoors. The highest concentrations were detected in Swedish day-care centres (Bergh et al., 2011b)**.**

Precipitation, storm water holding tank, river water

TBOEP levels in German storm water holding tanks (Regnery and Püttmann, 2010) were lower than those of TCIPP in the same samples. As TCIPP and TBOEP have similar water solubilities, this suggests TCIPP emissions in Germany are greater.

Table 1.16 *Available literature data on concentrations of TBOEP in dust samples*

n	Country	Year	Median (µg/g)	Mean (µg/g)	Range (µg/g)	Environment	Reference
16	US	2006	12	N/A	2.3-68	Home	(Dodson et al., 2012)
16	US	2011	11	N/A	0.79-170	Home	(Dodson et al., 2012)
41	Japan	2006	164	N/A	5.9-749	Home multisurface	(Kanazawa et al., 2010)
41	Japan	2006	1570	N/A	61.8-5890	Home floor	(Kanazawa et al., 2010)
8	Spain	2007	N/A	9.9	1.18-18.2	Home	(García et al., 2007b)
47	Romania	2010	1.5	2.7	<0.05 - 21	House/apartment	(Dirtu et al., 2012)
15	Belgium	2010	N/A	3.6	0.200-55.7	Store	(Van den Eede et al., 2011b)
33	Belgium	2010	N/A	2.0	0.360-67.6	Home	(Van den Eede et al., 2011b)
15	Kuwait	2011	0.855	11	0.031-140	Home	(Ali et al., 2013)
15	Kuwait	2011	4.465	5.27	0.012-12.5	Car	(Ali et al., 2013)
15	Pakistan	2011	0.016	0.029	<0.015-0.145	Home	(Ali et al., 2013)
15	Pakistan	2011	0.016	0.125	<0.015-1.5	Car	(Ali et al., 2013)
10	Sweden	N/A	4.0	8.5	0.6-30	Home	(Bergh et al., 2011b)
10	Sweden	N/A	1600	1900	31-4100	Day Care	(Bergh et al., 2011b)
10	Sweden	N/A	87	250	4.5-960	Work	(Bergh et al., 2011b)

Table 1.17 *Available literature data on atmospheric concentrations of TBEOP*

n	Country	Year	Median (ng/m^3)	Mean (ng/m^3)	Range (ng/m^3)	Environment	Reference
18	Japan	2002	1.8	N/A	<0.63-13.7	Houses	(Saito et al., 2007)
14	Japan	2002	0.97	N/A	<0.63-118	Office	(Saito et al., 2007)
8	Japan	2002	<0.63	N/A	<0.63-1.1	Outdoor	(Saito et al., 2007)
169	Sweden	N/A	N/A	Nd	N/A	Apartments	(Bergh et al., 2011a)
10	Sweden	N/A	Nd	0.5	nd-4.5	Houses	(Bergh et al., 2011b)
10	Sweden	N/A	84	130	nd-380	Day care centres	(Bergh et al., 2011b)
10	Sweden	N/A	5.8	17	nd-73	Work places	(Bergh et al., 2011b)
8	N/A	2010	N/A	N/A	Nd-0.080	Northern sea outdoor	(Möller et al., 2011)
a)	N/A	2010/11	N/A	N/A	nd-0.011	Arctic Ocean	(Möller et al., 2012)
a)	N/A	2010/11	N/A	N/A	0.015/0.081	Sea of Japan	(Möller et al., 2012)
a)	N/A	2010/11	0.004	N/A	nd-0.016	Northern Pacific Ocean	(Möller et al., 2012)
a)	N/A	2010/11	N/A	N/A	nd-0.077	East Indian Archipelago, Philippine Sea	(Möller et al., 2012)
a)	N/A	2010/11	0.017	N/A	nd-0.044	Indian Ocean	(Möller et al., 2012)
a)	N/A	2010/11	N/A	N/A	nd	Southern Ocean	(Möller et al., 2012)
27	US	2012	0.041	0.0041	N/A	Chicago	(Salamova et al., 2014)
22	US	2012	0.23	0.33	N/A	Cleveland	(Salamova et al., 2014)
16	US	2012	0.077	0.076	N/A	Sturgeon Point	(Salamova et al., 2014)
16	US	2012	0.058	0.067	N/A	Sleeping Bear Dunes	(Salamova et al., 2014)
26	US	2012	0.051	0.068	N/A	Eagle Harbor	(Salamova et al., 2014)

a) samples were taken on two cruises with a total of 30 samples included in the study

Table 1.18 *Concentrations of TBEOP in storm water holding tanks and precipitation in samples from Germany* (Regnery and Püttmann, 2010)

n	year	Median (ng/L)	Range (ng/L)	Comment
Storm water holding tank				
42	2007-2009	77	nd-1616	Frankfurt/Main
10	2007-2009	36	nd-77	Bekond
Precipitation				
90	2007-2009	21	nd-505	Frankfurt/Main
48	2007-2009	nd	nd-205	Bekond
29	2007-2009	17	nd-242	Kleiner Feldberg

1.4.4.4 Toxicology and health effects

There is a general lack of health studies about TBOEP (Dodson et al., 2012). In terms of human exposure, a metabolite of TBOEP (bis(2-butoxyethyl)phosphate - BBEP) was detected in 31 % of human adult urine samples (n=59) in Belgium. Given previous findings of high concentrations of TBOEP in Belgian indoor dust, this result surprised the authors who therefore questioned the bioaccessibility and absorption of TBOEP from indoor dust and also its metabolism, for which conclusive data is not yet available (Van den Eede et al., 2013b). Notwithstanding this, a recent study revealed that the diester metabolite might not be the main metabolic pathway for TBOEP. Instead, oxidative metabolism might be favoured, as the oxidative metabolites TBEOP-M9 and TBEOP-M10 were found in a preliminary screening of 16 urine samples. These metabolites were thus highlighted as potentially useful markers for monitoring in human blood and urine (Van den Eede et al., 2013a).

1.5 Dust sampling

The composition of indoor dust varies greatly between places and depends on a variety of factors e.g. season, location, and behaviour of room occupants. Air flow within a room (especially exchange with outdoor air), building age and its contents e.g. carpets and soft furnishings, humidity and temperature (heating/air condition), combined with cleaning frequency and effectiveness exert further substantial impacts on the dust and organic material (e.g. soil) loading in a room. Outdoor inputs can also impact indoor dust composition (Layton and Beamer, 2009).

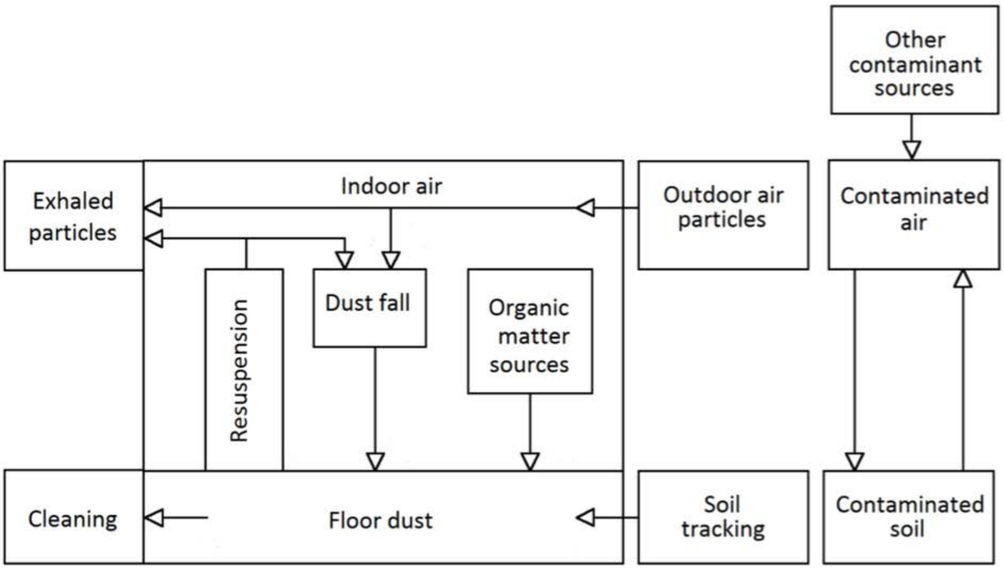


Figure 1.4 *Factors influencing indoor dust composition* (Layton and Beamer, 2009)

As established for PBDEs, indoor microenvironments tend to be more highly contaminated with PFRs than outdoor environments. This is due partly to low indoor ventilation rates, but also to the greater number and strength of indoor PFR sources, akin to previous observations for HBCDs (Harrad et al., 2009).

Dust itself is known to cause allergic reactions, and may also provide a vector of exposure to anthropogenic chemicals, e.g. flame retardants, plasticisers, and pesticides.

Human exposure to dust can occur via multiple routes and occurs in both indoor and outdoor environments via multiple pathways including oral ingestion, inhalation, and dermal contact depending on the type of dust (settled or suspended). While exposure to settled dust via ingestion is usually accidental, it may be deliberate for young children and some adults (Harrad, 2010). Moreover, as toddlers spend a greater amount of time on the floor crawling around and playing their ratio of ingestion: inhalation intake far exceeds than that for adults. As a result, dust ingestion has been highlighted as a particularly important pathway of exposure to chemicals like BFRs for toddlers (Harrad et al., 2010a).

Given the known presence of PFRs in settled indoor dust (Table 1.4, Table 1.9, Table 1.12 and Table 1.16), and the potential for exposure via contact with this dust, it is important that samples are taken to characterise PFR concentrations for exposure assessment purposes. The sampling method varies according to the microenvironment under study, and whether dust is sampled from the floor or other surfaces (e.g. shelves, tables, seats etc.). In view of such considerations, there are several approaches to collecting a settled dust sample in an indoor environment. In general they can be classed into two different groups: a) samples collected by a research group member ("researcher-collected") and b) samples collected by the individual 'dust-donor' with several subgroups. Table 1.19 lists advantages and disadvantages of various methods reported in the literature.

It was shown for PBDEs that there were significant differences in concentrations detected in samples derived from the same homes using the two sampling approaches of a whole vacuum cleaner dust bag and researcher-collected samples. This was attributed to differences in concentrations between different rooms sampled in the same home (Allen et al., 2008). To our knowledge, no data are available in the literature, which compares the two sampling approaches for PFRs. Furthermore, no data are available comparing the impact on concentrations of sampling a whole room versus only a small defined area. Indeed, at the time of writing there is no evidence in the literature that definitively identifies the most suitable approach for monitoring PFRs in indoor dust. A very recently published study, which compared researcher-collected dust sampling versus vacuum cleaner bag collection, showed good agreement for the two methods. Concentrations of TCIPP, TBEOP and TMPP were significantly higher in the researcher-collected samples, while EHDPP concentrations were significantly higher in the vacuum cleaner bag dust. (Fan et al., 2014) It needs to be noted though that this study did not use a standardised method for researcher collection of dust, which makes it difficult to be put in overall context.

An additional potential influence is the type of surface sampled. While most studies collect floor dust samples, (Ali et al., 2011; Van den Eede et al., 2011a) others collect elevated surface/ above floor samples. (Kanazawa et al., 2010) The influence of those two different sampling approaches on the PFR concentrations in dust samples is at this stage not known. A very recent indicative study showed that dust sample concentrations vary between floor dust and elevated surface dust within the room (Tajima et al., 2014). Given the preliminary nature of that study, more research is required, but given the likely variation in proximity of floor and elevated surface dust to different PFR sources, differences in PFR contamination of floor dust and elevated surface dust are plausible.

Although no such studies exist yet for PFRs, evidence exists that concentrations of BFRs will vary within different areas of the same room, likely dependent on the proximity of the sampled area to putative BFR sources. For example, (Harrad et al., 2008a) showed that concentrations of PBDEs in dust samples taken close to putative sources were higher than in samples taken further away. This can dramatically influence the concentrations on which human exposure assessment is based.

One solution to avoid sampling in a “hot-spot” area would be to collect a full room sample, instead of a smaller area within the room. This leads however to oversampling of the less frequented room areas and to a less biologically relevant dust sample than if sampling is confined to the most-frequented area(s) of the room. (Harrad, 2010).

Table 1.19 *Advantages and disadvantages of different sampling methods of settled dust for flame retardants reported in the literature*

	Advantage	Disadvantage
Researcher		
Sampling Sock	Controlled sample area	Time consuming for the researcher as each participant needs to be visited individually
	Cross-contamination is minimised	Potentially low dust mass in sample
	Sampling rate identical if same vacuum cleaner is used	
	Likely greater reproducibility as samples taken by the same person	
Dust donor		
Dust bag	Easily accessible	Unknown dust age in bag (can be accumulated over months if not a new dust bag is used for the study)
	High dust mass provided	Reflects all areas of the house and not just one individual room -> also areas which might not be used frequently (or even other houses/microenvironments)
	Reflects all areas of the house and not just one individual room	Different vacuum cleaner used
	Reflects individual cleaning habits	Samples taken by different people
Sampling sock	Convenient for the researcher	Donors may not conduct sampling correctly in accordance with the standard protocol
	Same advantages as for researcher-collected sampling sock method	Higher likelihood of cross-contamination if socks are not handled correctly
		Samples taken by different people

A further aspect meriting consideration is the extent of within-building variation in dust contamination with PFRs and related chemicals. (Bergh et al., 2011b) showed that the variation in concentrations of PFRs in dust from different rooms within the same multi-story building exceeded the inter-building variation in concentrations. This implies that the main sources of PFRs are items that vary in number and type between rooms (e.g. PCs, TVs etc.) rather than those specific to the building overall (e.g. paint, insulation material etc.).

1.6 Methods for Measuring Vapour Pressure of PFRs

Vapour pressure has important implications for the environmental behaviour of chemicals. For example, besides indicating the propensity for long-range atmospheric transport, it is a good indicator of the rate at which chemical volatilisation from products may occur. Vapour pressure can be predicted using quantitative structure property relationship (QSPR) modelling software. An alternative predictive approach is based on estimation based on the boiling point of the compound However, for several compounds, such predicted values are inaccurate. In addition to estimation methods, there exist several methods of making empirical measurements of vapour pressures. The mass balance method (Tremain, 2002a, 2002b) is one such approach. In this method, the compound of interest is heated in a small furnace, with a lid perforated with small holes of known diameter. The escaping vapour is directed onto a balance pan where the mass is measured. (OECD, 2002) Another approach is to measure using an isoteniscop (Dobry and Keller, 1957). Isotensicopes are based on the principle of the static method. The substance is heated under controlled conditions and the vapour pressure balanced with a known pressure of inert gas. (OECD, 2002)

The method used in this study was the GC-retention time (GC-RT) method (Hinckley and Bidleman, 1990; Koutek et al., 2001; Bidleman et al., 2003; Bidleman, 1984). This involves comparison of the retention time of the compound of interest with that of a reference standard of known vapour pressure. More detail of the theory and practice underpinning this method is provided in chapter 3.

The overall issue with the different approaches to measurement and estimation of vapour pressures, is that despite the importance of accurate vapour pressure measurements, there exist substantial inconsistencies between existing literature measurements of vapour pressures of PFRs. This hampers identification of the most accurate method for measurement of PFR vapour pressures.

1.7 Extraction and quantification methods for the determination of PFRs in environmental samples

In recent years, a growing number of laboratories have reported methods for the determination of PFRs in various sample matrices. The driver for this is a shift in focus from analysing PBDEs towards PFRs. While initial methods were hampered by a lack of suitable isotopically-labelled internal standards, this is being increasingly rectified as a growing range of deuterated PFR standards are becoming commercially available. This section gives an outline of the methods currently employed for the measurement of PFRs in environmental samples. An important point is that no standardised method exists for the determination of PFRs (Brandsma et al., 2013), an issue compounded by the current lack of any certified or standard reference materials that could be used to evaluate method accuracy.

In general, the sample matrix determines the type of extraction, clean-up and analytical instrumentation used. Especially in complex matrices like dust there might be many co-extractives, which potentially cause interferences during analysis. Moreover, PFRs are ubiquitous in the environment, and thus enormous care needs to be taken to ensure the sample does not get contaminated during analysis.

Extraction techniques include ultrasonication for dust (Van den Eede et al., 2011a; Dodson et al., 2012; Kanazawa et al., 2010; Van den Eede et al., 2011b; Ali et al., 2013; Bergh et al., 2010; Cristale and Lacorte, 2013), air (Saito et al., 2007), sludge and sediment (Cristale and Lacorte, 2013). Alternatives are: microwave extraction for dust (García et al., 2007a), and soxhlet extraction for air (Möller et al., 2012, 2011; Salamova et al., 2014) Each of these techniques employs a variety of solvents like: dichloromethane (DCM) (Van den Eede et al., 2011b; Möller et al., 2012, 2011), hexane /acetone (3:1) (Van den Eede et al., 2011a; Dodson et al., 2012; Dirtu et al., 2012; Ali et al., 2013), acetone (Kanazawa et al., 2010; García et al., 2007a; Bergh et al., 2010; Saito et al., 2007), hexane/acetone (1:1) (Salamova et al., 2014), ethyl acetate / cyclohexane (5:2) (Cristale and Lacorte, 2013), and acetonitrile/water (25:75) (Cao et al., 2012). Other approaches include: pressure filtration of water, rain and snow (Regnery and Püttmann, 2010).

Post-extraction, several methods for extract purification (clean-up) have been described in the literature. Florisil columns have been employed for purification of extracts of dust (Van den Eede et al., 2011a, 2011b; Dirtu et al., 2012; Ali et al., 2013; Dodson et al., 2012; Cristale and Lacorte, 2013) sediment and sludge samples (Cristale and Lacorte, 2013); while OASIS HLB SPE cartridges have been employed for clean-up of dust (García et al., 2007a), water (Bacaloni and Cavaliere, 2007; Cristale et al., 2013a, 2013b), and sediment sample extracts (Cao et al., 2012). Other methods include: deactivated silica gel for purification of air sample extracts (Möller et al., 2012, 2011) (Salamova et al., 2014), and styrene–divinylbenzene polymeric SPE cartridges for water, rain and snow sample extracts (Regnery and Püttmann, 2010).

Instrumental methods used to date for the determination of PFRs include: gas chromatography (GC) coupled to mass spectrometry (MS) (Van den Eede et al., 2011a; Regnery and Püttmann, 2010; Dodson et al., 2012; Kanazawa et al., 2010; Dirtu et al., 2012; Van den Eede et al., 2011b; Ali et al., 2013; Möller et al., 2012, 2011; Salamova et al., 2014; Cristale et al., 2013b, 2013a), GC-MS/MS (Bergh et al., 2011a, 2010; Cristale and Lacorte, 2013), GC coupled to nitrogen-phosphorus detection (NPD) (García et al., 2007a), GC coupled to flame photometric detection (FPD) (Saito et al., 2007), GC coupled to positive-ion chemical ionisation (PICI) mode (Björklund et al., 2004) and liquid chromatography (LC) coupled to MS/MS (Bacaloni and Cavaliere, 2007; Amini and Crescenzi, 2003). The method selected depends on the complexity of the matrix under study, as well as instrument availability. To date, GC-based methods are most favoured, notwithstanding reports of TCEP, TCIPP, and TDCIPP degradation on column, or in the injection port (Bergh et al., 2012; Bergh, 2011). Such issues are surmountable with care however, and are outweighed by the potential for signal suppression or enhancement due to matrix effects that has been reported for LC-MS/MS (Rodil et al., 2005).

In summary, PFR analysis is a relatively new area of study and there remains wide variation in the methods employed to date by studies of PFR contamination. Such variations must be borne in mind when comparing literature data, and this study will therefore apply identical sampling and analytical methodology to evaluate international trends in PFR contamination of indoor dust.

1.8 Concluding remarks

As shown in 1.4 PFRs are demonstrably present in the environment. This, combined with their known or suspected toxicity, implies a need for further research to evaluate human exposure to PFRs to facilitate understanding of the potential risk to human health. PFRs have been demonstrated to have the capacity to undergo long-range environmental transport, as exemplified by their detection in the Arctic. However, to our knowledge little research exists to date on their accumulation in the food chain. In contrast, research to date suggests indoor dust may be a major pathway of human exposure to PFRs. Hence greater knowledge of concentrations of PFRs in indoor dust is required to improve understanding of the risk posed by such contamination.

1.9 Aims and objectives of this project

The main aim of this project is to determine the magnitude of human exposure to PFRs via indoor dust ingestion. It also aims to augment significantly the currently sparse and conflicting database on the physicochemical properties of these contaminants by making empirical measurements of the vapour pressures of a range of PFRs.

The hypotheses to be tested in this project are that:

- The vapour pressures of PFRs can be satisfactorily determined via the GC-RT method
- Global variation in PFR use leads to a significant variation in the degree of contamination of indoor dust with PFRs as well as a country specific PFR pattern
- Indoor dust contamination varies between different microenvironments within the same country
- Couches represent a source of PFRs within living rooms
- Classroom dust has a distinctive PFR signature, which varies from that found in other microenvironments, is distinctive to a given country, and that PFR concentrations in classroom dust exceed significantly those of PBDEs
- Indoor dust ingestion is a substantial vector of human exposure to PFRs.

2 METHODOLOGY

Indoor dust samples were collected in order to address some of the hypotheses and aims outlined in Chapter 1. When sampling for human exposure estimation purposes, various critical issues need to be considered (see Figure 2.1). In this part of the project, settled indoor dust was identified as a likely major route of non-dietary human exposure to PFRs. The dust collection and extraction methods involved were specific for PFRs. All methodologies were developed from previous studies and modified to suit the equipment available. The methodology was based on an extraction method developed elsewhere (Van den Eede et al., 2011a) with the introduction of an additional internal standard as it came available during the course of this project, as well as a recovery standard for QA/QC purposes. The only amendment to the clean up procedure was that commercially-available pre-prepared florisil columns were replaced by self-prepared glass florisil columns. Sampling focused on the urban environment because of the relative ease of accessibility of the different microenvironments. The PFRs monitored are listed in Table 2.1 and include the most common compounds out of the three main PFR groups. They were chosen because of their high worldwide production volume and usage (see Chapter 1) and the available data on their concentrations in indoor dust globally. This study provides data on the largest range of PFRs reported in indoor dust samples to date and the first data on these contaminants in UK and Australian dust. This thesis also reports the first data on concentrations of PFRs in primary school dust with a study on nursery dust in Sweden the only previous comparable data. As the existing literature data on PFR vapour pressures are inconsistent, another aspect of this thesis was the determination of the vapour pressures of PFRs via the GC retention time method.

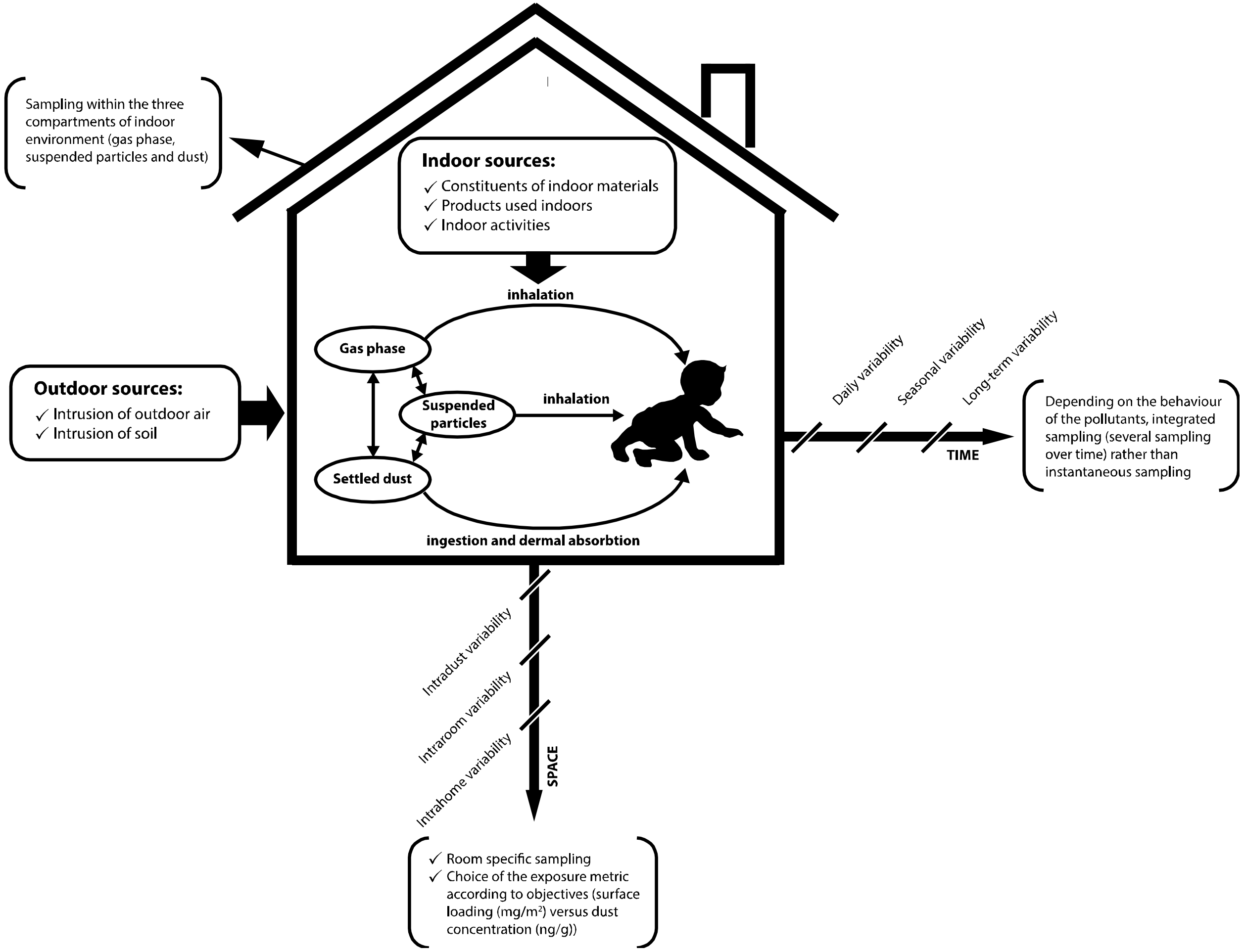


Figure 2.1 *Critical points to be considered when sampling indoor dust for exposure assessment purposes adapted from* (Mercier et al., 2011)

2.1 Chemicals

Most of the native analytes (TnBP, TCEP, TCIPP, TPHP, EHDPP, TBEOP, TDCIPP, TMPP) used in this project were supplied by Chiron, Norway. TnBP, TPHP and TMPP were purchased as stock solutions in iso-octane, while TDCIPP was only available as a stock solution in methanol. Stock solution concentrations were at 1 mg/mL. Neat TCEP, EHDPP, TCIPP, TBEOP were purchased, as no stock solutions were available at the beginning of this project. TEHP was provided neat by Sigma Aldrich, UK.

As those compounds are relatively insoluble (see Chapter 1) in nonpolar solvents, stock solutions were prepared in ethyl acetate at a concentration of 10 mg/mL for TCEP, EHDPP, TCIPP, TEHP and TBEOP, with subsequent dilutions prepared in iso-octane.

D_{15}-TPHP and d_{27}-TBP, which were used as internal standards, were purchased neat from Sigma Aldrich, UK with 10 mg/mL stock solutions prepared in iso-octane.

TAP, which was used as a recovery standard was provided by TCI Europe, Belgium. Standard details are provided in Table 2.1.

Table 2.1 *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	99.9
Tris(2-chloroethyl) phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	285.49	98.8
Tris(2-chloroisopropyl) phosphate	TCIPP	$C_9H_{18}Cl_3O_4P$	327.57	N/A
Triphenyl phosphate	TPHP	$C_{18}H_{15}O_4P$	326.29	99.8

Compound	Abbreviation	Molecular formula	Molecular weight	Purity (%)
2-Ethylhexyl diphenyl phosphate	EHDPP	$C_{20}H_{27}O_4P$	362.41	91.2
Tris(1,3-dichloroisopropyl) phosphate	TDCIPP	$C_9H_{15}Cl_6O_4P$	430.91	90.9
Tricresyl phosphate	TMPP	$C_{21}H_{21}O_4P$	368.37	>98.5
Tris(2-ethylhexyl) phosphate	TEHP	$C_{24}H_{51}O_4P$	434.65	N/A
Tris(2-butoxyethyl) phosphate	TBOEP	$C_{18}H_{39}O_7P$	398.48	95.8
Internal Standards				
Tri-n-butyl phosphate d_{27}	D_{27} TnBP	$C_{12}D_{27}O_4P$	293.48	98
Triphenyl phosphate-d_{15}	D_{15} TPHP	$C_{18}D_{15}O_4P$	341.38	98
Recovery Standard				
Triamylphosphate	TAP	$C_{15}H_{33}OP$	308.21	98

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, UK. Nitrogen used for solvent evaporation was oxygen free and supplied by BOC Gases, UK.

Even though included in the initial purchase of standards and also included in the vapour pressure analysis (see Chapter 3) TBEOP and TEHP were not determined in indoor dust samples in this study. TBEOP was excluded due to poor reproducibility exemplified by the highly inconsistent concentrations detected for this compound in SRM2585. It is known in the literature that TBEOP is problematic to analyse and its reported concentrations in SRMs are inconsistent in the literature (Brandsma et al., 2013). Concentrations of TEHP in dust are not reported here due to interferences with the qualifier ion (m/z 99). Problems with this ion are known in the literature due to its unspecificity as it is simply protonated phosphoric acid (H_4PO^{4+}), which does not give any further information about the R-group of the phosphate ester concerned (Ma and Hites, 2013). Furthermore the next suitable ion m/z 211 is insufficiently abundant (Brandsma et al., 2013). It was therefore just recently suggested to employ PCI for TEHP due to the fact that the $(M+H)^+$ ion produced is both abundant and interference problems are non-existent. (Ma and Hites, 2013) Unfortunately, PCI facilities were not available for use in this study at the time of analysis.

2.1.1 Sampling

UK dust sampling took place in Birmingham, the second most populous city in the UK, while German living room and car dust samples were taken from a wide range of locations throughout the country. Figure 2.2 shows the different sample locations in Germany. Dust samples in Australia originated from a number of locations, with main focus on the conurbations of of Brisbane and Sydney.

Figure 2.2 *Sampling locations in Germany*

2.1.1.1 Sampling procedure

Dust samples in the UK were collected using a corded handheld Black and Decker vacuum cleaner for indoor dust samples while a battery powered Black and Decker Flex was used to collect the car dust samples. Both vacuum cleaners were chosen to provide the most flexibility for the researcher, especially while carrying the sampling equipment on public transportation. Samples in Australia and Germany were collected with the sample donor's own vacuum cleaner. Most of the samples in Australia were provided directly by the room occupant ("dust-donor" samples). The dust-donor was provided with the sampling protocol and a sampling kit. Appendix 1 show the sampling protocol and sampling kit provided to the participants. Participants were also asked to fill out a questionnaire about putative sources of PFR contamination in the sampled microenvironment. The questionnaire given to participants is supplied as Appendix 2 - Appendix 6. Questionnaires for German participants were provided in German.

To reflect actual human exposure to PFRs, the sampling process was conducted under normal room conditions. Sampling in homes, offices, and cars was conducted according to clearly defined existing standard protocols used in previous studies of settled dust contamination (Harrad et al., 2008a). As there was no existing defined sampling protocol available for couch and mattress samples, the standard protocol was slightly adjusted for these microenvironments.

In carpeted rooms (living rooms, offices and bedrooms), 1 m^2 of carpet was vacuumed for 2 min while in rooms with bare (e.g. wooden or tiled) floors, a 4 m^2 area was vacuumed. In cars, only the seats and dashboard area were vacuumed for 2 min, while couch samples were acquired by vacuuming the couch for 2 min. Mattress samples were obtained by vacuuming the whole upper mattress area with linen removed but with mattress protector in place (if applicable). Car dust samples were collected by vacuuming the dashboards and seats only. Car floors were not included in the sampling process. Exact sampling areas are illustrated in Figure 2.3.

Table 2.2 *Dust collection protocol according to surface type*

Surface	**Area (m^2)**	**Time (min)**
Carpet (wall-to- wall)	1	2
Rug (larger than 1 m^2)	1	2
Bare floor	4	4
Car	N/A	2
Mattress	N/A	2
Couch	N/A	2

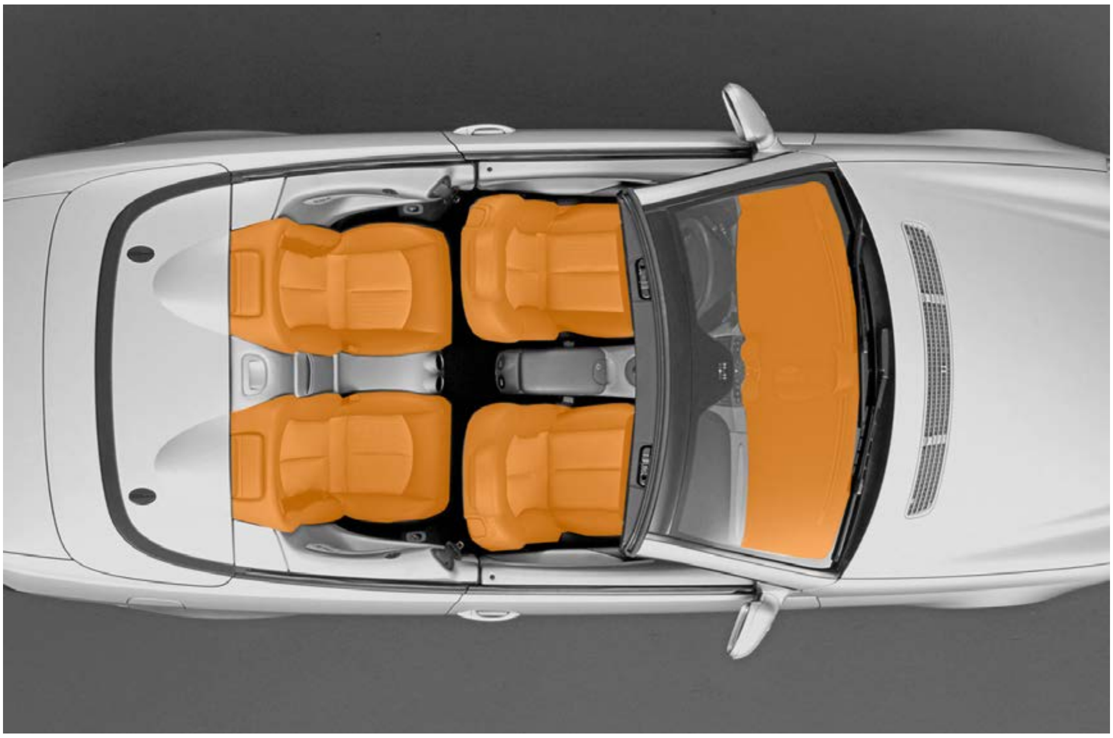


Figure 2.3 *Dust collection area for vehicles (highlighted regions)*

Samples were collected using a nylon sample sock (25 μm pore size, supplied by Allied Filter Fabric Pty Ltd, Australia), inserted within the furniture attachment of the vacuum cleaner. The sampling socks were closed after sampling with a twist tie, sealed in a plastic bag and stored in the dark at 4˚C.

The furniture attachment was cleaned thoroughly before and after sampling using a disposable baby wipe.

Classroom samples in Australia were collected by the Australian collaborator according to the same protocol used for the collection of living room dust samples. To obtain a larger dust mass and to be representative throughout a classroom, each classroom sample consists out of two separate one m^2 samples which were combined during the sieving process to achieve a single sample.

Sampling locations for the Australian classroom dust samples were located via acquaintances of the dust collector. Dust samples from UK classrooms were collected between March 2008 and March 2009 by former members of the POPs research group at Birmingham University (Harrad et al., 2010a) A list of the microenvironments sampled in this study is given in Table 2.3.

Table 2.3 *Numbers of dust samples analysed in this project*

Country	**Living room**	**Office**	**Couch**	**Mattress**	**Car**	**Classroom**	**Bedroom**
Germany	22	25			19		
UK	32	61	10		21	28	
Australia	42		41	57	39	28	11
Canada	14						
Kazakhstan	9	8					

Samples were sieved though an acetone rinsed 500 µm mesh aluminium sieve. Hair and long fibres were removed with acetone rinsed tweezers. After sieving, samples were weighed, stored in glass jars, closed with aluminium foil-lined lids and placed back into the cold room (4 °C) until extraction.

2.2 Extraction

Approximately 50 mg of dust was weighed accurately into an acetone pre-washed glass test tube and fortified with 100 µL ISTD solution (100 ng of d_{27}TBP and d_{15}TPHP). Two mL hexane/acetone (3:1 v/v) was added, the mixture vortexed for 1 min, sonicated for 5 min and vortexed for a further minute. The extract was then centrifuged at 2000 g for 2 min and the supernatant transferred into an acetone pre-washed glass test tube. The extraction process was repeated twice and all supernatants combined. The solvent was evaporated to incipient dryness under a gentle stream of nitrogen and redissolved in 1 mL hexane. The extract was transferred to a pre-cleaned (8 mL MeOH and 4 mL hexane) 1 g non-proprietary Florisil column. The first fraction (containing PBDEs) was eluted with 8 mL hexane (this fraction was only retained for the Australian school and some German dust samples). PFRs were eluted with 10 mL ethyl acetate. The elute was evaporated under a gentle steam of nitrogen and redissolved in 100 µL iso-octane containing 100 ng of TAP as a recovery standard and injected into the GC.

2.3 GC/MS analysis of PFRs

PFR analysis was conducted on an Agilent 5975C GC/MS fitted with a 30 m DB-5 MS column (0.25 mm id, 0.25 µm film thickness). Helium was used as carrier gas with a constant flow rate of 1.0 mL/min. The injector temperature was set at 290 °C under splitless conditions and the MS operated with a solvent delay of 3.8 min. The ion source, quadrupole and interface temperatures were set at 230 °C, 150 °C and 300 °C respectively. The GC temperature programme was 90°C, hold for 1.25 min, ramp 10 °C/min to 170, ramp 5 °C/min to 240 °C, hold for 10 min, ramp 20 °C/min to 310 °C, hold for 10 min. Resulting total run time was 46.75 min.

The MS was operated in EI mode and selected ion monitoring (SIM) mode was applied. An overview of selected Ions, which were monitored for identification and quantification purposes, can be found in Table 2.4.

TnBP, TCEP and TCIPP were quantified against d_{27}TnBP, while d_{12}TPHP was used to quantify TDCIPP, TPHP, EHDPP and TMPP. Dwell times were 30 ms for each ion.

Purchased standards of TCIPP, TDCIPP and TMPP contained different isomers. The commercial TCIPP mixture consists of 3 different isomers. As the third eluting isomer has a markedly lower response than the others, it can only be seen at higher concentrations. Due to this fact it is common practice to report TCIPP levels only as a sum of the 1st two eluting isomers only (referred to as TCIPP 1 and TCIPP 2) (Brandsma et al., 2013). This practice is adopted in this study. Where elevated concentrations of TCIPP were present, TCIPP 3 was used as an additional quality control step to confirm the elevated TCIPP concentration in the sample but this isomer is not reported. The commercial TDCIPP mixture consists of 2 different isomers with both reported. Hence reported TDCIPP concentrations in this study are the sum of both isomers. Similarly, four different peaks are distinguishable (referred to as TMPP1, 2, 3, and 4) in the commercial TMPP mixture when analysed via GC. TMPP concentrations in this study are therefore reported as the sum of these 4 peaks. At the outset of this study, standards for individual TMPP isomers were not available, and it is thus not possible to distinguish whether any of the 4 peaks represent any of the more toxic *o*-TMPP isomers.

Table 2.4 *Ions (m/z) monitored for PFRs*

Compound	**Quantification Ion**	**Identification Ion**
TnBP	211	155
TCEP	249	251
TCIPP 1	277	279
TCIPP 2	277	279
TPHP	326	325
TBEOP	299	199
TDCIPP 1	381	379
TDCIPP 2	381	379
EHDPP	251	250
TEHP	211	99
TMPP 1	368	367
TMPP 2	368	367
TMPP 3	368	367
TMPP 4	368	367
D_{27} TnBP	103	167
D_{15} TPHP	341	339
TAP	239	169

Figure 2.4 displays the elution order of the standards, while Figure 2.5 shows a sample with PFR concentrations at the lower end of the range observed in this study. Finally, Figure 2.6 shows a sample chromatogram with elevated EHDPP levels.

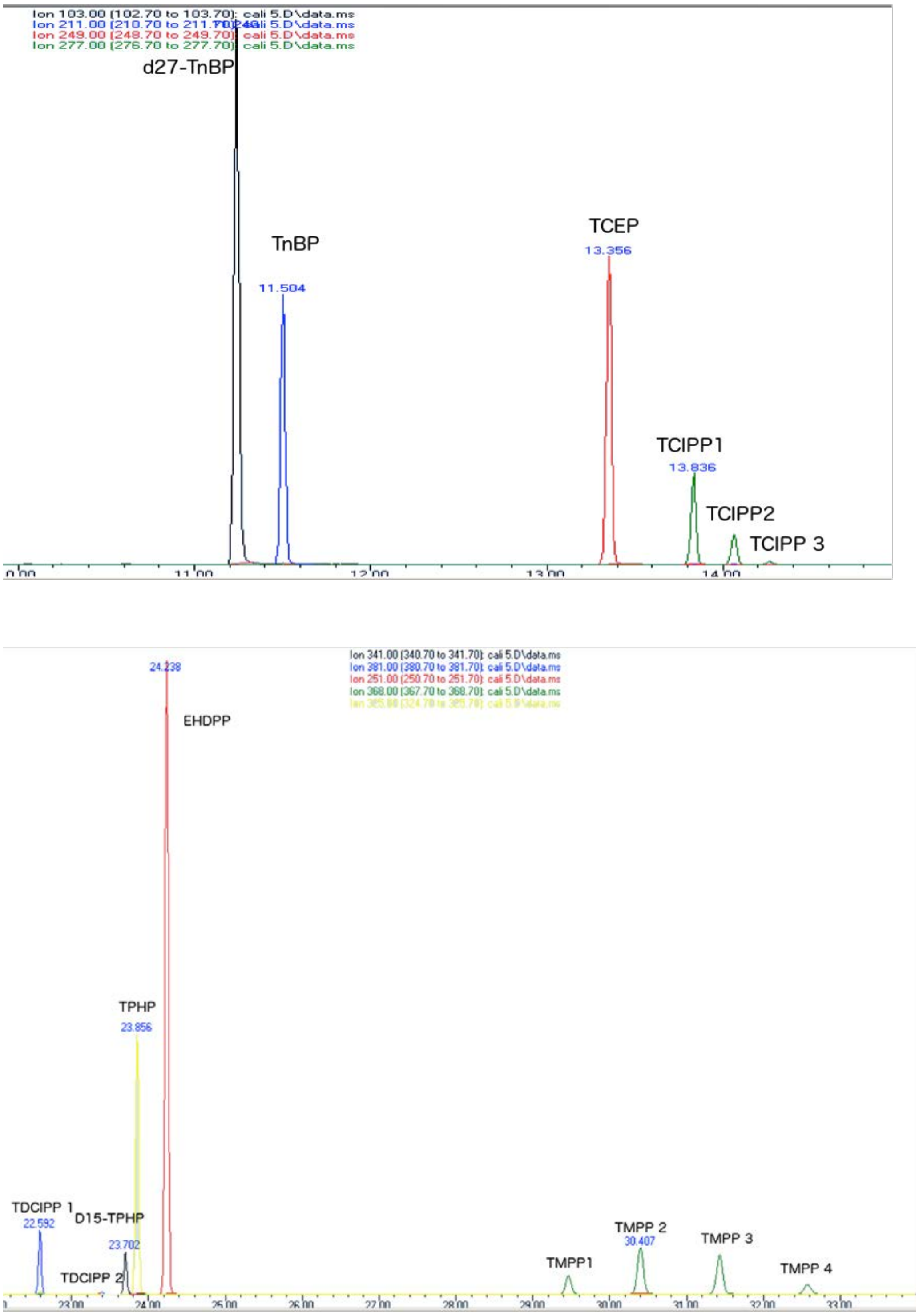


Figure 2.4 *Elution order of standards*

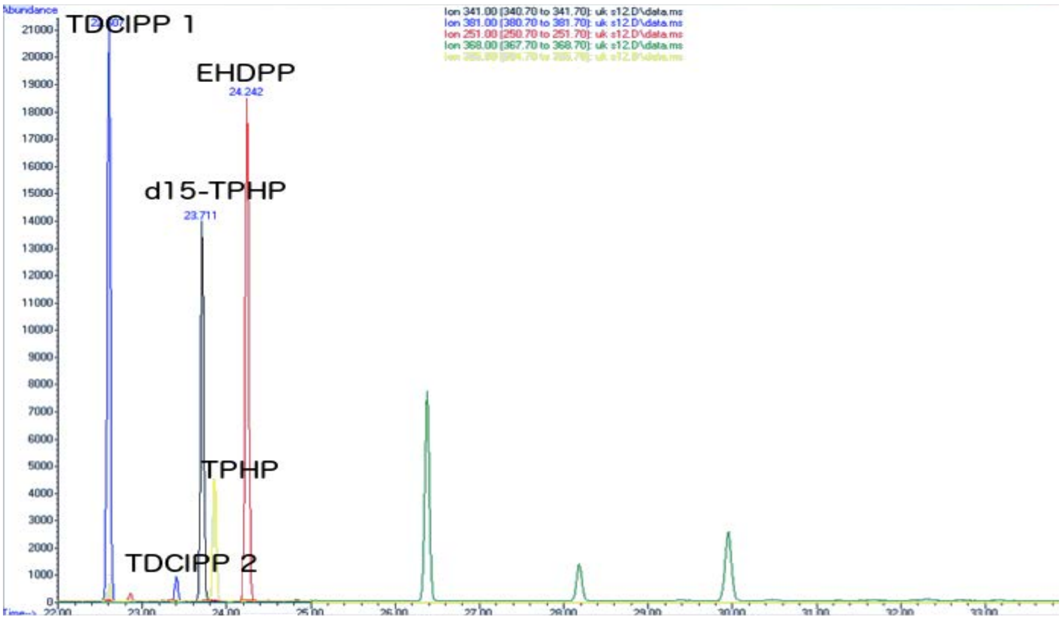


Figure 2.5 *Example chromatogram of a school dust sample with comparatively low PFR contamination*

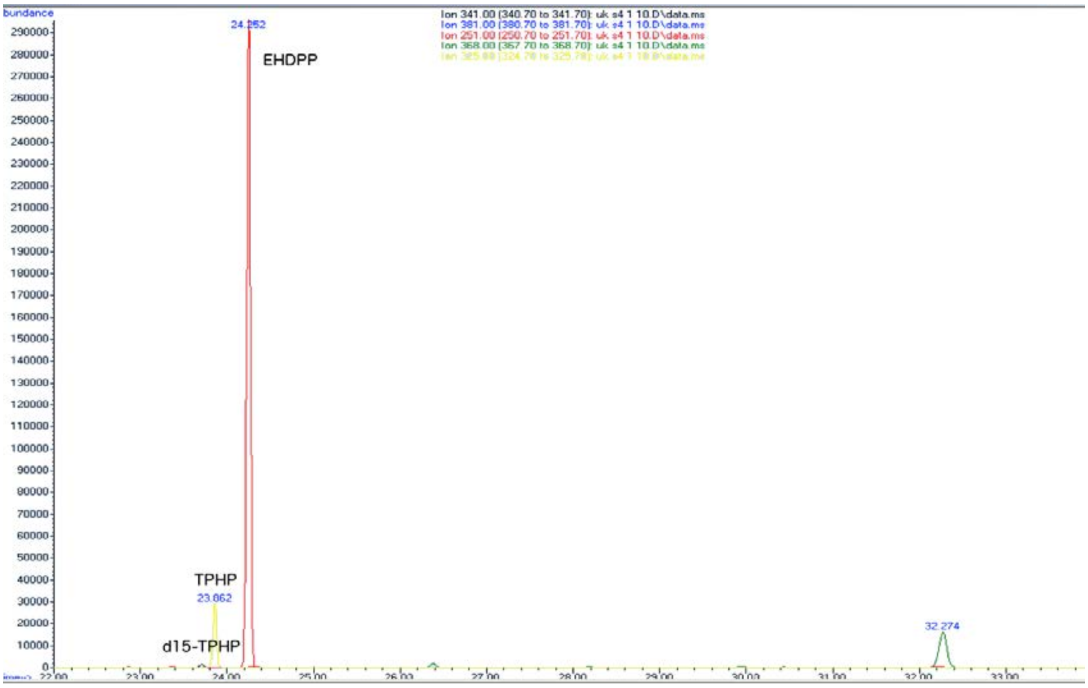


Figure 2.6 *Example chromatogram of a school dust sample with comparatively high PFR contamination (final extract 1/10 dilution to avoid EHDPP overload)*

2.4 Quality Assurance/Quality Control

The GC-MS was calibrated at the beginning of each sample batch analysed, and after any instrument shutdown and maintenance. Initially, a seven point calibration was conducted. The calibration point concentrations used were 0.05, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 ng/µL. Subsequently, continuing calibration for each sample batch run on the GC-MS was achieved by determining the RRFs for each analyte for one of the calibration standards (e.g. 1.0 ng/µL). This continuing calibration was conducted at the start and the end of each sample batch. Continuing calibration was considered successful provided that the RRFs determined were within ±25% of those determined in the initial calibration. Daily calibration data were used to derive relative response factors (RRFs) for each individual native compound (NAT). The RRF compares the response (peak area) of the NAT with that of the corresponding internal standard (IS) for the respective concentrations (c) of each analyte. The algorithm to calculate RRFs is given as Equation 2.1 with RRF values for each native standard given in Table 2.5

Equation 2.1

$$\mathbf{RRF} = \frac{\mathbf{A_{NAT}}}{\mathbf{A_{IS}}} \times \frac{\mathbf{c_{IS}}}{\mathbf{c_{NAT}}}$$

Calculated RRFs for each standard compound should be essentially identical at each concentration level of native standard. Ideally, the relative standard deviation (i.e. $(\sigma_{n-1}/\text{average})\times 100\%$) of RRFs derived at each of the concentration levels should not exceed 10% for each target compound.

The mass of the analytes in a sample was calculated using Equation 2.2. RRF_{STD} is the relative response factor calculated with Equation 2.1 while M_{IS} represents the mass of the internal standard added to the sample and M_S the sample mass.

Equation 2.2

$$\mathbf{Mass} = \frac{\mathbf{A_{NAT}}}{\mathbf{A_{IS}}} \times \frac{\mathbf{1}}{\mathbf{RRF_{STD}}} \times \frac{\mathbf{M_{IS}}}{\mathbf{M_S}}$$

Table 2.5 *Relative response factors for all native standards*

Calibration Standard (ng μL^{-1})	**TnBP**	**TCEP**	**TCIPP 1**	**TCIPP 2**	**TDCIPP 1**	**TDCIPP 2**	**EHDPP**	**TPHP**	**TMPP 1**	**TMPP 2**	**TMPP 3**	**TMPP 4**
0.05	9.44	10.8	3.95	1.27	23.2	nd	284	147	15.3	36.5	32.6	9.61
0.20	8.95	9.64	3.44	1.09	22.8	0.69	270	146	14.4	37.3	32.4	8.76
0.5	9.17	11.0	3.51	1.15	24.7	0.64	294	150	15.4	40.9	35.3	9.80
1	9.15	11.3	3.47	1.16	25.2	0.63	305	152	15.1	40.5	34.9	9.58
2	9.26	11.7	3.54	1.14	26.7	0.79	317	156	16.8	42.9	36.6	9.74
5	9.30	11.9	3.54	1.19	27.5	0.73	321	154	16.0	43.2	37.3	10.2
10	8.90	11.7	3.44	1.15	27.5	0.73	319	148	16.3	43.5	37.7	10.4
Mean	9.17	11.2	3.56	1.16	25.3	0.70	301	150	15.6	40.7	35.3	9.73
Stdev	0.19	0.78	0.18	0.05	1.94	0.06	19.7	3.77	0.79	2.84	2.13	0.53
RSD	2.10	7.00	5.09	4.68	7.65	8.45	6.53	2.50	5.05	6.99	6.04	5.48

- TCIPP levels are reported as the sum of TCIPP 1 and TCIPP 2; TDCIPP levels are reported as the sum of TDCIPP 1 and TDCIPP 2; TMPP levels are reported as the sum of TMPP 1, TMPP 2, TMPP 3 and TMPP 4
- TnBP, TCEP and TCIPP were quantified with TBP; while TPHP was used for TDCIPP, TPHP, EHDPP, TMPP
- Nd = not detected

2.4.1 Internal Standards

Due to the fact that the number of suitable commercially available isotope-labelled standards was very limited at the start of this study, only two deuterated standards were employed in this project. Use of internal standards obviates the need for correction for analyte recovery when calculating concentrations in the samples. However for QA/QC purposes recoveries of internal standards were still measured. For each IS an acceptable recovery was deemed to lie between 30 and 150%. Note that factors such as matrix effects, mean that the recovery of the IS can exceed 100%. In addition to the IS recovery falling within this range, the signal:noise ratio of the IS must exceed, as a minimum, 20:1, to be considered valid. IS recoveries for all samples in this study are summarised in Table 2.6. In cases where a sample was identified to have an IS recovery outside the acceptable range it was discarded and the sample re-extracted and analysed again.

Table 2.6 *Internal Standard recovery from dust samples analysed in this study (%)*

Standard	n	Mean	Median	Range	Stdev	RSD
D_{27} TnBP	598	77	77	36-133	19	24
D_{15} TPHP	598	89	91	34-139	16	18

2.4.2 Precision and on-going method performance

QA/QC for the entire method was checked via analysis of at least one aliquot of SRM 2585 (provided by National Institute of Standards and Technology (NIST), purchased from Greyhound Chromatography and Allied Chemicals, UK) per sample batch. As there were no certified values available for SRM 2585, this SRM was initially analysed as 5 replicates and the values obtained compared to literature data. Concentration data obtained for the SRM aliquot analysed with each sample batch subsequently was required to fall within 30% of the average values obtained from the initial replicate analyses.

SRM 2585 was used as a test sample for an interlaboratory study in early 2013. The interlaboratory study of PFRs gave also another quality check for the results obtained with this method. The values obtained in our study were - with the exception of TnBP - within the ranges obtained in the interlaboratory study. (Figure 2.7). This is of some mild interest as TnBP values reported in this study fell within those reported previously in the literature. Specifically, (Bergh et al., 2012)'s reported value for TnBP was 0.19 ± 0.02 µg/g, while (Van den Eede et al., 2011b) reported the concentration of this PFR in SRM2585 to be 0.18 ± 0.02 µg/g. While overall, our data for SRM2585 agree well with values reported elsewhere, the uncertainty over TnBP, underlines that certified values for PFRs are urgently required in both dust and other environmental matrices.

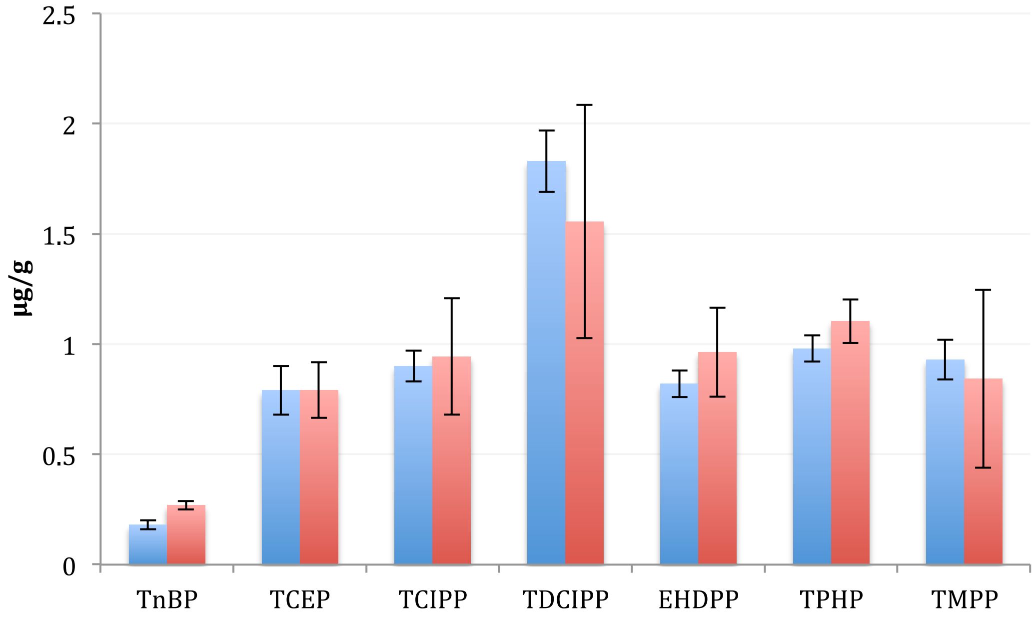


Figure 2.7 *Comparison of SRM 2585 values obtained in this study (blue) versus the interlaboratory study (red)* (Brandsma et al., 2013)

Table 2.7 *PFR concentrations detected in SRM2585 in this study (µg/g)*

SRM (n=57)	**TnBP**	**TCEP**	**TCIPP**	**TDCIPP**	**EHDPP**	**TPHP**	**TMPP**
Mean	0.18	0.79	0.90	1.83	0.82	0.98	0.93
Minimum	0.15	0.65	0.76	1.48	0.70	0.81	0.79
Maximum	0.22	1.00	1.04	2.05	0.93	1.1	1.1
SD	0.02	0.11	0.07	0.14	0.06	0.06	0.09
%RSD	10	14	7.8	7.9	7.1	6.4	10

2.4.2.1 Blank contamination

At least one blank was run with every sample batch (thus every 6th sample was a blank). A blank sample consisted of pre-baked Na_2SO_4 treated as sampled dust. Na_2SO_4 was introduced from the sieving step in the lab and further on treated thereafter. Additionally to that, field blanks were collected for samples taken in living room, car and couch samples collected in Birmingham. Due to logistics no field blanks were taken in Australia and Germany. Field samples consisted of pre-baked Na_2SO_4, which was taken to the sample location, spread on aluminium foil and vacuumed into a sock and treated as a normal sample from there on. As Canadian and Kazakhstani dust samples were archived dust samples collected by a previous group member no field blanks were available for those samples as well. Acceptable blank concentrations were deemed those where the concentration of the target analyte was less than 5% of the lowest concentration in that batch. Where the analyte concentration in the blank fell between 5% and 20% of the concentration in samples from that batch, concentrations were corrected accordingly via subtraction of the blank concentration. If blank concentrations exceeded 20% of those in samples from the same batch, all samples in that batch were discarded and reanalysed. Even though utmost care was taken not to contaminate samples, e.g. baking all glassware and prepared columns before use at 450 °C for 6 hours; concentrations of TCEP, TCIPP and TPHP were detected frequently in blanks. When TPHP was detectable in blanks, concentrations were usually close to the LOQ, while those of all other target analytes were below the LOQ. As no significant differences were seen between the field blank and laboratory blanks, it appears that contamination with PFRs may occur at some point during handling in the laboratory.

Table 2.8 *Dust sample blank concentrations (ng/g); assuming 50 mg of dust analysed*

Compound	**N**	**Mean**	**Median**	**Range**	**Stdev**	**RSD (%)**
TnBP	107	<34	<34	<34	-	-
TCEP	107	28	23	<17-95	20	72
TCIPP	107	67	30	<11-385	87	130
TPHP	107	13	6	<6-81	18	135
EHDPP	107	<3	<3	<3	-	-
TDCIPP	107	<29	<29	<29	-	-
TMPP	107	<11	<11	<11	-	-

2.4.2.2 Determination of Detection Limits

Table 2.9 reports the instrument limit of detection (LOD) and sample limit of quantification (LOQ) for each individual PFR. LODs are defined as the quantity of analyte, which provides a signal to noise ratio of 3:1.

The LOQ was determined as the lowest measurable concentration in the extracted sample, 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). It is calculated according to Equation 2.3.

Equation 2.3

$$\mathbf{LOQ} = \frac{\mathbf{LOD \times FEV}}{\mathbf{SS \times VFEI}} \times \frac{\mathbf{100}}{\mathbf{\%IS\ Rec}}$$

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

In the majority of cases, LOQs were not exceeded by the blank concentrations. In cases where the blank contained detectable (but acceptable – see 2.4.2.1) levels, an effective LOQ (also called the Minimum reported value, MRV) was calculated as the mean PFR concentration plus 3 times the standard deviation of the PFR concentrations detected in the 10 blank samples containing quantifiable concentrations. This MRV was used instead of the LOQ for those samples (see Table 2.10).

In samples where concentrations were below the LOQ/MRV, half the LOQ/MRV was used as the concentration for the purposes of calculating descriptive statistics.

Table 2.9 *Instrument and sample detection limits in this study*

Compound	LOD (pg/injection)	LOQ (ng/g)	MRV (ng/g)
TnBP	12	34	
TCEP	6	17	56
TCIPP	4	11	46
TPHP	2	6	10
EHDPP	1	3	
TDCIPP	10	29	
TMPP	4	11	

Table 2.10 *Calculation of MRV values (ng/g) for TCEP, TCIPP, and TPHP)*

	TCEP	TCIPP	TPHP
Blank 1	29.1	23.2	1.3
Blank 2	29.2	29.0	2.1
Blank 3	0.0	0.9	2.0
Blank 4	25.5	13.2	3.0
Blank 5	27.0	27.8	1.9
Blank 6	30.3	8.7	8.2
Blank 7	28.6	10.8	5.3
Blank 8	18.8	24.5	5.1
Blank 9	35.3	17.6	3.4
Blank 10	24.9	17.3	3.6
Mean	24.9	17.3	3.6
SD	10.3	9.6	2.2
3 x SD	30.9	28.8	6.7
MRV	56	46	10

In case of concentrations being below either LOQ or MRV half the LOQ/MRV was used as the concentrations of PFRs in samples for the purposes of calculating descriptive statistics.

2.5 Determination of vapour pressures of PFRs

PFRs, retention time reference compounds HCB or *p,p'*-DDT, and other calibration compounds were co-chromatographed according to previously described techniques (Hinckley and Bidleman, 1990; Bidleman, 1984) during a placement at the laboratories of Environment Canada/ University of Toronto, Canada. Samples of 1 to 2 µL (≈2 ng PFR on column) in isooctane were injected in splitless mode on a DB-1 capillary column (1.0 m x 0.25 mm i.d., 0.25 µm film, J & W Scientific, USA) installed in an Agilent 6890N GC - 5973 Mass Selective Detector (MSD). Injector and detector temperatures were 220°C. Isothermal runs were made between 60 to 90 °C for TCEP and TCIPP and 110 to 140 °C for other PFRs. Flow rates varied between 1 to 5 mL min^{-1}, the faster flow rates were used for the lower temperature runs, as reported previously (Bidleman et al., 2003). Data was collected using Agilent Chemstation.

2.6 Statistical analysis

To examine the data resulted from this study, a variety of statistical analyses were conducted, to e.g. compare concentrations and relative abundances of PFRs between different microenvironments and countries (see Chapter 4 and 5). As datasets were highly skewed and arithmetic mean values would be misleading due to being driven by a small number of highly elevated concentrations; median concentrations were preferred for direct comparison. Nevertheless, in some cases (especially when comparing to literature data) it was not possible to use median concentrations, as the literature only reported arithmetic mean values. To show the overall distribution of the data, interquartile ranges are also reported.

T-test analysis and analysis of variance (ANOVA) were applied as appropriate, to data sets for testing of significant differences between arithmetic means. Due to the fact that the data were highly skewed (tested via Shapiro-Wilk test) such tests were conducted on log transformed data. In addition, principal component analysis was used when assessing differences in contamination patterns between sample groups of different origins (e.g.

country, microenvironment etc.). Statistical analysis of data was conducted using a combination of Microsoft Excel for Mac (Microsoft Office for Mac 2011) and SPSS for Mac (version 21.0). The minimum confidence limit was set to 95% (i.e. significant level (p) = 0.05) even though a higher significance level of 99 % was reported if determined in the data set.

Furthermore, questionnaire data was used to collect data on potential sources of PFRs and other factors that might influence PFR concentrations in indoor environments, e.g. number of electronics, building age, presence/absence of carpet, and cleaning interval etc.. The questionnaires used are included as Appendix 2 to Appendix 6.

3 DETERMINATION OF PFR VAPOUR PRESSURES VIA THE GC RETENTION TIME METHOD

3.1 Introduction

Examination of the existing literature reporting vapour pressures at 298 K/ 25°C (p_{298}) of PFRs reveals substantial disparities between values reported by different studies for the same compounds. Moreover, many of the available data are estimates derived via application of predictive algorithms, with further problems arising from the fact that even different versions of the same predictive software can generate different estimated values of vapour pressure for the same PFR. Against this backdrop, there is a clear need for experimental measurements of PFR vapour pressures. Hinckley and Bidleman (1990) applied the GC retention-time (GC-RT) method to determine p_{298} of seven organophosphate insecticides and three PFRs (TEHP, TBOEP and p-TMPP). Resulting p_{298} values fell within the 95% confidence interval of some literature values, but overestimated reported p_{298} for others. At that time it was not clear whether the discrepancies were due to systematic overestimation of p_{298} by the GC-RT method for moderately polar compounds (by early elution from the nonpolar stationary phase) (Hinckley and Bidleman, 1990; Bidleman, 1984) or simply inadequacies of the literature database. This chapter will describe the determination of p_{298} and enthalpies of vaporisation ($\Delta_l{}^gH$) of 11 PFRs by the GC-RT method and evaluate the accuracy of the values obtained by comparison to previously reported *in silico* estimates and experimental measurements.

3.2 Theoretical framework underpinning the GC retention time method for determining vapour pressures

Jensen and Schall (1966) initially described the relationship between the retention volumes (V_R) and vapour pressures (p) for two compounds run under the same chromatographic conditions as:

Equation 3.1 $V_{R1}/V_{R2} = t_1/t_2=p_1/p_2$

Where t is the retention time of the substance.

(Hamilton, 1980) pointed out the error in this formula, as the substance with the higher vapour pressure will be first to elute from the column, which leads to:

Equation 3.2 $t_1/t_2=p_2/p_1$

Therefore it follows that:

Equation 3.3 $V_{R1}/V_{R2} =P_2/p_1 = t_1/t_2$

Vapour pressure and latent heat data can be correlated starting off with the Clausius-Clapeyron equation for vaporisation of a liquid (Othmer, 1940):

Equation 3.4 $dp/dT = L /(V-v)T$

where T= absolute temperature (Kelvin) , L= latent heat per mole (J/mol) , V= vapour volume per mole (m^3/mol) and v= liquid volume per mole(m^3/mol).

Under the assumption that the perfect gas law is followed and v is very small compared to V it follows that:

Equation 3.5 $dp/dT = Lp/(RT^2)$

$\Rightarrow$ $1/L \; d \log p = 1/RT^2 \; dT$

This function can also be described over the temperature and pressure range where L can be regarded as constant. (Hamilton, 1980)

This means for substance 1 and 2 at the same temperature:

$$1/L_1 \; d \log p_1 = 1/RT^2 \; dT$$
$$1/L_2 \; d \log p_2 = 1/RT^2 \; dT$$

Equation 3.6 $d \ln p_1 = L_1/L_2 \; d \ln p_2$

It has been shown that this is more useful over a wider temperature range and that especially for related compounds L_1/L_2 will be more or less constant, as their behaviour will follow the same law, which stabilises the remaining quotient. (Othmer, 1940; Hamilton, 1980)

Integration of Equation 3.6 results in:

Equation 3.7 $\log p_1 = L_1/L_2 \log p_2 + c$

With c being a constant

Taking the logarithms of Equation 3.3 it follows that:

Equation 3.8 $\log p_1 = \log p_2 - \log t_1/t_2$

A combination of Equation 3.7 and Equation 3.8 results in:

$$\log p_2 - \log (t_1/t_2) = L_1/L_2 \log p_2 + c$$

Equation 3.9 $\log (t_1/t_2) = (1-L_1/L_2) \log p_2 - c$

Equation 3.3 and Equation 3.9 form the theoretical basis of the GC retention time method. Plotting log (t_1/t_2) versus log p_2 results in a line with a slope (m) of ($1-L_1/L_2$) and an intercept of –c. t_1/t_2 is the ratio of the retention time of the test compound to that of a reference compound (i.e. one for which the vapour pressure is already known) and p_2 the vapour pressure of the reference compound at the given temperature. The ratio of L_1/L_2 is equal to ratio of vaporization enthalpies ($\Delta_l{}^gH_1/\Delta_l{}^gH_2$). The vapour pressure of compound 1 at a given temperature (e.g. 25˚C) can be calculated using the known vapour pressure (p_2) of the reference compound (compound 2) at the same temperature and the slope and y-intercept of the above linear regression.

From Equation 3.3 and Equation 3.9 one can obtain:

$$\log p_{2\ 25\ °C} - \log p_{1\ 25\ °C} = (1-L_1/L_2) \log p_{2\ 25\ °C} - c$$

Equation 3.10
$$\log p_{1\ 25\ °C} = L_1/L_2 \log p_{2\ 25\ °C} + c$$

The GC-RT method has been widely used to determine vapour pressure of organic compounds (Lei et al., 2004; Hinckley and Bidleman, 1990; Koutek et al., 2001; Lei et al., 2002; Bidleman, 1984; Bidleman et al., 2003; Wong et al., 2001; Goel et al., 2007; Lei et al., 1999).

3.3 Results

As previously mentioned in 3.2 this GC method makes the assumption that the infinite dilution activity coefficients in the GC stationary phase are the same for test and reference compounds, and that the ratio of vaporisation enthalpies is constant over the temperature range of measurements (Hinckley and Bidleman, 1990; Koutek et al., 2001), which might not be true. The reference compound is chosen to have well-established $\Delta_l{}^gH_{ref}$ and $p_{\mathrm{ref,T}}$ values over the temperature range of measurements.

Examination of the literature revealed that the range of vapour pressures for our target organophosphate flame retardants may cover up to three orders of magnitude. Such a wide potential range makes the selection of an appropriate reference compound problematic. As a result, two different reference compounds were used and our target PFRs divided into 2 groups: (a) those of higher volatility (TCEP, TCIPP) and (b) those of relatively low volatility (all others). Relative retention times (RRTs) were very reproducible with relative standard deviations for three replicate GC runs averaging 0.2% (Table 3.1)

As described in the literature (Bidleman et al., 2003; Falconer and Bidleman, 1994; Bidleman, 1984) a log-log plot of RRTs of test (x) and reference compounds $(t_x/t_{ref})_T$ versus $p_{\mathrm{ref},T}$ (ref = *p,p'*-DDT or HCB) was made at the different temperatures (*T*) according to Equation 3.9.

To calculate the vapour pressures at different temperatures for HCB the thermodynamically consistent “final adjusted value” (FAV) was used. This, which takes all previously measured physicochemical properties for HCB into account, was 0.094 Pa at 25°C (Shen and Wania, 2005).

The FAV internal energy of phase change for solubility in air ($\Delta_l^{\,g} U_{HCB}$) *is* 65690 J/mol (Shen and Wania, 2005). To convert this internal energy to enthalpy, 2391 J/mol needs to be added (Beyer et al., 2002) and follows to $\Delta_l^{\,g} H_{HCB}$ =68082 J/mol with R = 8.314 J/mol×K.

So the temperature coefficients for the FAV vapour pressure could be calculated according thus:

M value: -68082/(2.303×8.314) = -3556

resulting in

log 0.094 = b- 3556/298.16

➔ b= 10.90

Table 3.1 *Relative retention times ($t_{compound}/t_{reference}$) at different temperatures for analysed compounds*

	140 °C			**130°C**			**120°C**			**110°C**		
Compound	**Average**	**SD**	**RSD**	**Average**	**SD**	**RSD**	**Average**	**SD**	**RSD**	**Average**	**SD**	**RSD**
TDCIPP	0.99	0.003	0.28	1.01	0.002	0.17	1.02	0.003	0.26	1.04	0.003	0.33
TPHP	1.25	0.002	0.13	1.27	0.005	0.37	1.30	0.001	0.08	1.35	0.004	0.29
TBEOP	2.00	0.002	0.08	2.18	0.005	0.24	2.38	0.002	0.09	2.72	0.005	0.18
o-TMPP	2.78	0.003	0.10	2.98	0.013	0.42	3.18	0.002	0.06	3.50	0.009	0.25
TEHP	2.96	0.003	0.10	3.30	0.008	0.25	3.72	0.003	0.09	4.34	0.013	0.30
m-TMPP	3.87	0.002	0.04	4.28	0.012	0.28	4.73	0.001	0.03	5.39	0.009	0.17
p-TMPP	5.41	0.007	0.13	6.07	0.013	0.22	6.81	0.007	0.10	7.89	0.024	0.30
TIPPP	7.08	0.016	0.23	8.10	0.008	0.10	9.27	0.016	0.17	11.01	0.037	0.33

	90 °C			**80°C**			**70°C**			**60°C**		
	Average	**SD**	**RSD**	**Average**	**SD**	**RSD**	**Average**	**SD**	**RSD**	**Average**	**SD**	**RSD**
TCEP	1.41	0.003	0.20	1.55	0.002	0.10	1.74	0.001	0.07	2.10	0.006	0.27
TCIPP	1.76	0.003	0.16	1.99	0.001	0.06	2.31	0.002	0.09	2.89	0.007	0.25

Leading to the final equation of:

Equation 3.11 $\log P_{L\ HCB}\ (Pa) = 10.90 - 3556/T$

where $\log P_{L\ HCB}$ (Pa) = the logarithm of the vapour pressure of HCB at temperature T (in Kelvin)

Equation 3.11 gives $p_{HCB,T}$ that are about 60% of those which were used as reference values (not from FAVs) in the GC-RT determination of P_L for fluorinated chemicals(Lei et al., 2004).

For *p,p'*-DDT a previously established equation (Bidleman et al., 2003) was used, which was based on five reports for the vapour pressure of solid *p,p'*-DDT and four experimental values for the entropy of fusion ($\Delta_s{}^l S_{DDT,m}$/J•mol^{-1}•K^{-1}), which was used to convert solid- to liquid-phase vapour pressure:

Equation 3.12 $\log P_{L\ pp'\text{-}DDT}\ (Pa) = 12.38 - 4665/T$

Resulting values for the plot can be found in Table 3.2 and the plot for compounds measured against HCB and p,p'-DDT given in Figure 3.1 and Figure 3.2. All the resulting values from the measurement against the reference compound are listed in Table 3.3.

Table 3.2 *Log t_R vs. HCB or p,p'- DDT*

Compound/ temperature	**60°C**	**70°C**	**80°C**	**90°C**	**110°C**	**120°C**	**130°C**	**140°C**	**Reference compound**
TCEP	0.323	0.242	0.189	0.149					HCB
TCIPP	0.461	0.363	0.299	0.245					HCB
TDCIPP					0.016	0.009	0.002	-0.002	*p,p'*-DDT
TPhP					0.132	0.114	0.105	0.097	*p,p'*-DDT
EHDPP					0.295	0.255	0.224	0.189	*p,p'*-DDT
TBEOP					0.435	0.376	0.339	0.301	*p,p'*-DDT
o-TMPP					0.545	0.503	0.475	0.445	*p,p'*-DDT
TEHP					0.637	0.570	0.519	0.471	*p,p'*-DDT
m-TMPP					0.732	0.675	0.631	0.588	*p,p'*-DDT
p-TMPP					0.897	0.833	0.783	0.733	*p,p'*-DDT
TIPPP					1.042	0.967	0.909	0.850	*p,p'*-DDT

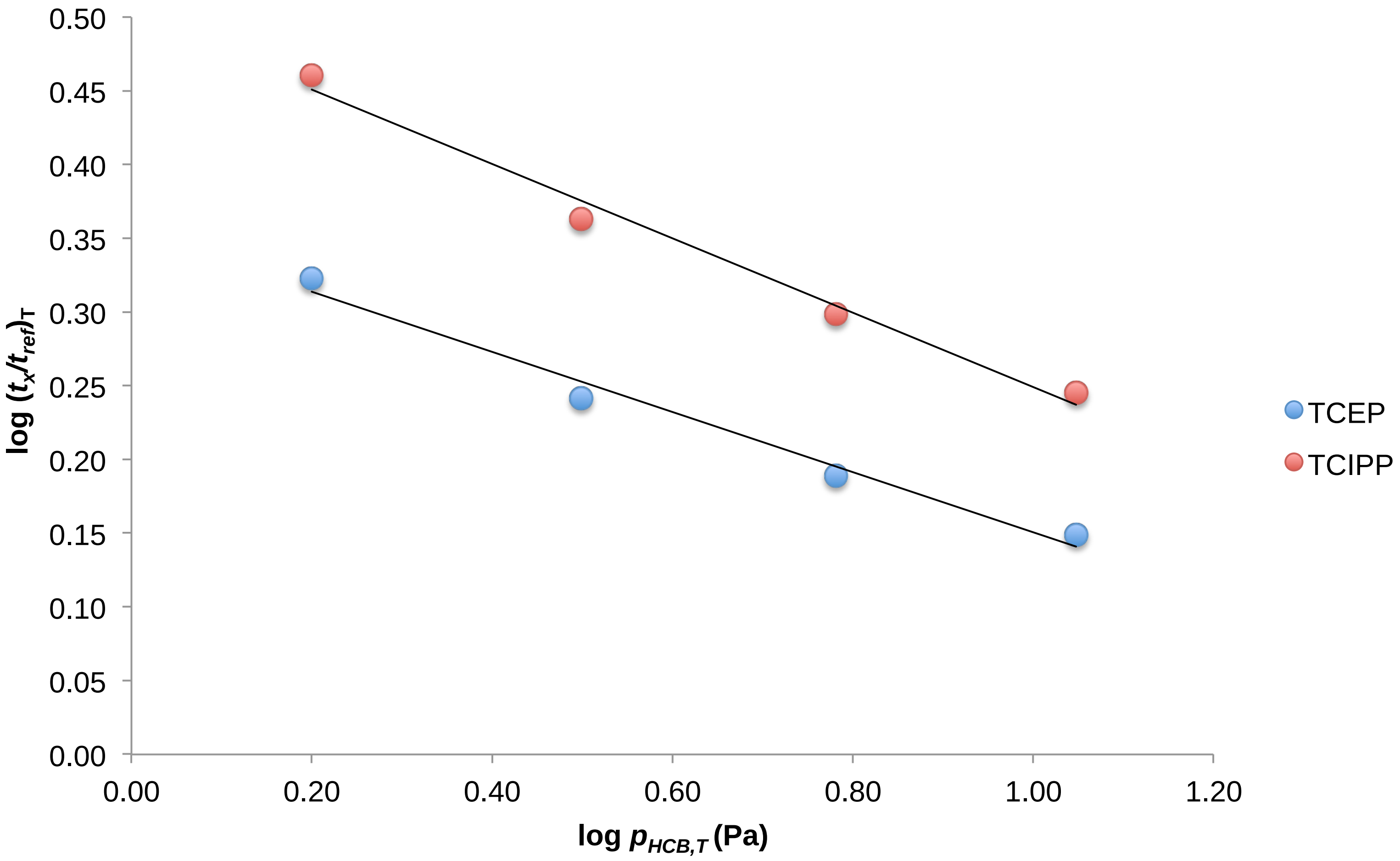


Figure 3.1 *Determination of* $\Delta_l^g H_x / \Delta_l^g H_{HCB}$ *for TCEP and TCIPP*

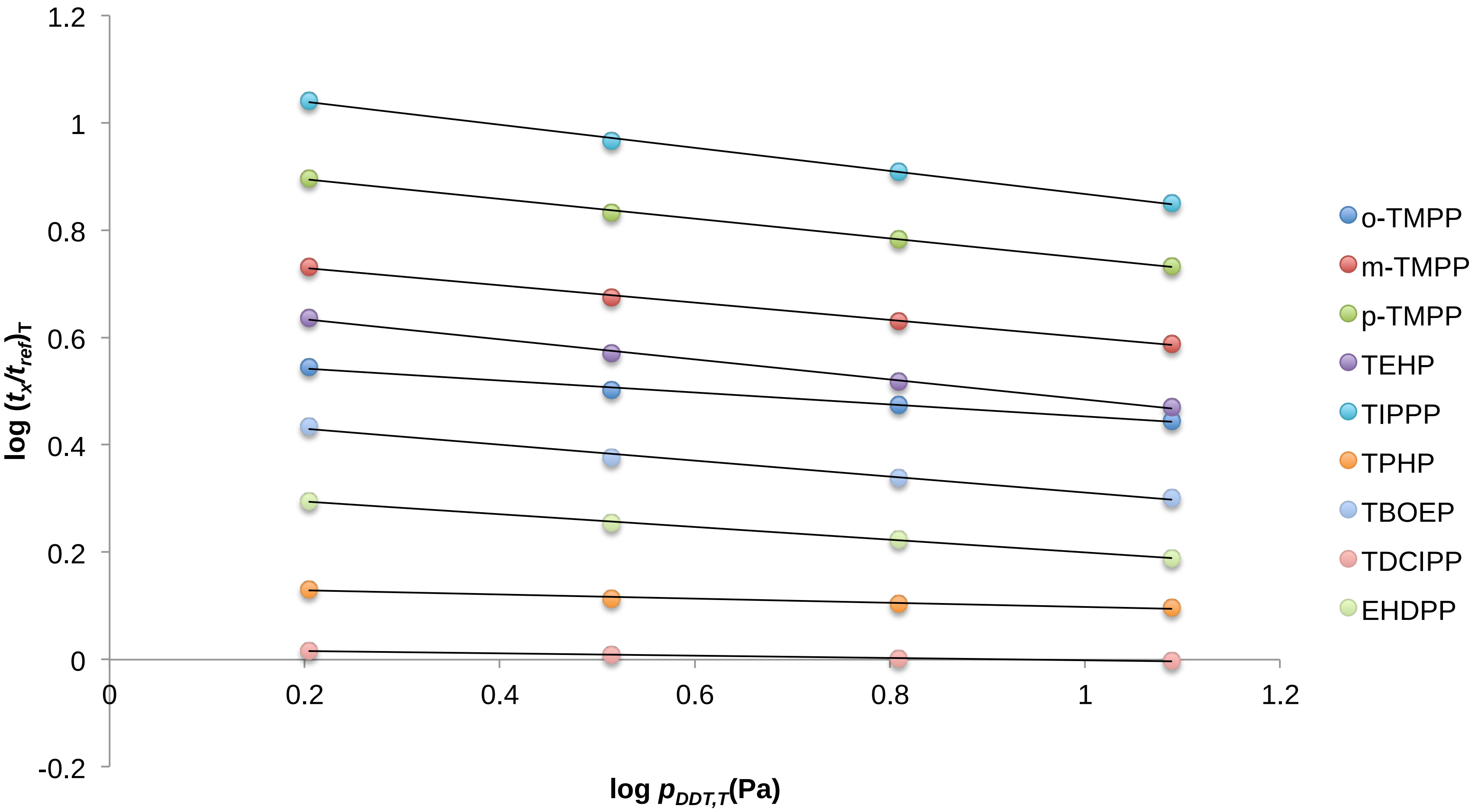


Figure 3.2 *Determination of* $\Delta_l{}^gH_x/\Delta_l{}^gH_{DDT}$ *for other PFRs*

Table 3.3 *GC Data for vapour pressure determination*

Compound	m (1- L_1/L_2)	-C	L_1/L_2	r^2	$p_{GC,298}$ (Pa)
TCEP	-0.204	0.355	1.204	0.981	0.0256
TCIPP	-0.252	0.501	1.252	0.987	0.0163
o-TMPP	-0.111	0.565	1.111	0.995	6.38×10^{-5}
m-TMPP	-0.161	0.762	1.161	0.998	2.78×10^{-5}
p-TMPP	-0.184	0.932	1.184	0.998	1.59×10^{-5}
TEHP	-0.187	0.672	1.187	0.997	2.82×10^{-5}
TIPPP	-0.215	1.083	1.215	0.998	8.87×10^{-6}
TPhP	-0.039	0.137	1.039	0.967	2.95×10^{-4}
TBEOP	-0.149	0.460	1.149	0.991	6.13×10^{-5}
TDCIPP	-0.022	0.020	1.022	0.993	4.39×10^{-4}
EHDPP	-0.119	0.318	1.119	0.998	1.07×10^{-4}

Various studies have shown that the activity coefficient can vary and that such effects require correction. This can be done by making a log-log calibration plot of p_{298} vs. $p_{GC,298}$ for a series of low-polarity compounds (usually polycyclic aromatic hydrocarbons and chlorinated hydrocarbons) for which values of p_{298} have been measured or estimated by methods other than GC-RT(Lei et al., 2004; Hinckley and Bidleman, 1990; Bidleman, 1984; Bidleman et al., 2003; Lei et al., 1999; Wong et al., 2001). In this study two different calibration plots were prepared. FAVs were selected wherever possible.

One plot was made with lower molecular weight compounds Phenanthrene, Anthracene, Pyrene, Fluoranthene, *alpha*-HCH, *gamma*-HCH, *beta*-HCH, and PCB-29 using HCB as a reference compound to determine $p_{GC,298}$. This plot was used to estimate p_{298} of TECP and TCIPP from measured $p_{GC,298}$. and values used can be found in Table 3.4.

The resulting regression equation (r^2 = 0.88) was:

Equation 3.13 $$\text{Log } p_{298}\text{ (Pa)} = 0.718 \log p_{GC,298}\text{ (Pa)} - 0.177$$

Table 3.4 *Values used for the HCB calibration plot*

Compound	Log $p_{GC,298}$ (Pa)	Log p_{298} (Pa)	Reference
Phenanthrene	-1.24	-1.00	(Hinckley and Bidleman, 1990)
Anthracene	-1.28	-1.03	(Hinckley and Bidleman, 1990)
Pyrene	-2.49	-1.84	(Hinckley and Bidleman, 1990)
Fluoranthene	-2.63	-2.20	(Hinckley and Bidleman, 1990)
a-HCH	-0.95	-0.61	(Xiao et al., 2004)
g-HCH	-1.04	-1.12	(Xiao et al., 2004)
b-HCH	-1.19	-1.28	(Xiao et al., 2004)
PCB-29	-1.74	-1.34	(Li et al., 2003)

A second calibration plot (Figure 3.4) based on *p,p'*-DDT as reference compound was made for higher molecular weight compounds *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, PCB-209, benz[*a*]anthracene and benzo[*a*]pyrene. Additionally, the inclusion of log p_{GC} values for 6 compounds (PCB-15, PCB-61, PCB-52, PCB-101, PCB-155 and PCB-202) previously measured (Hinckley and Bidleman, 1990) showed good agreement (r^2 = 0.95). Hence, these values were included in the calibration plot for the PFRs measured with *p,p*'-DDT as a reference compound. The values used for the pp'-DDT calibration plot can be found in Table 3.5.

The resulting regression equation was:

Equation 3.14 $\text{Log } p_{298} \text{ (Pa)} = 1.083 \log p_{GC,298} \text{ (Pa)} + 0.252$

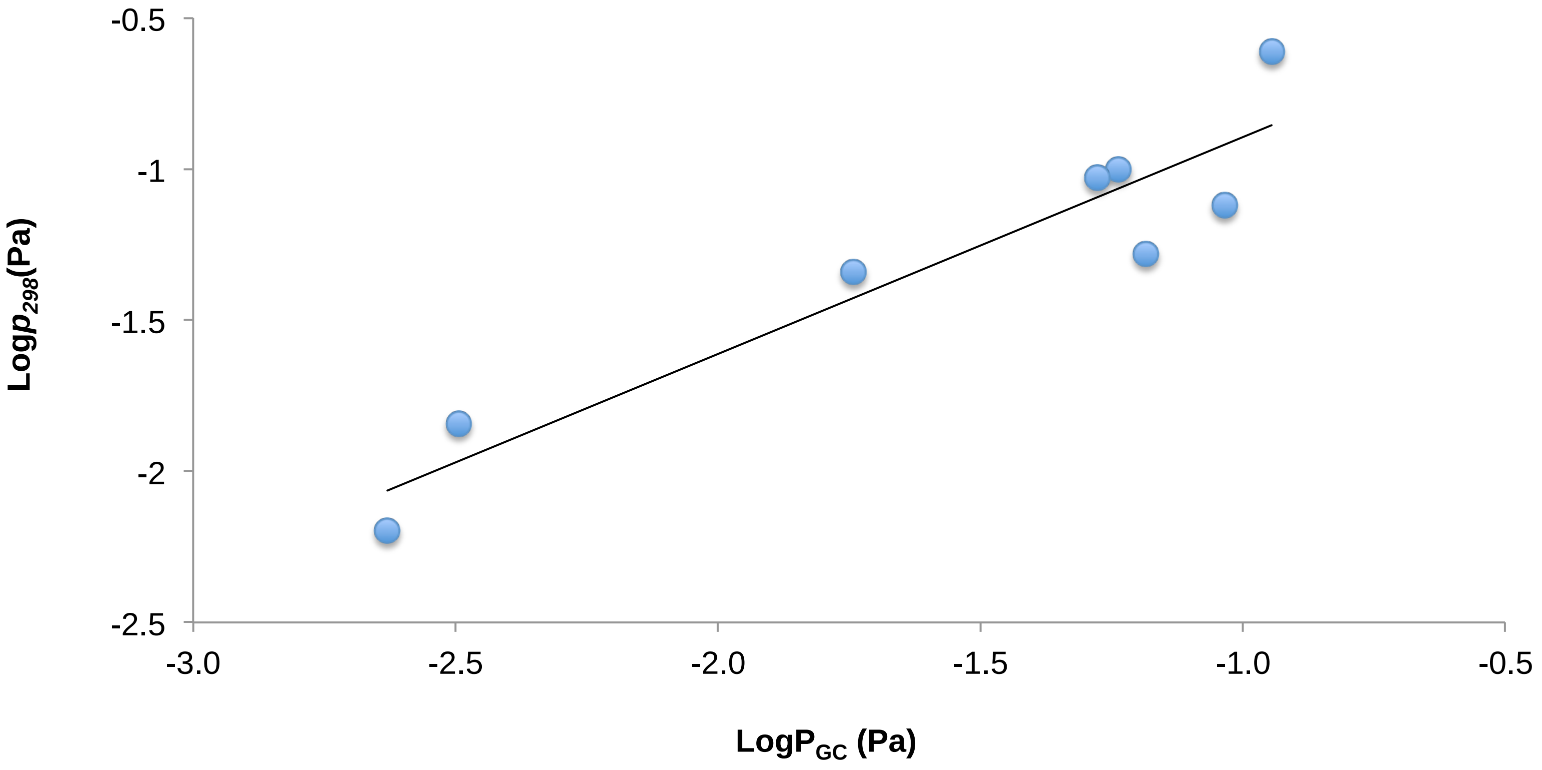


Figure 3.3 *Calibration plot for HCB for estimating* p_{298} *from* p_{GC}

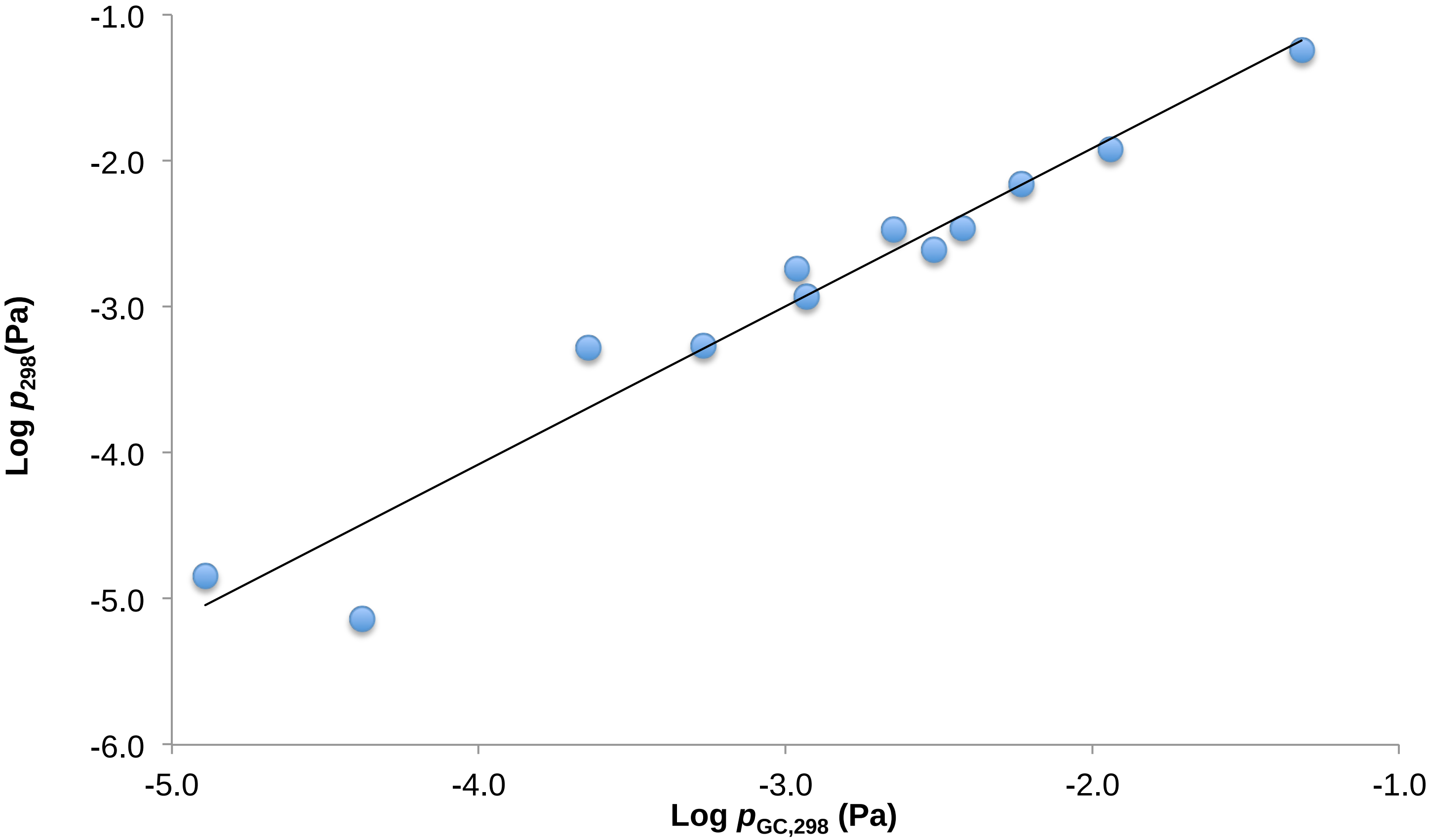


Figure 3.4 *Calibration plot for p,p'-DDT for estimating* p_{298} *from* $p_{GC,\ 298}$

Table 3.5 *Values used for the p,p'-DDT calibration plot*

Compound	Log $p_{GC,298}$ (Pa)	Log p_{298} (Pa)	Reference
PCB-15	-1.32*	-1.24	(Li et al., 2003)
PCB-61	-2.23*	-2.16	(Li et al., 2003)
PCB-52	-1.94*	-1.92	(Li et al., 2003)
PCB-101	-2.52*	-2.61	(Li et al., 2003)
PCB-155	-2.42*	-2.46	(Li et al., 2003)
***p,p'*-DDE**	-2.65	-2.47	(Shen and Wania, 2005)
***p,p'*-DDD**	-2.93	-2.93	(Shen and Wania, 2005)
***o,p'*-DDT**	-2.96	-2.74	(Hinckley and Bidleman, 1990)
PCB-202	-3.64*	-3.28	(Hinckley and Bidleman, 1990)
PCB-209	-4.89	-4.84	(Hinckley and Bidleman, 1990)
benz[*a*]anthracene	-3.27	-3.27	(Hinckley and Bidleman, 1990)
benzo[*a*]pyrene	-4.38	-5.14	(Hinckley and Bidleman, 1990)

* values taken from (Hinckley and Bidleman, 1990)

The equations were used to calculate p_{298} (Pa) values of PFR compounds from their measured $p_{GC,298}$ values at 25°C.

The temperature dependence of p for our target PFRs was expressed by the Clausius-Clapeyron equation:

Equation 3.15 $\log p = A_L + B_L/T$

where $B_L = -\Delta_l{}^gH/2.303 \cdot R$ (as in Equation 3.11 and Equation 3.12). The $\Delta_l{}^gH$ was calculated from the slope of Equation 3.10 and $\Delta_l{}^gH_{ref}$ for either HCB (TCEP and TCIPP) or *p,p'*-DDT (other PFRs).

As discussed previously (Bidleman et al., 2003), uncertainties in RRTs are relatively minor and most of the uncertainty in the GC-RT method lies in relating $p_{GC,298}$ to p_{298} through the log-log calibration plots. Standard uncertainties of estimates (u_e) in these plots were 0.188 (Figure 3.3) and 0.271 (Figure 3.4). From these, the standard prediction uncertainties (u_p) of log p_{298} (Pa) from log $p_{GC,298}$ (Pa) were calculated as previously described (Bidleman et al., 2003).

3.4 Vapour pressures and enthalpies of vaporisation

Table 3.6 summarises log $p_{GC,298}$, log p_{298} , $\Delta_l{}^gH$, and parameters of Equation 3.15 for the 11 PFRs, based on this study's GC-RT measurements. Log p_{298} cover four orders of magnitude, from –1.32 for TCEP to –5.22 for TIPPP. The u_p for the GC-RT determinations of log p_{298} ranged from 0.20 for TCEP and TCIPP to 0.28-0.33 for the heavier PFRs. 95% prediction windows of the calibration plots for log p_{298} are ±0.47 for TCEP and TCIPP, and ±0.62-0.73 for heavier compounds.

The $\Delta_l{}^gH$ values obtained here from GC-RT measurements ranged from 82-109 kJ•mol^{-1} with most >90 kJ•mol^{-1}, which is similar to the range of $\Delta_l{}^gH$ for tri- to hexabrominated PBDEs (Wong et al., 2001), PAHs with four or more rings(Hinckley and Bidleman, 1990; Lei et al., 2002), PCBs with four or more chlorines (Hinckley and Bidleman, 1990; Puri et al., 2001), and some chlorinated pesticides (Hinckley and Bidleman, 1990).

3.4.1 Comparison of GC-RT measurements to other values

A survey was performed to retrieve published measurements or *in silico* predictions of p_{298} for the target compounds. Values of p_{298} were also predicted using SPARC (SPARC Performs Automatic Reasoning in Chemistry) (ARChem, 2013), version 5.1 and MPBPWIN in the Estimation Program Interface (EPI) Suite (U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012), version 4.11.

Table 3.6 *log* $p_{GC,298}$ *(Pa), log* p_{298} *(Pa) with standard uncertainties u,* $\Delta_l^{g}H$ *(kJ/mol) and* Equation 3.15 *for analysed PFRs*

PFR	**log $p_{GC,298}$(Pa)**	**log p_{298}(Pa)**	**u logp_{298} (Pa)**	**p_{298} (Pa)**	**$\Delta_l^{g}H$ (kJ•mol^{-1})**	**B_L**	**A_L**
TCEP	-1.60	-1.32	0.20	4.8×10^{-2}	82.0	-4281	13.04
TCIPP	-1.79	-1.46	0.20	3.5×10^{-2}	85.2	-4452	13.47
TDCIPP	-3.36	-3.38	0.28	4.1×10^{-4}	91.3	-4766	12.63
TPHP	-3.53	-3.57	0.29	2.7×10^{-4}	92.8	-4846	12.72
EHDPP	-3.97	-4.05	0.28	8.9×10^{-5}	99.9	-5218	13.53
o-TMPP	-4.20	-4.29	0.20	5.1×10^{-5}	99.3	-5185	13.20
TBOEP	-4.21	-4.31	0.30	4.9×10^{-5}	102.6	-5359	13.76
TEHP	-4.55	-4.68	0.31	2.1×10^{-5}	106.0	-5538	14.02
m-TMPP	-4.56	-4.68	0.31	2.1×10^{-5}	103.7	-5418	13.62
p-TMPP	-4.80	-4.95	0.32	1.1×10^{-5}	105.7	-5523	13.72
TIPPP	-5.05	-5.22	0.33	6.0×10^{-6}	108.5	-5669	13.96

The resulting values can be found in Table 3.7, along with our GC-RT determinations and estimates using SPARC and EpiSuite. Adjustment by using the parameters of Equation 3.15), or by extrapolation of temperature-dependent data in the original report were performed for literature values of p at temperatures other than 298.15 K.

A striking observation is that reported p_{298} values often vary by more than an order of magnitude for an individual PFR.

This study's GC-RT determinations of log p_{298} (Pa) were compared with: 1. SPARC estimates, 2. EpiSuite estimates, and 3. arithmetic mean literature values of log p_{298} (Pa), based on previous reports of experimental measurements other than GC-RT and *in silico* estimates other than SPARC. The log p_{298} (Pa) values of Hinckley et al. (Hinckley and Bidleman, 1990) for TEHP, TBOEP and *p*-TMPP were not included because these were obtained also via GC-RT and the intent was to evaluate GC-RT versus other methods.

Log $(p_{298}/\mathrm{Pa})_{\mathrm{RT}}$ was closely correlated with log $(p_{298}/\mathrm{Pa})_{\mathrm{SPARC}}$ ($r^2 = 0.94$) (Figure 3.5), but with a strong bias away from the 1:1 line which increased at lower vapour pressures. The average deviation of log $(p_{298}/\mathrm{Pa})_{\mathrm{RT}}$ from the 1:1 line was 0.84 log units.

The correlations of log $(p_{298}/\mathrm{Pa})_{\mathrm{RT}}$ vs. log $(p_{298}/\mathrm{Pa})_{\mathrm{EpiSuite}}$ (Figure 3.6) and mean log $(p_{298}/\mathrm{Pa})_{\mathrm{lit}}$ (Figure 3.7) showed $r^2 = 0.77$ and 0.69 and only slight overall bias, with average deviations from 1:1 of 0.05 and 0.20 log units.

Table 3.7 *Vapour pressures determined in this study compared with calculated and literature values (mean literature levels and literature SD values used for comparison are given as well) X: values included for comparison, P: predicted, E: experimental*

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (°C)	Reference	Method	Comments
TCEP						
	4.80×10^{-2}	-1.32	25	This study	E	GC-RT
x	0.22	-0.66	25	This study	P	SPARC
x	1.44×10^{-2}	-1.84	25	(Bergh, 2011; Bergman et al., 2012)	P	ACD/Labs Software V.9.04, V.11.02
	1.14×10^{-3}	-2.94	20	(European Union, 2009; Verbruggen et al., 2005)	E	Industrial data, 137-196˚C, extrapolated to 20˚C
x	2.15×10^{-3}	-2.67	25			Above extrapolated to 25 ˚C, using $\Delta_l{}^gH$ in Table 3.6
	13.3	1.12	25	(Bergman et al., 2012)	P	EpiSuite SRC EPIWIN v.2b, Modified Grain, extrapolated from boiling point Quoted from industry report(outlier)
x	5.21×10^{-2}	-1.28	25	(Verbruggen et al., 2005; Beyer et al., 2002)	P	EpiSuite, MBBPVPWIN, v. 3.11, 4.11, Modified Grain, extrapolated from boiling point
x	8.2	0.91	25	(SRC, 2013; ATSDR, 2012; Sjögren et al., 2010; Verbruggen et al., 2005; Dobry and Keller, 1957)	E	Isoteniscope (outlier)
		-1.92				mean literature (inc. SPARC)
		1.00				SD (inc. SPARC)
		-2.23				mean literature (no SPARC)
		0.95				SD (no SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (°C)	Reference	Method	Comments
TCIPP						
x	3.47×10^{-2}	-1.46	25	This study	E	GC-RT
x	4.73×10^{-2}	-1.33	25	This study	P	SPARC
x	7.00×10^{-3}	-2.15	25	(Bergh, 2011)	P	ACD/Labs Software V9.04
x	2.69×10^{-3}	-2.57	25	(Bergman et al., 2012; SRC, 2013; ATSDR, 2012; Sjögren et al., 2010)	P	ACD/Labs Software V11.02
x	1.4×10^{-3}	-2.85	25	(European Union, 2008a; Verbruggen et al., 2005; Tremain, 2002a)	E	Vapour pressure balance (effusion)
x	7.52×10^{-3}	-2.12	25	(Verbruggen et al., 2005; U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012)	P	EpiSuite, MPBPVPWIN, v.1.42, 3.11, 4.11. Modified Grain, extrapolated from boiling point
		-2.21				mean literature (inc. SPARC)
		0.58				SD (inc. SPARC)
		-2.43				mean literature (no SPARC)
		0.35				SD (no SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (°C)	Reference	Method	Comments
TDCIPP						
	4.13×10^{-4}	-3.38	25	This study	E	GC-RT
x	3.61×10^{-5}	-4.44	25	This study	P	SPARC
x	5.43×10^{-6}	-5.27	25	(Bergh, 2011; Bergman et al., 2012)	P	ACD/Labs Software V.9.04, V.11.02
x	5.6×10^{-6}	-5.25	25	(European Union, 2008b; Tremain, 2002b)	E	Vapour pressure balance (effusion)
x	3.97×10^{-5}	-4.40	25	(SRC, 2013; Verbruggen et al., 2005; U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012)	P	EpiSuite, MPBPVPWIN, v.3.11 and 4.11. Modified Grain, extrapolated from boiling point
		-4.84				mean literature (inc. SPARC)
		0.48				SD (inc. SPARC)
		-4.97				mean literature (no SPARC)
		0.50				SD (no SPARC)

Compound	p_{298} **(Pa)**	**Log (p_{298}/Pa)**	**T (°C)**	**Reference**	**Method**	**Comments**
TEHP						
	2.11×10^{-5}	-4.68	25	This study	E	GC-RT
x	7.34×10^{-7}	-6.13	25	This study	P	SPARC
x	2.94×10^{-3}	-2.53	25	(Verbruggen et al., 2005)	E	industrial data, 160-200˚C, extrapolated.
x	2.72×10^{-4}	-3.57	25	(Bergh, 2011)	P	ACD/Labs Software V.9.04
x	1.1×10^{-5}	-4.96	25	(Bergman et al., 2012)	P	ACD/Labs Software V11.02
	1.1×10^{-5}	-4.96	25	(Hinckley and Bidleman, 1990; Sjögren et al., 2010)	E	GC-RT
x	3.03×10^{-5}	-4.52	25	(Verbruggen et al., 2005)	E	Effusion
x	8.09×10^{-5}	-4.09	25	(Verbruggen et al., 2005; U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012)	P	EpiSuite, MPBPVPWIN, v.1.42, 3.11 and 4.11. Modified Grain, extrapolated from boiling point
		-4.30				mean literature (inc. SPARC)
		1.23				SD (inc. SPARC)
		-3.93				mean literature (no SPARC)
		0.94				SD (no SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (°C)	Reference	Method	Comments
TBOEP						
	4.89×10^{-5}	-4.31	25	This study	E	GC-RT
x	1.60×10^{-5}	-4.80	25	This study	P	SPARC
	2.8×10^{-5}	-4.55	25	(Hinckley and Bidleman, 1990; Sjögren et al., 2010; WHO, 2000b)	E	GC-RT
x	1.48×10^{-4}	-3.83	25	(Bergh, 2011)	P	ACD/Labs Software V.9.04
x	3.33×10^{-6}	-5.48	25	(Bergman et al., 2012)	P	ACD/Labs Software V11.02
x	2.41×10^{-5}	-4.62	25	(Small et al., 1948; Sjögren et al., 2010)	E	Effusion
x	1.64×10^{-4}	-3.79	25	(Verbruggen et al., 2005; U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012),	P	EpiSuite, MPBPVPWIN, v.1.42, 3.11 and 4.11. Modified Grain, extrapolated from boiling point
		-4.50				mean literature (inc. SPARC)
		0.71				SD (inc. SPARC)
		-4.43				mean literature (no SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (^{o}C)	Reference	Method	Comments
		0.80				SD (no SPARC)
TPHP						
	2.68×10^{-4}	-3.57	25	This study	E	GC-RT
x	6.87×10^{-5}	-4.16	25	This study	P	SPARC
x	1.65×10^{-4}	-3.78	25	(Bergh, 2011)	P	ACD/Labs Software V9.04
x	8.37×10^{-4}	-3.08	25	(Bergman et al., 2012)	P	ACD/Labs Software V11.02
x	1.20×10^{-4}	-3.92	25	(Environment Agency, 2009d; Boethling and Cooper, 1985)	E	Estimated from boiling point at reduced pressure
x	8.52×10^{-4}	-3.07	25	(Sjögren et al., 2010; Verbruggen et al., 2005; Dobry and Keller, 1957)	E	Isoteniscope
	8.81×10^{-2}	-1.06	100	(Verbruggen et al., 2005; Small et al., 1948)	E	Effusion
x	4.77×10^{-5}	-4.32	25			Above adjusted to 25 ˚C, using $\Delta_l{}^gH$ in Table 3.6
x	4.1×10^{-3}	-2.39	25	(Verbruggen et al., 2005; Environment Agency, 2009d)	E	Data from 20-350^{o}C, extrapolated using $\Delta_l{}^gH$ in ref. (Environment Agency, 2009d)
x	6.29×10^{-5}	-4.20	25	(Verbruggen et al., 2005; U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012)	P	EpiSuite, MPBPVPWIN, v.1.42, 3.11 and 4.11. Modified Grain, extrapolated from boiling point
		-3.62				mean literature (inc. SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (°C)	Reference	Method	Comments
		0.69				SD (inc. SPARC)
		-3.54				mean literature (no SPARC)
		0.71				SD (no SPARC)
***o*-TMPP**						
	5.11×10^{-5}	-4.29		This study	E	GC-RT
x	1.36×10^{-6}	-5.87	25	This study	P	SPARC
x	7.98×10^{-5}	-4.10	25	(Boethling and Cooper, 1985)	P	Extrapolated from boiling point.
x	6.33×10^{-3}	-2.20	25	(Verbruggen et al., 2005)	P	EpiSuite, MPBPVPWIN, v.4.11, Modified Grain, extrapolated from boiling point
x	2.26×10^{-4}	-3.65	25	(Verbruggen et al., 2005; Dobry and Keller, 1957)	E	Isoteniscope.
	5.5×10^{-5}	-4.26	20	(Verbruggen et al., 2005; Environment Agency, 2009c)	P	Extrapolated from high temperature data
x	1.10×10^{-4}	-3.96	25			Above adjusted to 25 ˚C, using $\Delta_l{}^gH$ in Table 3.6
		-4.15				mean literature (inc. SPARC)
		1.02				SD (inc. SPARC)
		-3.73				mean literature (no SPARC)
		0.40				SD (no SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (°C)	Reference	Method	Comments
***m*-TMPP**						
	2.08×10^{-5}	-4.68	25	This study	E	GC-RT
x	2.42×10^{-6}	-5.62	25	This study	P	SPARC
	9.9×10^{-5}	-4.00	20	(Verbruggen et al., 2005; Environment Agency, 2009c)	E	Extrapolated from boiling point using $\Delta_l{}^gH$ of commercial TMPP
x	1.78×10^{-4}	-3.75	25	(Verbruggen et al., 2005; Environment Agency, 2009c)		Above adjusted to 25 ˚C, using $\Delta_l{}^gH$ in Table 3.6
x	3.74×10^{-6}	-5.43	25	(Verbruggen et al., 2005; Small et al., 1948)	E	Effusion
x	3.94×10^{-6}	-5.41	25	(Verbruggen et al., 2005; Small et al., 1948)	E	Effusion
x	1.21×10^{-5}	-4.92	25	(Verbruggen et al., 2005; Small et al., 1948)	E	Effusion
x	1.45×10^{-5}	-4.84	25	(ATSDR, 2012; Verbruggen et al., 2005)	E	EpiSuite, MPBPVPWIN, v.1.42, 3.11 and 4.11. Modified Grain, extrapolated from boiling point
x	1.84×10^{-6}	-5.74	25	(Verbruggen et al., 2005; Dobry and Keller, 1957)	E	Isoteniscope
		-5.10				mean literature (inc. SPARC)
		0.68				SD (inc. SPARC)
		-5.01				mean literature (no SPARC)
		0.70				SD (no SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (°C)	Reference	Method	Comments
***p*-TMPP**						
	1.13×10^{-5}	-4.95	25	This study	E	GC-RT
x	1.55×10^{-6}	-5.81	25	This study	P	SPARC
x	8.0×10^{-5}	-4.10	25	(Bergman et al., 2012)	P	ACD/Labs Software V11.02
	6.10×10^{-6}	-5.21	25	(Hinckley and Bidleman, 1990)	E	GC-RT
x	1.47×10^{-5}	-4.83	25	(U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012)	E	EpiSuite, MPBPVPWIN 4.11. Modified Grain, extrapolated from boiling point
x	2.94×10^{-6}	-5.53	25	(Small et al., 1948; Sjögren et al., 2010)	E	Effusion
	4.4×10^{-5}	-4.36	20	(Verbruggen et al., 2005; Environment Agency, 2009c)	E	Extrapolated from boiling point using the $\Delta_l{}^gH$ of commercial TMPP
x	9.04×10^{-5}	-4.04	25	(Verbruggen et al., 2005; Environment Agency, 2009c)	E	Above adjusted to 25 ˚C, using $\Delta_l{}^gH$ from Table 3.6
		-4.86				mean literature (inc. SPARC)
		0.81				SD (inc. SPARC)
		-4.63				mean literature (no SPARC)
		0.70				SD (no SPARC)

Compound	**p_{298} (Pa)**	**Log (p_{298}/Pa)**	**T (^{o}C)**	**Reference**	**Method**	**Comments**
EHDPP						
	8.91×10^{-5}	-4.05	25	This study	E	GC-RT
x	2.35×10^{-5}	-4.63	25	This study	P	SPARC
x	8.65×10^{-5}	-4.06	25	(Bergh, 2011)	P	ACD/Labs Software V9.04
x	4.44×10^{-3}	-2.35	25	(U.S. Environmental Protection and Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC), 2012)	P	EpiSuite, MPBPVPWIN, v.1.42, 4.11. Modified Grain, extrapolated from boiling point
x	2.50×10^{-5}	-4.60	25	(Environment Agency, 2009a)	P	EpiSuite SRC MBBPWIN v.1.28, Modified Grain, extrapolated from boiling point
x	6.20×10^{-4}	-3.21	25	(Environment Agency, 2009a)	E	extrapolated from data in 140-250^{o}C range.
		-3.77				mean literature (inc. SPARC)
		0.98				SD (inc. SPARC)
		-3.56				mean literature (no SPARC)
		0.99				SD (no SPARC)

Compound	p_{298} (Pa)	Log (p_{298}/Pa)	T (^{o}C)	Reference	Method	Comments
TIPPP						
	6.03×10^{-6}	-5.22	25	This study	E	GC-RT
x	1.97×10^{-8}	-7.71	25	This study	P	SPARC
x	3.89×10^{-7}	-6.41	25	(Bergman et al., 2012)	P	ACD/Labs Software V11.02
x	8.76×10^{-6}	-5.06	25	(Environment Agency, 2009b)	P	EpiSuite, SRC MPBPVPWIN, v.1.28, 4.11. Modified Grain, extrapolated from boiling point
	7.77×10^{-4}	-3.11	70	(Environment Agency, 2009b)	E	Industrial data
	2.3×10^{-6}	-5.64	20	(Environment Agency, 2009b)	E	Above adjusted to 25 ˚C, using $\Delta_l{}^gH$ from reference (Environment Agency, 2009b)
x	4.15×10^{-6}	-5.32	25	(Environment Agency, 2009b)	E	Above adjusted to 25 ˚C, using $\Delta_l{}^gH$ in Table 3.6
		-6.12				mean literature (inc. SPARC)
		1.21				SD (inc. SPARC)
		-5.60				mean literature (no SPARC)
		0.72				SD (no SPARC)

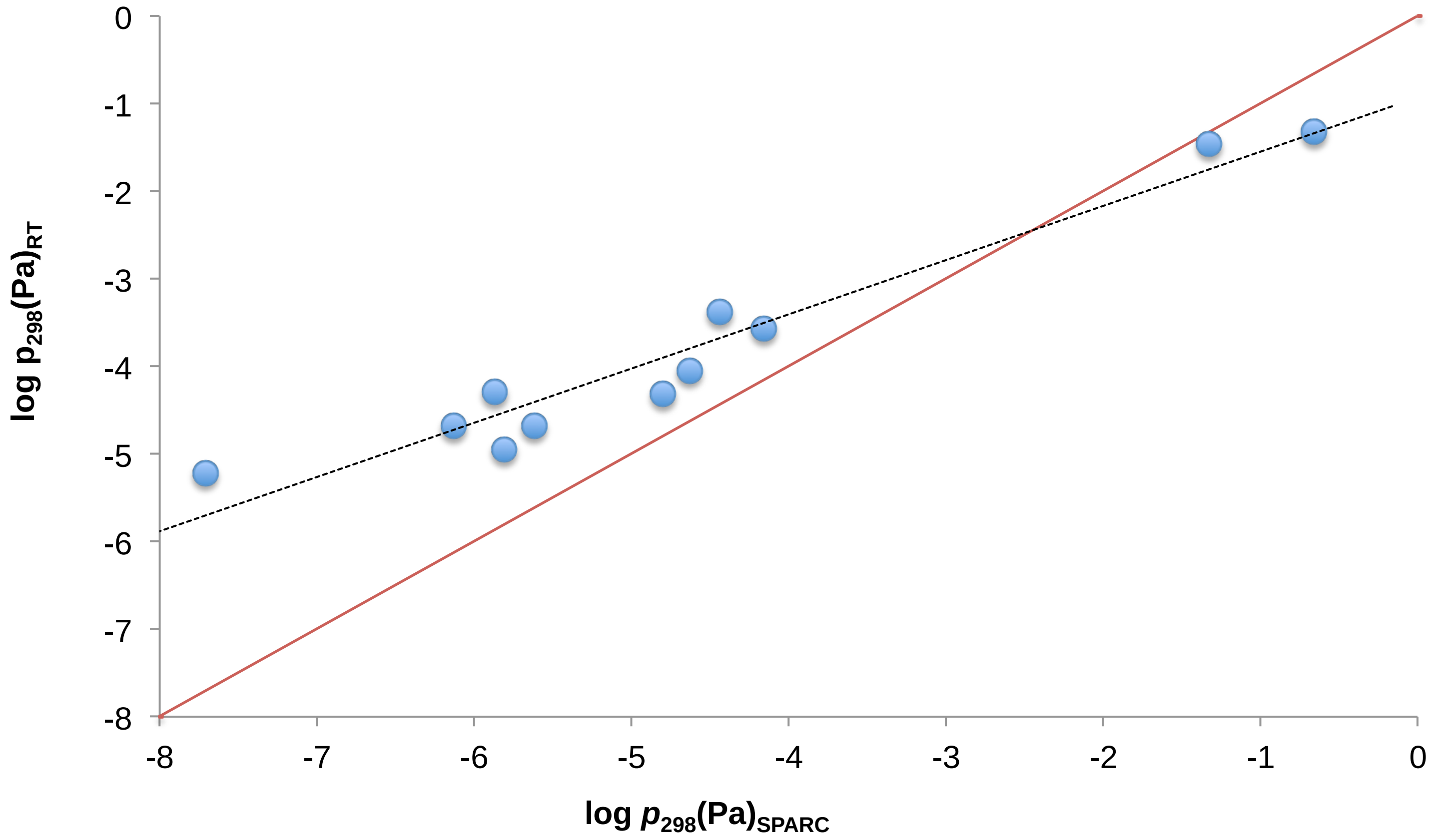


Figure 3.5 *log (p_{298}/Pa)$_{RT}$ versus log (p_{298}/Pa)$_{SPARC}$ (red line is 1:1 relationship; dotted line equals regression line; regression parameters are: $y = 0.619x – 0.930$, $R^2 = 0.944$)*

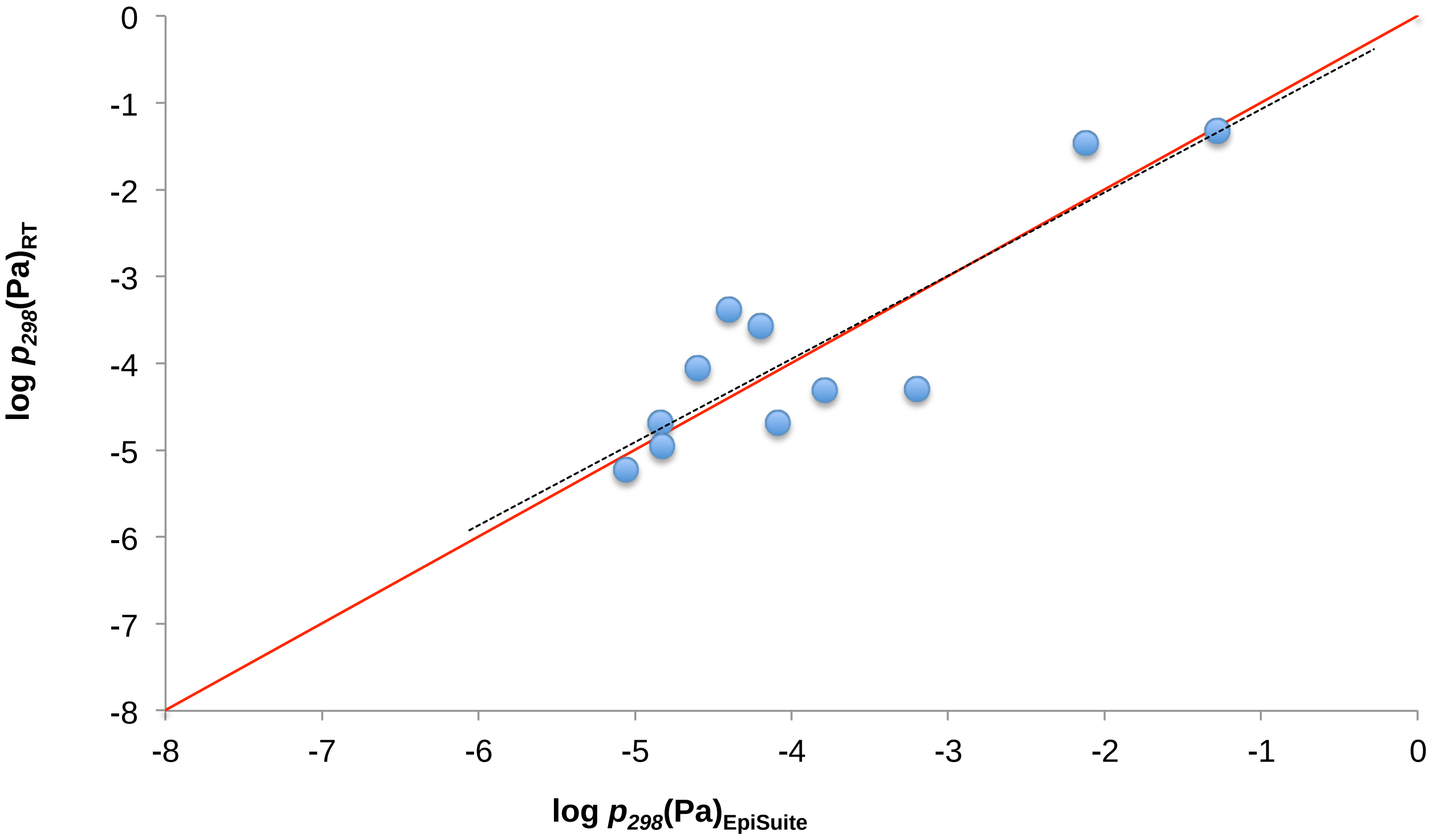


Figure 3.6 *log (p_{298}/Pa)$_{RT}$ versus log (p_{298}/Pa)$_{EpiSuite}$ (red line is 1:1 relationship; dotted line equals regression line; regression parameters are: $y = 0.959x – 0114$, $R^2 = 0.769$)*

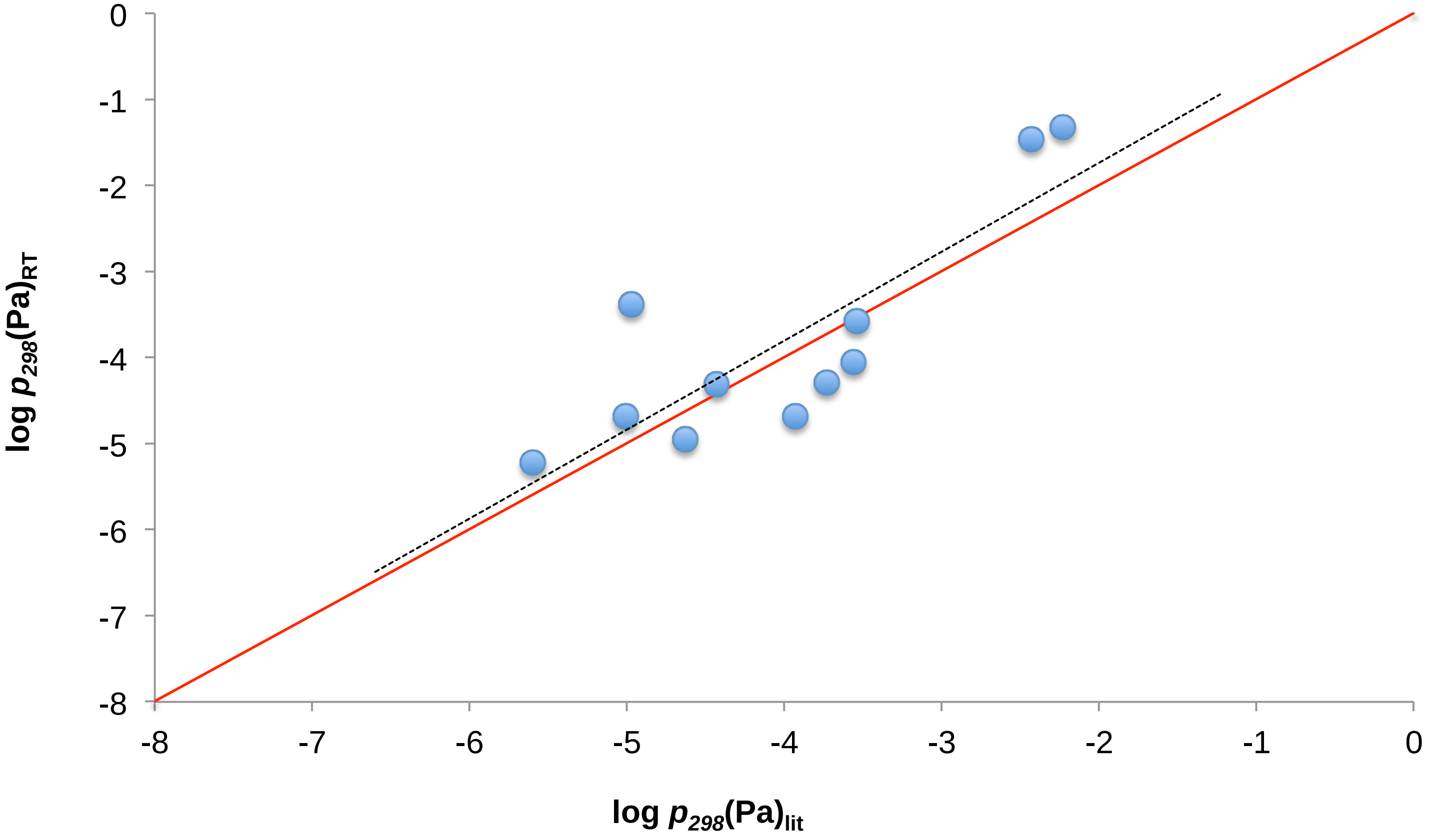


Figure 3.7 *log (p_{298}/Pa)$_{RT}$ versus mean log (p_{298}/Pa)$_{lit}$ (red line is 1:1 relationship; dotted line equals regression line; regression parameters are: $y = 1.034x + 0.3311$, $R^2 = 0.691$)*

The good correspondence between log (p_{298}/Pa)$_{RT}$ and log (p_{298}/Pa)$_{EpiSuite}$ or mean log (p_{298}/Pa)$_{lit}$ indicates that the bias in Figure 3.5 is due to underestimation by SPARC, especially for the low vapour pressure PFRs (Hinckley and Bidleman, 1990) expressed concern that the GC-RT method overestimates p_{298} for polar compounds. Figure 3.6 and Figure 3.7 suggest little or no overall bias for PFRs, though individual compounds may be problematic. The greatest deviations from the 1:1 line in Figure 3.7 are for TDCIPP and *o*-TMPP, which are higher and lower by about 1 log unit, respectively. Figure 3.7 suggests a high bias for the chlorinated PFRs TCEP, TCIPP and TDCIPP (above the 1:1 line by 0.91, 0.97 and 1.6 log units). However, the log p_{298} (Pa)$_{EpiSuite}$ and mean log p_{298}(Pa)$_{lit}$ values on the X-axes of these plots have their own uncertainties. EpiSuite predictions are based on the Modified Grain Method, which extrapolates from the boiling point at atmospheric pressure. Accurate boiling points for these compounds are often difficult to obtain and uncertain (European Union, 2008a; Environment Agency, 2009b, 2009a, 2009c, 2009d). Standard uncertainties (*u*) of log p_{298}(Pa)$_{lit}$ values range from 0.35-0.99 log units (mean u = 0.71 log unit).

3.4.2 Implications for Environmental Behaviour of PFRs

The distribution of semivolatile compounds between the particulate and gaseous phases in air is critical to understanding their long-range transport potential (Scheringer, 2009) and exposure through inhalation as opposed to indoor dust (US EPA, 2011). The Junge-Pankow (J-P) equation is commonly used to estimate the particulate fraction (ϕ) in ambient air from p and the surface area available for adsorption, θ = cm^2 aerosol/cm^3 air (Pankow, 1987; Bidleman, 1988).

Equation 3.16 $$\Phi = c \bullet \theta / (p + c \bullet \theta)$$

where c is often assumed to be 17.2 Pa•cm (Bidleman, 1988). Estimates of ϕ for the PFRs investigated here were made for urban air and clean continental background air, using the θ-values of $1.1 \bullet 10^{-5}$ and $4.2 \bullet 10^{-7}$ cm^2 aerosol/cm^3

air typical of these regimes (Bidleman, 1988) and *p* at 15^{o}C, the average temperature of the earth's surface (calculated from parameters in Table 3.6).

Until now the Junge-Pankow model has only been applied to outdoor air and to our knowledge it and related models have not been applied to the prediction of the particulate fraction in indoor air. This is presumably because θ-values are only available for outdoor air. We hence used the data in Table 3.8 to derive a q-value for indoor air.

Table 3.8 *Indoor particle size distribution data from one townhouse in Virginia* (Ogulei et al., 2006)

Particle size diameter (µm)	Particle size radius (µm)	Average volume particulate matter (µm^3/cm^3)	Average size radius (µm)	Average area (µm^2/cm^3)	Average area (cm^2/cm^3)
0.01–0.05	0.005-0.025	0.0797	0.015	15.94	1.59×10^{-7}
0.05–0.1	0.025-0.05	0.398	0.0375	31.84	3.18×10^{-7}
0.1–0.5	0.05-0.25	2.21	0.15	44.20	4.42×10^{-7}
0.5–1.0	0.25-0.5	0.33	0.375	2.64	2.64×10^{-8}
1.0–2.5	0.5-1.25	0.673	0.875	2.31	2.31×10^{-8}
2.5–10.0	1.25-5.0	3.73	3.125	3.58	3.58×10^{-8}
10.0–20.0	5.0-10.0	6.90	7.5	2.76	2.76×10^{-8}

Assuming a particle density of 1 g/cm^3 (Ogulei et al., 2006) it follows from Table 3.8 where the summed average volume of particulate matter per unit volume of air is 14.32 µm^3/cm^3, that the particle mass is 1.43×10^{-11} g/cm^3 air. Taking the average size radius of each particle size group into account, it follows from the relationship between volume and the surface area of a sphere that the q-value for indoor air is the sum of the particle surface area per unit air volume values for all particle size ranges = i.e. 1.0×10^{-6} cm^2 aerosol/cm^3.

Figure 3.8 shows the modelled distributions in urban and background air at 288 K. In urban air, TCEP and TCIPP are predicted to exist almost entirely in the gas phase, while 60% or more of the other PFRs are forecast to be associated with aerosols. Predicted particulate-bound percentages in background air are 10% or less for TCEP, TCIPP, TDCIPP and TPHP, and

20-80% for the other PFRs. Even though when this estimation is done for a typical seasonal temperature range (273 K and 298K, see Table 3.9) TCEP and TCIPP still show predicted particulate bound fractions of less than 20 %. In contrast, field studies have shown that PFRs are predominantly in the particle phase, even for TCEP and TCIPP, in both urban air (Salamova et al., 2014) and marine air over the North Sea (Möller et al., 2012, 2011). This suggests that these polar compounds may be more strongly sorbed to aerosols than predicted by the J-P model, and/or to glass fibre filters used for air sampling. For indoor air sampling SPE cartridges are commonly applied (van der Veen and de Boer, 2012), which do not distinguish between the two phases. To our knowledge, no approaches to passive air sampling have been applied to PFRs, which would enable the particle/gas distribution to be determined for indoor air without use of an air pump, as has been conducted for BFRs (Abdallah and Harrad, 2010).

TIPPP has the lowest estimated vapour pressure of all PFRs targeted in this study with literature values reported as low as 2.06×10^{-8} Pa. However the determined vapour pressure in this study of 6.03×10^{-6} Pa is two orders of magnitude higher than the lowest estimated value reported in the literature. Moreover, extrapolation of experimental literature data available at higher temperatures to 25 ˚C resulted in similar vapour pressures to those determined in this study. Therefore this compound might be more volatile and environmentally mobile than previously forecasted via prediction software. This is in line with the detection of TIPPP in sediments from Japan and the US (Environment Agency, 2009b). Published studies of TIPPP in air, dust and water are to our knowledge not available to date but preliminary data suggests that TIPPP was found very infrequently in 1-2% of dust samples from Canadian and Turkish homes (Liiisa Jantunen personal communication). Moreover, screening for TIPPP in Canadian ambient/outdoor reveals concentrations to be <10pg/m^3 (Liisa Jantunen personal communication). This is consistent with its relatively low vapour pressure and indicates that air is unlikely to be a dominant source of human exposure to TIPPP.

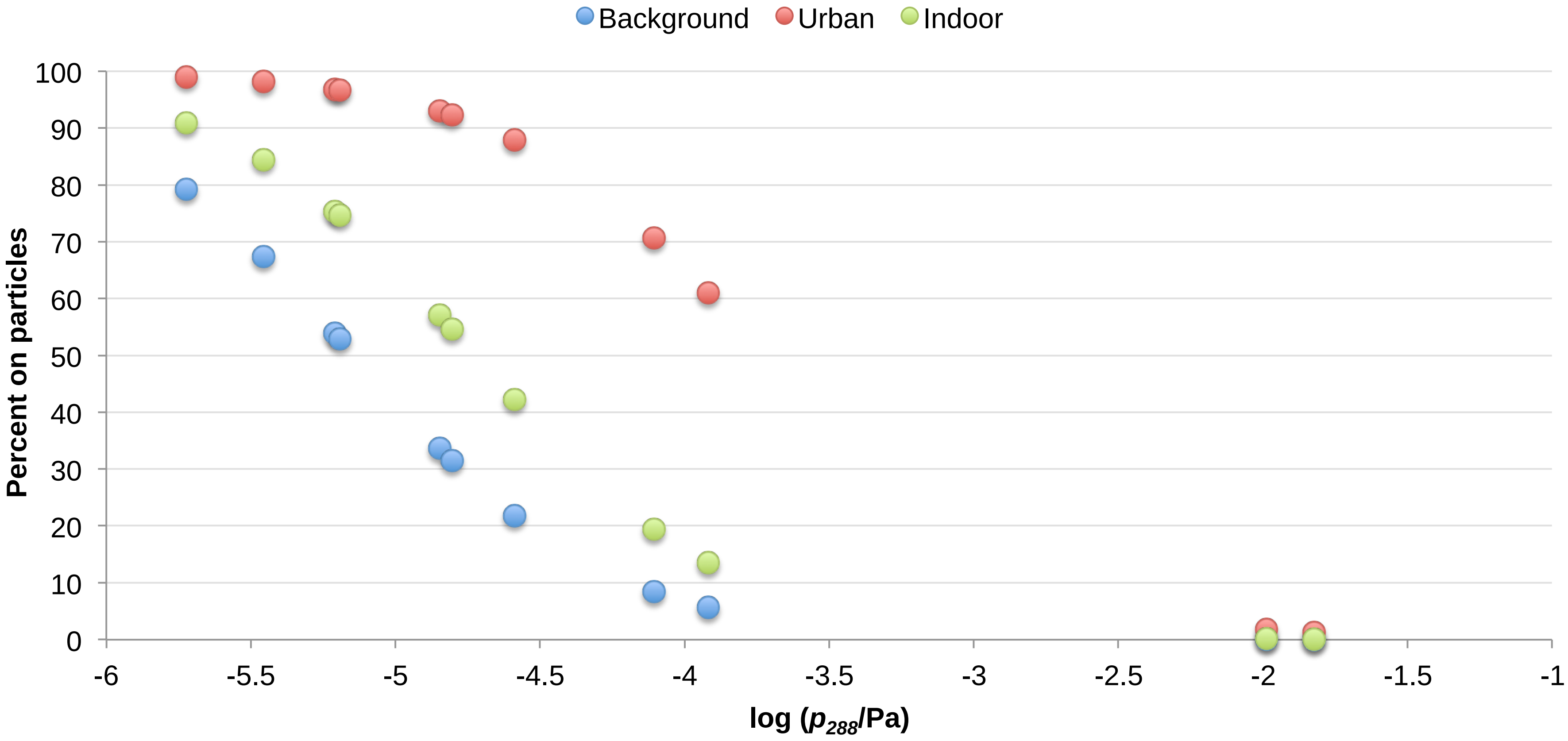


Figure 3.8 *Distributions of PFRs between the particle/gas phases in background, indoor and urban air at 15° C, modelled with the Junge-Pankow adsorption equation (Pankow, 1987; Bidleman, 1988)*

Table 3.9 *Junge-Pankow estimates of the percent particulate-bound fraction of individual PFRs at 3 different temperatures*

	Clean Background Air (%)	**Urban Air (%)**	**Indoor Air (%)**
298 K			
TCEP	0.0	0.4	0.0
TCIPP	0.0	0.6	0.1
TDCIPP	1.6	30.4	4.2
TPHP	2.5	39.7	6.2
EHDPP	6.5	64.4	15.3
o-TMPP	10.3	75.0	23.0
TBOEP	10.8	76.0	24.0
m-TMPP	20.8	87.3	40.8
TEHP	20.9	87.4	40.9
p-TMPP	32.0	92.5	55.2
TIPPP	45.5	95.6	68.7
288 K			
TCEP	0.0	1.2	0.1
TCIPP	0.1	1.8	0.2
TDCIPP	5.7	61.1	13.6
TPHP	8.4	70.7	19.5
EHDPP	21.9	88.0	42.3
o-TMPP	31.5	92.3	54.6
TBOEP	33.7	93.0	57.1
m-TMPP	52.9	96.7	74.7
TEHP	53.9	96.8	75.4
p-TMPP	67.4	98.2	84.4
TIPPP	79.3	99.0	90.9
273 K			
TCEP	0.3	7.7	0.8
TCIPP	0.5	11.5	1.3
TDCIPP	32.7	92.7	56.0
TPHP	43.7	95.3	67.0
EHDPP	73.5	98.6	87.9
o-TMPP	81.8	99.2	92.1
TBOEP	84.3	99.3	93.3
m-TMPP	92.4	99.7	97.0
TEHP	93.0	99.7	97.2
p-TMPP	95.9	99.8	98.4
TIPPP	97.9	99.9	99.2

Furthermore the vapour pressure of *o*-TMPP of 5.11×10^{-5} Pa was two orders of magnitude higher than the previous predicted values. A reason for this might lie with the credibility of the published literature values. According to these, *o*-TMPP should have a vapour pressure nearly three orders of magnitude higher than its isomer *p*-TMPP, which does not seem plausible. Furthermore, recalculation with the latest version of the SPARCs software yields a value of 1.36×10^{-6} Pa, which is one magnitude lower than the average literature value of *m*-TMPP. This may suggest that *o*-TMPP is more likely to be found in e.g. soil rather than air.

As noted above, TCIPP and TDCIPP showed the greatest deviations from the available literature data. A possible explanation is that the only previous experimental measurements of vapour pressure for these PFRs were obtained via the vapour pressure balance method (European Union, 2008a); which resulted both times in values towards the higher end of the literature data spectrum. More experimental data is necessary for these compounds to determine which experimental method is more suitable for determining the vapour pressure of TCIPP and TDCIPP.

3.4 Conclusions

This chapter reports experimentally-derived vapour pressures and enthalpies of vaporisation for selected PFRs. In general, log $p_{298}(\mathrm{Pa})_{\mathrm{RT}}$ agreed well with log $p_{298}(\mathrm{Pa})_{\mathrm{EpiSuite}}$ and with mean log $p_{298}(\mathrm{Pa})_{\mathrm{lit}}$. A bias toward higher values by GC-RT, as might be expected from chromatography of polar compounds on a nonpolar stationary phase, was not seen overall, although this is suggested for the chlorinated compounds TCEP, TCIPP and TDCIPP. The SPARC model seriously underestimated p, especially for the less volatile compounds.

Application of the Junge-Pankow (J-P) adsorption model using p_{288} 15°C indicates that most of the PFRs except TCEP and TCIPP are expected to be predominantly particulate-bound in urban air but more equally distributed between the particulate and gas phases in background air. Data from field studies indicates even higher proportions to be associated with the particulate phase, which suggests stronger sorption of PFRs to aerosols or to air sampling filters than predicted by the J-P model.

Further experimental measurements are necessary to confirm those reported in this chapter as most of the literature data available to date are *in silico* estimates and subject to substantial variation between studies resulting in standard deviations of up to nearly two orders of magnitude. Moreover, this study is based on the assumption that non-polar compounds display similar behaviour to polar PFRs, which might not be the case. Ideally therefore, the reference compound used in future studies would be a more polar compound with an established FAV value. While organochlorine pesticides of suitable polarity and vapour pressures exist that would make appropriate calibration compounds, such compounds still require FAV values to be determined. In summary, provision of accurate vapour pressure data for PFRs has important implications for understanding of their phase distribution and their environmental fate and behaviour. Hence accurate vapour pressure data are much needed by modellers, risk assessors and legislators.

4 IS THERE A DIFFERENCE IN PFR PATTERN/CONCENTRATIONS BETWEEN DIFFERENT COUNTRIES OR MICROENVIRONMENTS?

This chapter addresses the hypothesis that significant differences exist in absolute and the relative abundance of different PFRs in indoor dust from: (a) similar microenvironments from different countries, and (b) different microenvironments from the same country. To do so, PFRs are measured in dust from living rooms from five countries, from cars and offices from three countries, and from couches from two countries.

4.1 Introduction

Car dust samples were collected from three countries, namely Australia (n=39), Germany (n=19) and the UK (n=21), covering a wide range of manufacturers, models and ages. In addition to car dust samples collected specifically for this study, 9 samples of archived car dust collected in 2009 were included.

Office dust samples were taken from Germany (n=25), Kazakhstan (n=8) and the UK (n=61). While the German and UK samples were acquired specifically for this study, those from Kazakhstan were archived material procured in 2009. Finally, couch dust samples were taken from Australia (n=41) and the UK (n=10).

PFR concentrations were determined in dust from living rooms (Australia, UK, Germany, Canada, Kazakhstan), offices (UK, Germany, Kazakhstan), and cars (Australia, UK, Germany). In Australia, samples were also taken from couches (n=41) and mattresses (n=57), as well as from the floors of children's bedrooms (n=11). These samples provide additional insights into PFR contamination in the domestic environment.

This chapter assesses whether international differences exist in PFR contamination of indoor dust by evaluating parallels and differences between PFR concentrations and patterns in Europe, Australia, North America and Asia. It also tests the hypothesis that PFR concentrations in indoor dust vary significantly between different microenvironment categories.

To our knowledge this is the most extensive comparison of PFR concentrations/patterns conducted to date. A particular strength of this study is that it employs similar dust collection and identical analytical methods throughout. This eliminates the possibility when comparing data from different studies conducted by different research groups, that apparent differences in PFR concentrations and patterns between microenvironment categories and/or countries, might be artefacts due to the different sampling and analytical methods used. Examples of such issues highlighted by (Brandsma et al., 2013) include: employment of different internal standards, and the use of LC rather than GC which has been shown to yield significantly lower concentrations of ΣTMPP.

Finally, this chapter reports to our knowledge for the first time, concentrations of PFRs in Australian, UK and Kazakhstani dust samples, as well as the most comprehensive survey to date of PFR concentrations in German indoor dust.

4.2 International variation in concentrations of PFRs in indoor dust

This section evaluates the existence of significant differences in PFR contamination between different countries for the same microenvironment.

4.2.1 Living room dust

Living room dust samples were collected according to the sampling procedure described in Chapter 2 from five countries, namely Australia (n=42), Canada (n=14), Kazakhstan (n=9), Germany (n=22), and the UK (n=32). While samples from Canada and Kazakhstan were archived samples collected by others within our research group in 2008 and 2009 respectively; those from Australia, Germany, and the UK were collected specifically for this study. Samples from homes were primarily collected from living rooms of houses and apartments but also included rooms from student halls of residence (UK only).

Data for individual living room dust samples analysed in this study can be found in Appendix 7, a statistical data summary in Appendix 8, while median and range concentrations are displayed in Table 4.1. Concentrations below detection limit were replaced by half the LOQ for all statistical analyses.

Concentrations of ΣPFRs in UK living room dust samples were the highest with a median ΣPFR level of 44 µg/g. Australia (median 7.9 µg/g), Kazakhstan (median 7.3 µg/g) and Canada (median 5.8 µg/g) showed broadly similar ΣPFR levels, while those from Germany were the least contaminated living room samples (ΣPFR median 2.7 µg/g) analysed in this study.

The high concentrations of ΣPFRs in the UK samples are mainly driven by high concentrations of TCIPP (median 21 µg/g), which is ~20 times the median concentrations found in samples from other countries, which ranged from 1.0 µg/g (Kazakhstan and Germany) to 1.8 µg/g Australia.

Table 4.1 *Median and Range of Concentrations (µg/g) of PFRs in Living Room Dust Samples from Australia, Canada, Germany, Kazakhstan, and the UK (µg/g)*

TnBP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.03	<0.03	<0.03	<0.03	<0.03
Median	0.06	0.13	<0.03	0.11	<0.03
Maximum	8.4	1.2	0.25	0.23	0.09
TCEP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.06	0.19	<0.06	0.62	<0.06
Median	0.60	0.69	0.21	1.4	0.81
Maximum	24	37	5.7	6.8	28
TCIPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	0.24	0.12	0.33	0.42	3.7
Median	1.8	1.2	1.0	1.0	21
Maximum	24	37	5.7	6.8	28
TPHP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	0.24	0.02	0.07	1.2	0.49
Median	1.2	1.6	0.23	3.8	3.3
Maximum	31	37	18	9.2	110
EHDPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.01	0.01	<0.01	0.06	0.18
Median	0.38	0.39	0.14	0.27	1.6
Maximum	5.1	0.73	0.56	1.2	130
TDCIPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.03	0.03	<0.03	<0.03	0.06
Median	0.32	1.1	0.08	0.11	0.71
Maximum	11	3.2	14	2.0	14
TMPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.01	<0.01	<0.01	<0.01	<0.01
Median	0.04	<0.01	0.14	<0.01	0.02
Maximum	3.0	0.67	1.3	1.1	44
ΣPFR	Australia	Canada	Germany	Kazakhstan	UK
Minimum	1.1	0.38	1.3	5.5	7.9
Median	7.9	5.8	2.7	7.3	44
Maximum	67	94	340	15	260

4.2.1.1 Statistical evaluation of differences in absolute concentrations of PFRs in living room dust from different countries

Inspection of Table 4.1 indicates potential differences in concentrations of PFRs in dust samples from living rooms in different countries. These differences were explored further via subjecting log-transformed data for each target PFR to an ANOVA test with a Tukey post hoc test. The data were log-transformed as Shapiro-Wilk test showed that concentrations of all PFRs were significantly skewed.

Statistically significant differences ($p<0.05$) in absolute concentrations of individual PFRs in living room dust from the five different countries studied, are listed in Table 4.2. If not listed in Table 4.2, no significant differences were detected. As observed for BFRs like PBDEs (Harrad et al., 2008b), such differences do exist and – while the relatively small sample size is acknowledged – these likely reflect international variations in PFR use. Interestingly, while concentrations of most PFRs targeted in this study are significantly elevated in Australia, Canada, and the UK; concentrations of TCEP and TPHP are significantly greater in house dust from Kazakhstan than Germany. Our data suggest that PFR usage in Germany has been low in an international context. Moreover, TCIPP concentrations are significantly higher in UK dust compared to that in the other countries studied.

Table 4.2 *Summary of Statistically Significant (p<0.05) Differences in Concentrations of PFRs in Living Room Dust from Different Countries*

PFR	Significant differences		
TnBP	Australia, Kazakhstan	>	UK
TCEP	UK, Australia, Canada, Kazakhstan	>	Germany
TCIPP	UK	>	Germany, Canada, Kazakhstan, Australia
TPHP	UK, Canada, Australia, Kazakhstan	>	Germany
TDCIPP	UK, Canada, Australia	>	Germany

4.2.1.2 Significant differences in PFR contamination pattern of living room samples

To compare PFR contamination patterns between living room samples from different countries, a principal component analysis (PCA) was employed. We therefore subjected our data to a series of PCA, using the relative proportions of individual PFRs to ΣPFR in each sample as input. This approach allows separation of samples according to differences in the relative abundance of individual PFRs (which may indicate different categories of source inputs), rather than their absolute concentrations, as would be the case if unnormalised concentrations were entered into PCA, and which would mainly indicate differences in source *strengths*. This method has been used successfully for the elucidation of trends in contamination patterns in studies of organic contaminants in a wide variety of matrices over several decades, including international trends in contamination of indoor dust with PBDEs (Harrad et al., 2008b)

PCA was conducted for all measured PFRs in living room dust samples from the UK, Germany, Australia, Canada and Kazakhstan Kazakhstan (see Figure 4.1)German living room samples analysed in Belgium (n=6) were not included in the PCA as no EHDPP data was available for those samples.

PC 1 and PC 2 account for 24 and 19% of the total variance in the data. The rotated component matrix (see Table 4.3) shows the relative contribution of each PFR to each principal component score.

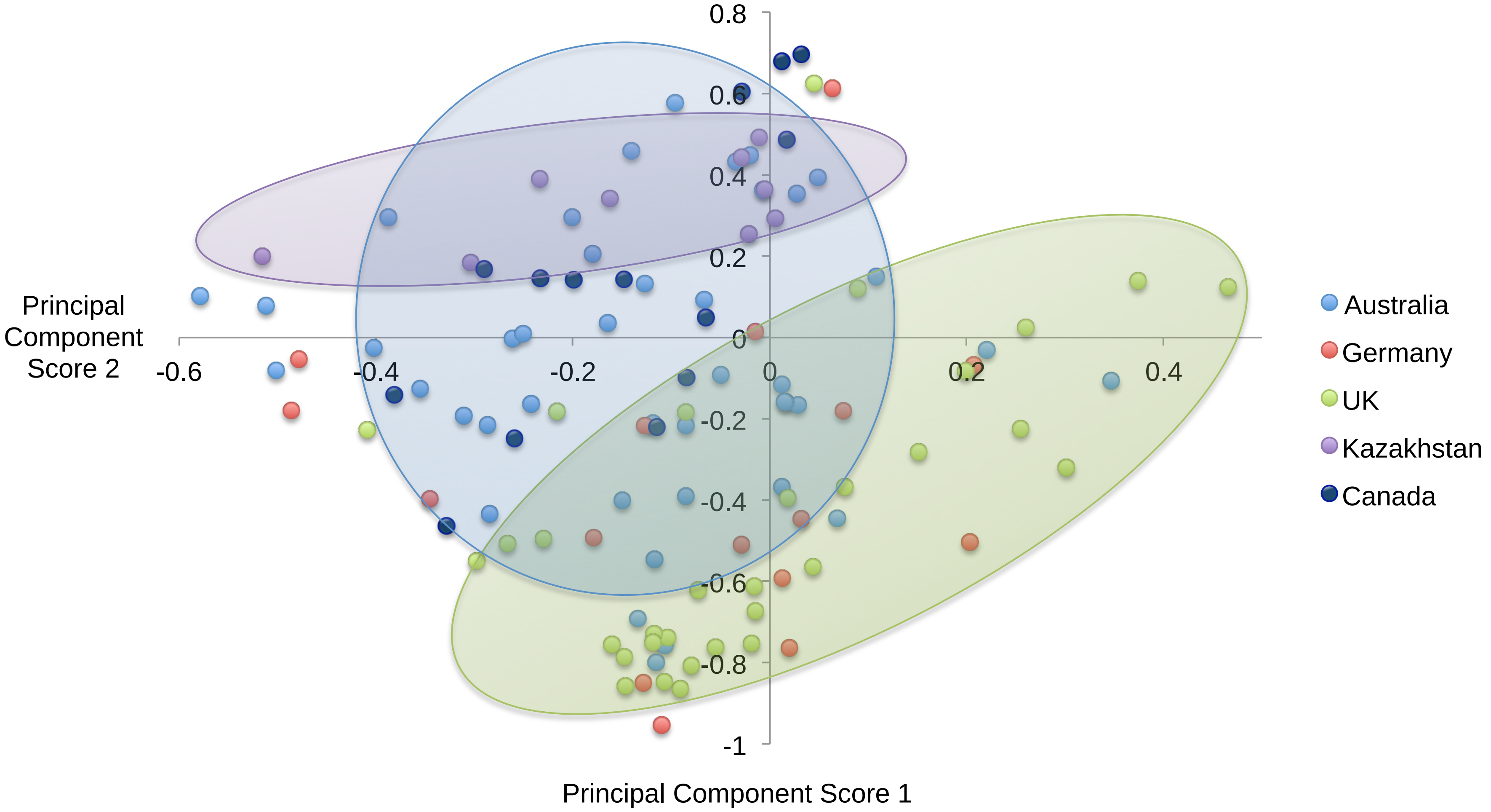
Samples with a high relative abundance of TPHP show a positive PC 1 score, with more negative PC1 scores driven by a high relative abundance of TCIPP. Similarly, PC 2 scores are positively driven by EHDPP and negatively driven by TDCIPP and TCEP.

Table 4.3 *Rotated Component Matrix for Living room Dust Samples*

	Component	
	1	**2**
TnBP	0.149	0.257
TCEP	0.188	-0.665
TCIPP	-0.957	-0.109
TPHP	0.810	0.064
EHDPP	0.030	0.705
TDCIPP	0.199	-0.740
TMPP	-0.530	0.541

The resulting Figure 4.1 indicates the existence of pattern differences in PFR contamination between the different countries. The samples group into three broadly defined clusters. Cluster 1 (green) represents all the values below the 1:1 line. The majority of the analysed UK samples were found in this cluster with primarily negative PC 1 scores, which is due to the relative high abundance of TCIPP in those samples.. Only 5 UK dust samples showed positive PC 1 values. Cluster 2 (purple) displays all the samples from Kazakhstan, which were the only samples with positive PC 1 scores. Cluster 3 (blue) represents the majority of Australian dust samples. Samples from Australia primarily exhibited negative scores for PC 2. Note that the third cluster is overlapping with the other two clusters. No indicative clusters were found for the German and Canadian dust samples, which might be due to the lower sample number compared to Australian and UK samples. Besides that German concentrations were overall significant lower than determined in other countries, which results in a non-siginificant pattern due to variability within the sample set.

Figure 4.1 *PCA for living room samples from Australia, Germany, UK, Kazakhstan and Canada*



4.2.1.3 Comparison with available literature data on living room dust concentrations

To our knowledge, there are no previous reports of concentrations of PFRs in Australian living room dust. However, one study is available for living room floor dust from New Zealand (Ali et al., 2012). The pattern in the 34 New Zealand samples analysed was dominated primarily by TPHP (median 0.6 µg/g) and TCIPP (median 0.35 µg/g), which were also the dominant PFRs in the Australian samples analysed in this study (TCIPP (median 1.8 µg/g), TPHP (median 1.2 µg/g)). Literature data on PFR concentrations in Canadian house dust are also scarce. One study found average TDCIPP concentrations in dust collected in 2010 to be 0.28 µg/g (Goosey et al., 2012). This is lower than the average concentration of 1.2 µg/g in the samples analysed in this study which were collected in 2008. While another very recently published study determined median concentrations of TCIPP in Canadian "fresh" house dust of 1.4 µg/g and Canadian vacuum cleaner bag samples of 1.1 µg/g. (Fan et al., 2014), which is inline with the median TCIPP concentrations in our Canadian dust samples, TPHP levels reported in that study agreed as well very well with the concentrations detected in our sample set. However, Fan et al (2014) reported TDCIPP concentrations that at up to 101 µg/g, were nearly an order of magnitude higher than the maximum TDCIPP concentration detected in Canadian dust samples in this study.

Elsewhere in North America, median concentrations of TDCIPP in US living room dust were 2.8 µg/g and 2.1 µg/g in 2006 and 2010 respectively (Dodson et al., 2012). Noteworthy is the observation that the maximum TDCIPP concentration reported by Dodson et al (2012) was – at 44 µg/g – substantially higher compared to the maximum concentration of 3.2 µg/g found in this study. While TCIPP concentrations in the UK are with a median of 21 µg/g, an order of magnitude higher than those reported by Dodson et al (2012) (median 2.1 µg/g), concentrations of TDCIPP in our UK samples (median 0.71 µg/g) are lower than those in the US. Combined, these observations lead to the conclusion that TCIPP is preferred in the UK, while

TDCIPP is the preferred choice in the US.

Even though TCIPP concentrations in UK house dust are significantly elevated compared to the other countries studied here, they are of a comparable order to TCIPP concentrations detected in Japanese floor dust in 2006 (median 19 µg/g). The Japanese study also reported maximum concentrations twice those detected in UK dust in this study (100 µg/g) while it was shown by (Kanazawa et al., 2010) that living room dust concentrations were even higher when taken as a multisurface sample (i.e. including dust from tables, shelves as well as floors etc.) and not just as floor dust. To our knowledge, to date Japan displays the highest PFR concentrations in living room dust samples worldwide.

It is slightly surprising that TCIPP, the PFR with the third highest vapour pressure of our target compounds, is the most abundant in all microenvironments studied except Kazahkstani homes. However, the relative abundance of TCIPP may possibly be attributed to its greater use. In other words, the relative abundance of an individual PFR in air and dust will be an integral of the extent to which it is used, and its physicochemical properties. An example of the potential influence of physicochemical properties is the high vapour pressure of TMPP. This means it partitions preferentially to the vapour phase, consistent with its low detection frequency in floor dust, which is potentially exacerbated further by comparatively low use.

Moreover, a very recently published study of simultaneously-collected indoor air and dust samples from Norwegian homes, indicated that concentrations of TCIPP, TnBP, TCEP and TBEOP were significantly correlated in air and dust (Cequier et al., 2014). The authors suggested that the dust:air partition coefficient for a given PFR would likely be proportional to K_{OA}. If so, the authors proposed that knowledge of the concentration in dust of a given PFR of known K_{OA}, would facilitate calculation of the corresponding air concentrations in the same microenvironment. This highlights the influence of physicochemical properties of PFRs on their indoor fate.

4.2.2 PFR concentrations in car dust

Car dust samples were collected according to the sampling procedure described in Chapter 2 from three countries, namely Australia (n=39), Germany (n=19) and the UK (n=21). As only 12 UK car dust samples were collected specifically for this study, nine archived dust samples previously analysed for perfluorinated compounds by a former group member were additionally analysed. The vehicles sampled covered a wide range of manufacturers, models, and ages.

PFR concentrations in individual car dust samples analysed in this study can be found in Appendix 9, a statistical data summary in Appendix 10, while median and range concentrations are provided in Table 4.5. Concentrations below detection limit were replaced by half the LOQ for all statistical analyses.

4.2.2.1 Significant differences in absolute PFR contamination of car dust samples

Table 4.5 indicates potential differences in concentrations of PFRs in dust samples from cars in different countries. For example, median concentrations of ΣPFRs in Australian, German, and UK car dust were 90, 20, and 110 µg/g respectively. These differences were explored further via ANOVA with a Tukey post hoc test. Statistical analysis was conduced on log-transformed data as a Shapiro-Wilk test of normality showed that concentrations of all PFRs were significantly positively skewed. Table 4.4 displays the statistically significant differences ($p<0.05$) observed in absolute concentrations of individual PFRs detected in car dust samples for the three different countries studied. If not listed in Table 4.4 no significant differences were observed.

Several key observations arise from this comparison. Firstly, concentrations of TCIPP were significantly higher in UK and Australian samples compared to Germany. Secondly, EHDPP was significantly more abundant in samples from the UK compared to Australia. Thirdly, TDCIPP levels were significantly higher in UK samples compared to those in samples from Australia and Germany. Furthermore, concentrations of TnBP were significantly higher in

Australian car dust compared to those from UK vehicles. This is mainly due to TnBP levels being mostly below the LOD in the UK sample set.

Table 4.4 *Summary of Statistically Significant ($p<0.05$) Differences in Concentrations of PFRs in Car Dust Samples from Australia, Germany and UK*

PFR	**Significant differences**		
TnBP	Australia	>	UK
TCIPP	UK, Australia	>	Germany
EHDPP	UK	>	Australia
TDCIPP	UK	>	Australia, Germany

4.2.2.2 Differences in PFR contamination pattern of car dust samples

PCA was conducted for the analysed car dust samples from Australia, Germany, and the UK. Car samples from Germany, which were analysed in Belgium, were excluded from the PCA analysis, as no EHDPP data were available for those samples.

PC 1 and PC 2 respectively account for 25 % and 23 % of the total variance in the data. The rotated component matrix shows the relative contribution of each PFR to each principal component score (Table 4.6). In the case of car dust samples PC 1 is mainly positively driven by a high abundance of TnBP, TCEP, TPHP and EHDPP, while negatively driven by a high relative abundance of TCIPP and TDCIPP. PC 2 is positively driven by a high relative abundance of TCIPP while negatively driven by a high relative abundance of TDCIPP.

Table 4.5 *Median and Range of PFR Concentrations (µg/g) in Car Dust Samples from Australia, Germany, and UK*

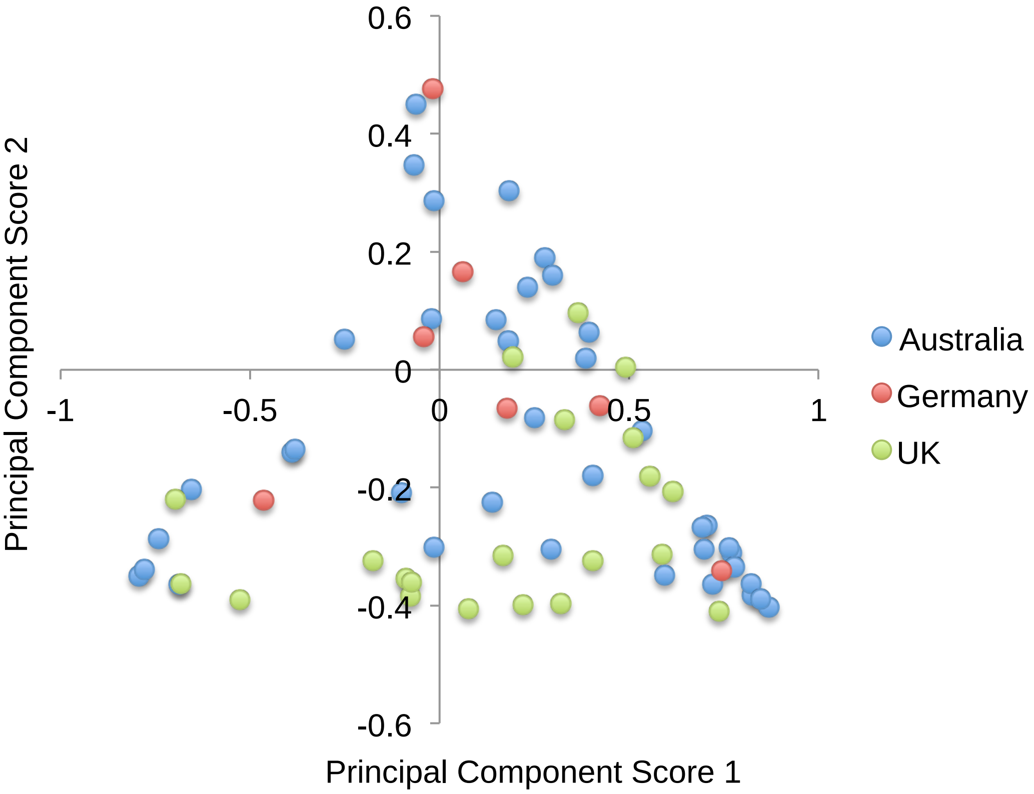
	TnBP	Australia	Germany	UK	**TCEP**	Australia	Germany	UK
Minimum		<0.03	<0.03	<0.03		<0.06	<0.06	<0.06
Median		0.11	<0.03	<0.03		2.0	0.40	1.23
Maximum		8.4	0.63	1.2		62	5.1	8.7
	TCIPP	Australia	Germany	UK	**TPHP**	Australia	Germany	UK
Minimum		0.31	0.29	2.4		0.33	0.33	0.27
Median		24	2.9	53		3.7	1.8	3.3
Maximum		310	100	370		85	11	170
	EHDPP	Australia	Germany	UK	**TDCIPP**	Australia	Germany	UK
Minimum		0.18	0.01	0.29		0.06	<0.03	0.11
Median		0.63	1.17	2.2		2.3	4.1	31
Maximum		4.9	1.9	11		730	620	740
	TMPP	Australia	Germany	UK	**ΣPFR**	Australia	Germany	UK
Minimum		<0.01	<0.01	<0.01		2.6	1.3	6.1
Median		0.31	0.86	0.59		90	20	110
Maximum		240	150	5.6		850	640	940

Table 4.6 *Rotated component matrix for car dust samples*

	Component	
	1	**2**
TnBP	0.65	-0.004
TCEP	0.584	-0.114
TCIPP	-0.424	0.888
TPHP	0.582	-0.036
EHDPP	0.405	0.151
TDCIPP	-0.402	-0.897
TMPP	0.311	0.015

Results of the PCA suggest that overall there is relatively little difference in the PFR contamination pattern observed in car dust, regardless of whether the vehicles sampled are from Australia, Germany, or the UK. This is perhaps unsurprising given the substantial international trade in motor vehicles, which means that – e.g. cars purchased in the UK may have been manufactured in a number of locations worldwide. Notwithstanding this, there is a slight indication that the UK car dust samples generally display more negative PC2 scores than those from Australia and Germany. This reflects the greater contribution of TDCIPP in many UK car dust samples, suggesting greater use of this PFR in UK than in Australia or Germany.

Figure 4.2 *PCA for car dust samples from Germany, UK and Australia*



4.2.2.3 Comparison with available literature data on car dust concentrations

Comparison of these data with relevant literature is difficult due to the very sparse database on PFR concentrations in car dust samples. Car dust samples from Kuwait (Ali et al., 2013) showed elevated TDCIPP concentrations, which is similar to the samples analysed this study, even though the median concentration (7.6 µg/g) was four times lower than that detected in our UK samples. It appears though that Australian, German and UK cars are more contaminated with PFRs than cars in Pakistan. (Ali et al., 2013) showed that cars in Pakistan had TDCIPP median concentrations of only 0.03 µg/g with a maximum concentration of 1.2 µg/g, which is lower than all the median concentrations determined in this study. (Ali et al., 2013) suggested that the higher concentrations in cars from Kuwait might be due to the fact that Kuwait imports most of their vehicles from countries like Japan, USA and the EU, while Pakistanis buy locally assembled cars, which most likely have less strict fire regulations than those produced in developed countries. Another reason could lie with the composition of the dust, as the authors noted that the Pakistani dust samples had a uniformly very sandy texture, while samples from Kuwait were more heterogeneous in nature indicating e.g. abrasion as a source for PFRs. Car samples collected in the US showed a geometric mean TDCIPP concentration of 26 µg/g (Webster et al., 2010) with a maximum value approaching 1 mg/g, which exceeds slightly the maximum value found in this study.

4.2.3 Office dust

Office samples were procured from a variety of office types, ranging from closed single occupant office space, through home offices, to open plan offices for up to nine people for UK samples. Maximum occupancy for German offices was two people. There are indications that open plan offices (which contain more PFR sources compared to smaller offices) are much more common in the UK than there are in Germany. No questionnaire data was available for the archived Kazakhstan samples. Concentrations of PFRs in individual office dust samples analysed in this study are reported in Appendix 11, a statistical data summary in Appendix 12, while median and range concentrations are reported in Table 4.8. Concentrations below detection limit were replaced by half the LOQ for all statistical analyses.

4.2.3.1 Concentrations of PFRs in office dust from different countries

Table 4.7 summarises the statistically significant differences ($p<0.05$) in absolute concentrations of individual PFRs detected in office samples for the three different countries studied. If not listed in Table 4.7, no significant differences were observed. Note that TCIPP, EHDPP and TDCIPP concentrations in UK offices are significantly higher than in their German counterparts. Even though, due to the small sample numbers, results for samples from Kazakhstan are only indicative; observed concentrations in these office samples were significantly lower for TCIPP and EHDPP compared to the samples from the UK. It is interesting that no significant differences in absolute concentrations between samples from Kazakhstan and Germany were observed. This further underlines the fact that, as seen for the living room samples, PFR use in Germany appears less than in other countries.

Table 4.7 *Summary of Statistically Significant (p<0.05) Differences in Concentrations of PFRs in office samples from Kazakhstan, Germany and UK*

PFR	**Significant differences**		
TCIPP	UK	>	Germany, Kazakhstan*
EHDPP	UK	>	Germany, Kazakhstan*
TDCIPP	UK	>	Germany

*preliminary result as less than 10 samples included for comparison

Table 4.8 *Median and Range of PFR Concentrations (μg/g) in Office Dust Samples from Germany, Kazakhstan and UK*

	TnBP	Germany	Kazakhstan	UK	**TCEP**	Germany	Kazakhstan	UK
Minimum		<0.03	<0.03	<0.03		<0.06	0.95	<0.06
Median		0.17	0.07	<0.03		0.13	2.5	0.87
Maximum		0.76	0.48	1.3		12	5.8	160
	TCIPP	Germany	Kazakhstan	UK	**TPHP**	Germany	Kazakhstan	UK
Minimum		0.18	0.87	3.6		0.20	0.39	0.56
Median		1.6	2.2	33		1.5	5.3	4.3
Maximum		13	100	230		8.8	48	50
	EHDPP	Germany	Kazakhstan	UK	**TDCIPP**	Germany	Kazakhstan	UK
Minimum		0.13	0.08	0.15		<0.03	<0.03	<0.03
Median		0.36	0.26	5.3		0.14	0.91	0.48
Maximum		3.8	0.57	81		2.2	4.0	51
	TMPP	Germany	Kazakhstan	UK	**ΣPFR**	Germany	Kazakhstan	UK
Minimum		<0.01	0.01	<0.01		0.75	8	10
Median		<0.01	0.38	<0.01		6.4	22	47
Maximum		1.9	9.99	5.3		28	111	280

4.2.3.2 International differences in PFR contamination pattern of office dust samples

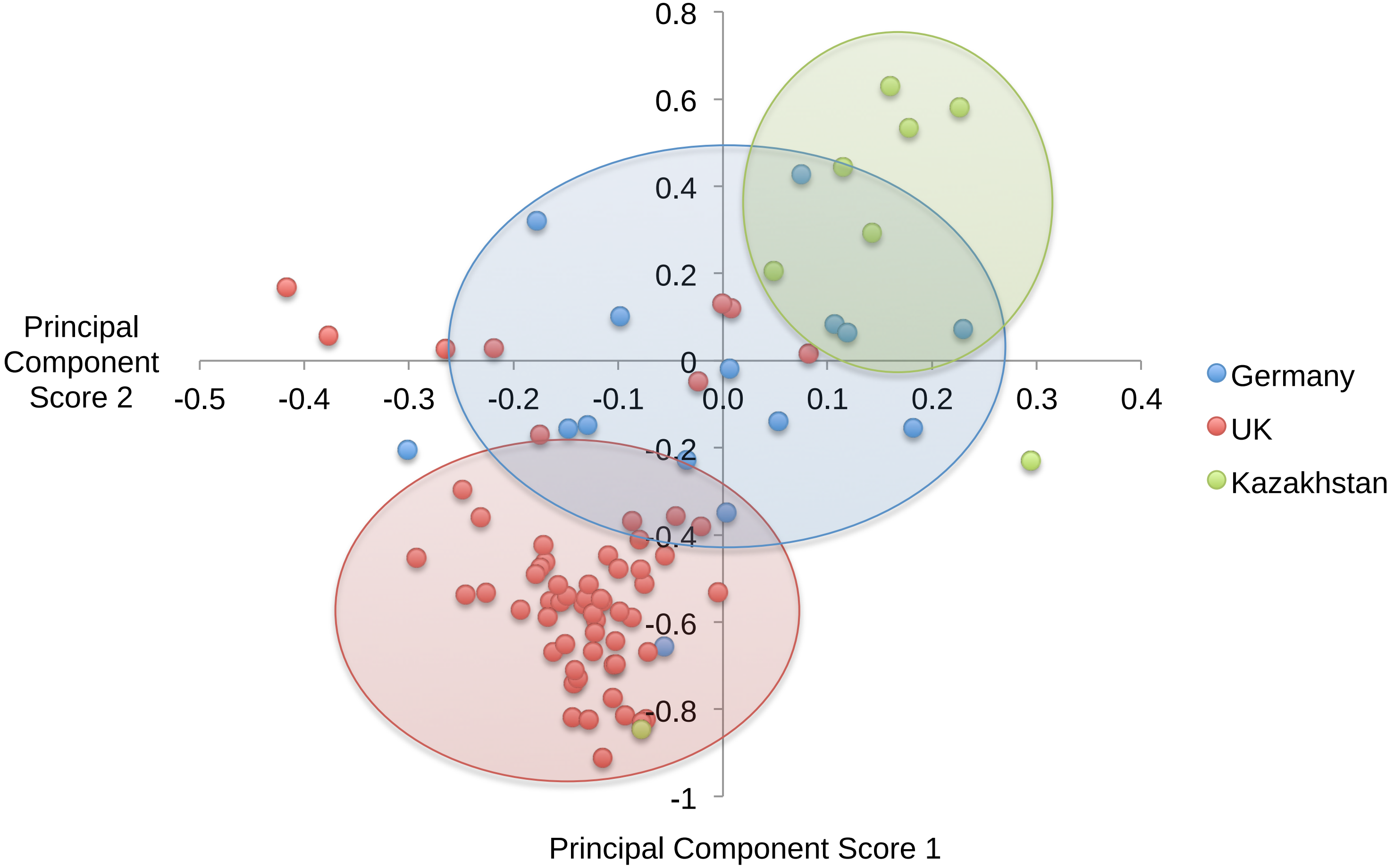
A PCA was conducted for all measured PFRs in office dust samples from the UK, Germany and Kazakhstan (Table 4.9). German office samples analysed in Belgium (n=10) were not included in the PCA as there were no EHDPP data available for those samples. PC 1 and PC 2 account for 31% and 19% of the total variance in the data. The rotated component matrix shows the relative contribution of each PFR to each principal component score (Table 4.9). In this case, PC 1 is mainly positively driven by a high relative abundance of TPHP, while negatively driven by a high abundance of TCIPP. PC 2 is positively driven by relative high abundance of TDCIPP and TMPP while substantially negatively driven by a relative high abundance of EHDPP.

Table 4.9 *Rotated Component Matrix for office dust samples*

	Component	
PFR	**1**	**2**
TnBP	0.584	-0.244
TCEP	0.422	0.124
TCIPP	-0.955	-0.111
TPHP	0.755	0.156
EHDPP	0.189	-0.729
TDCIPP	0.179	0.545
TMPP	0.145	0.675

It can be clearly seen in Figure 4.3 that there are three different clusters. Cluster 1 (red) represents the majority of UK samples. The majority of UK samples were mainly driven in a negative direction for both PCs. In contrast, cluster 2 (blue) represents the majority of German office samples. German office samples were not highly driven in either a positive or negative direction for either PC, which results in them occupying a central region of component space. Finally, the 3rd cluster that occupies the top right quadrant of component space is mainly occupied by office dust samples from Kazakhstan.

Figure 4.3 *PCA for office samples from Germany, UK and Kazakhstan*



These Kazakhstani samples showed (except for one sample) positive scores for both PC 1 and PC 2.

4.2.3.3 Comparison with available literature data on office dust concentrations

As with car dust samples, the available literature data on concentrations of PFRs in office dust are relatively few, which makes comparison with our data rather difficult. A study on US office dust (Carignan et al., 2013b) showed geometric mean TDCIPP levels of 6.6 µg/g which is about one order of magnitude higher than the geometric mean of 0.54 µg/g detected in the UK samples analysed in this study.

On the other hand, preliminary results from the same study published as a conference contribution (Webster et al., 2010) indicate that the geometric mean TPHP concentration of 4.1 µg/g detected within US office dust samples, is comparable to the 3.6 µg/g detected in the UK samples in this study. This suggests greater use of TDCIPP within the office environment in the US, while use of TPHP appears of similar magnitude in both the UK and US. No TPHP results were published in the (Carignan et al., 2013b) paper.

4.2.4 Couch dust

To provide an indication of the role of couches as a PFR source in indoor environments, couch dust samples were collected according to the sampling procedure described in Chapter 2 from two countries, namely Australia (n=41) and the UK (n=10). As the numbers of UK couch dust samples are low, the acquired data must be viewed as indicative only

Concentrations of PFRs in individual couch dust samples are provided in Appendix 13, a statistical data summary in Appendix 14, while median and range concentrations are given in Table 4.10. Concentrations below detection limit were replaced by half the LOQ for all statistical analyses.

Table 4.10 *Median and Range of Concentrations (µg/g) of PFRs in Couch Dust Samples from Australia (Aus) and the UK*

	TnBP		**TCEP**		**TCIPP**	
	UK	Aus	UK	Aus	UK	Aus
Minimum	<0.03	<0.03	<0.06	<0.06	1.8	0.82
Median	0.34	<0.03	<0.06	0.72	610	2.9
Maximum	4.8	3.0	3.4	27	1900	550
	TPHP		**EHDPP**		**TDCIPP**	
	UK	Aus	UK	Aus	UK	Aus
Minimum	0.18	0.37	0.28	0.08	0.16	<0.03
Median	2.4	1.8	1.4	0.39	2.0	0.58
Maximum	8.4	29	2.5	11	700	7.5
	TMPP		**ΣPFR**			
	UK	Aus	UK	Aus		
Minimum	<0.01	<0.01	5.2	1.3		
Median	0.62	<0.01	620	6.4		
Maximum	2.8	6.6	2600	640		

4.2.4.1 Significant differences in absolute PFR contamination of couch dust samples

Comparison via t-test of log-transformed PFR concentrations in couch dust from Australia with that from the UK revealed concentrations of TnBP, TCIPP, EHDPP, TDCIPP, TMPP to be significantly ($p<0.01$) higher in UK than Australian samples. In comparison, concentrations of TCEP were significantly elevated ($p<0.01$) in Australian compared to UK couch dust. To our knowledge this is the first time that concentrations of PFRs in couch dust have been reported. While previously polyurethane foam from couches (Stapleton et al., 2012) and furniture foam in general (Stapleton et al., 2009) have been studied, we believe that couch dust has potentially, especially for adults, more relevance for human exposure. As flame retardants are usually added to polyurethane foam at percent levels, a threshold at 0.2 mg/g for “low detection” was applied to polyurethane foam from couches. (Stapleton et al., 2012) Applying the same threshold to our dust samples it is highly likely that the UK couches were treated with TCIPP and TDCIPP, while the Australian couches were either treated with TCIPP or another type of flame retardant. As (Stapleton et al., 2012) focused their study on the V6 impurity TCEP, TPHP (an ingredient of Firemaster 550), TDCIPP, and another flame retardant mixture called AC073 (which contains 38-48% TPHP); no data are available on the concentrations of TCIPP in US couch foam. But as the Californian flammability standard TB 117 is very strict, there is a high likelihood that TDCIPP is being replaced by TCIPP in countries with less strict flammability standards due to the cost of the former.

4.3 Differences in absolute concentrations and relative abundances of PFRs observed in dust from different microenvironment categories

Concentrations and relative abundances of PFRs in dust from different microenvironment categories from the same country were compared. This was conducted to elucidate whether particular microenvironments display significantly elevated contamination with one or more PFRs.

4.3.1 Australia

Australian indoor dust samples were collected from living rooms (n=42), cars (n=39), couches (n=41), mattresses in adult bedrooms (n=48), children’s bedrooms (n=11) and mattresses from the children’s bedrooms (n=9). As described in chapter 2, samples came mainly from Sydney and Brisbane. Additionally, samples from smaller cities and more remote regions were analysed. As Australia is such a large country, the climate differs between Sydney and Brisbane, which may influence PFR concentrations in dust via enhanced volatilisation from putative sources, balanced to an unknown extent by reduced partitioning to dust from air at higher temperatures. Moreover, a great variety of cars were studied with a range of ages, manufacturers and models included in the sample set.

Concentrations of PFRs in individual samples can be found in Appendix 7, Appendix 9, Appendix 13, Appendix 15 and Appendix 16, while summaries are displays in Table 4.1,Table 4.10, Table 4.11 and Table 4.12. PFRs were present in all samples analysed, with TCIPP and TPHP being the two most abundant PFRs in Australian samples.

Comparison of the median concentrations of individual PFRs in dust from the various microenvironment categories studied in Australia is displayed in Figure 4.4. Concentrations of PFRs in Australian indoor dust samples displayed a positively skewed distribution; hence log-transformed concentrations were subjected to ANOVA analysis with Tukey post-hoc tests. The outcome of this data analysis is summarised in Table 4.13, which lists those PFRs and microenvironments for which significant ($p<0.05$) differences in concentration exist.

Table 4.11 *Descriptive Statistical Summary of PFR Concentrations (μg/g) in Mattress Dust Samples from Australia*

	TnBP	**TCEP**	**TCIPP**	**TPHP**	**EHDPP**	**TDCIPP**	**TMPP**	**ΣPFR**
Minimum	<0.03	<0.06	0.04	0.04	<0.01	<0.03	<0.01	0.32
5th percentile	<0.03	<0.06	0.20	0.17	<0.01	<0.03	<0.01	1.1
Median	<0.03	0.32	1.3	1.1	0.15	0.09	<0.01	3.9
Geometric mean	0.04	0.16	1.2	1.0	0.13	0.10	0.03	4.1
Average	0.11	0.52	2.8	2.0	0.24	0.35	0.24	6.2
95th percentile	0.52	1.5	9.8	5.6	0.57	1.5	1.3	17
Maximum	2.0	6.5	31	21	0.91	4.1	4.1	34
Standard Deviation	0.30	0.99	4.9	3.3	0.20	0.73	0.67	6.7
Relative Standard Deviation	260	190	180	170	85	210	270	110

Table 4.12 *Descriptive Statistical Summary of PFR Concentrations (μg/g) in Bedroom Floor Dust Samples from Australia*

	TnBP	**TCEP**	**TCIPP**	**TPHP**	**EHDPP**	**TDCIPP**	**TMPP**	**ΣPFR**
Minimum	<0.03	<0.06	0.46	0.20	0.12	<0.03	<0.01	2.7
5th percentile	<0.03	<0.06	0.50	0.37	0.14	0.03	<0.01	2.8
Median	<0.03	0.41	1.6	1.6	0.24	0.31	<0.01	7.6
Geometric mean	0.04	0.37	1.6	1.5	0.30	0.21	0.02	6.4
Average	0.05	1.3	2.4	2.34	0.37	0.67	0.18	7.3
95th percentile	0.15	4.2	6.3	6.4	0.85	2.6	0.79	12
Maximum	0.19	4.3	7.4	6.6	0.95	3.8	1.4	13
Standard Deviation	0.06	1.7	2.3	2.2	0.27	1.1	0.40	3.6
Relative Standard Deviation	100	130	94	94	74	170	220	49

Figure 4.4 *Median dust PFR concentration (µg/g) for different microenvironments in Australia*

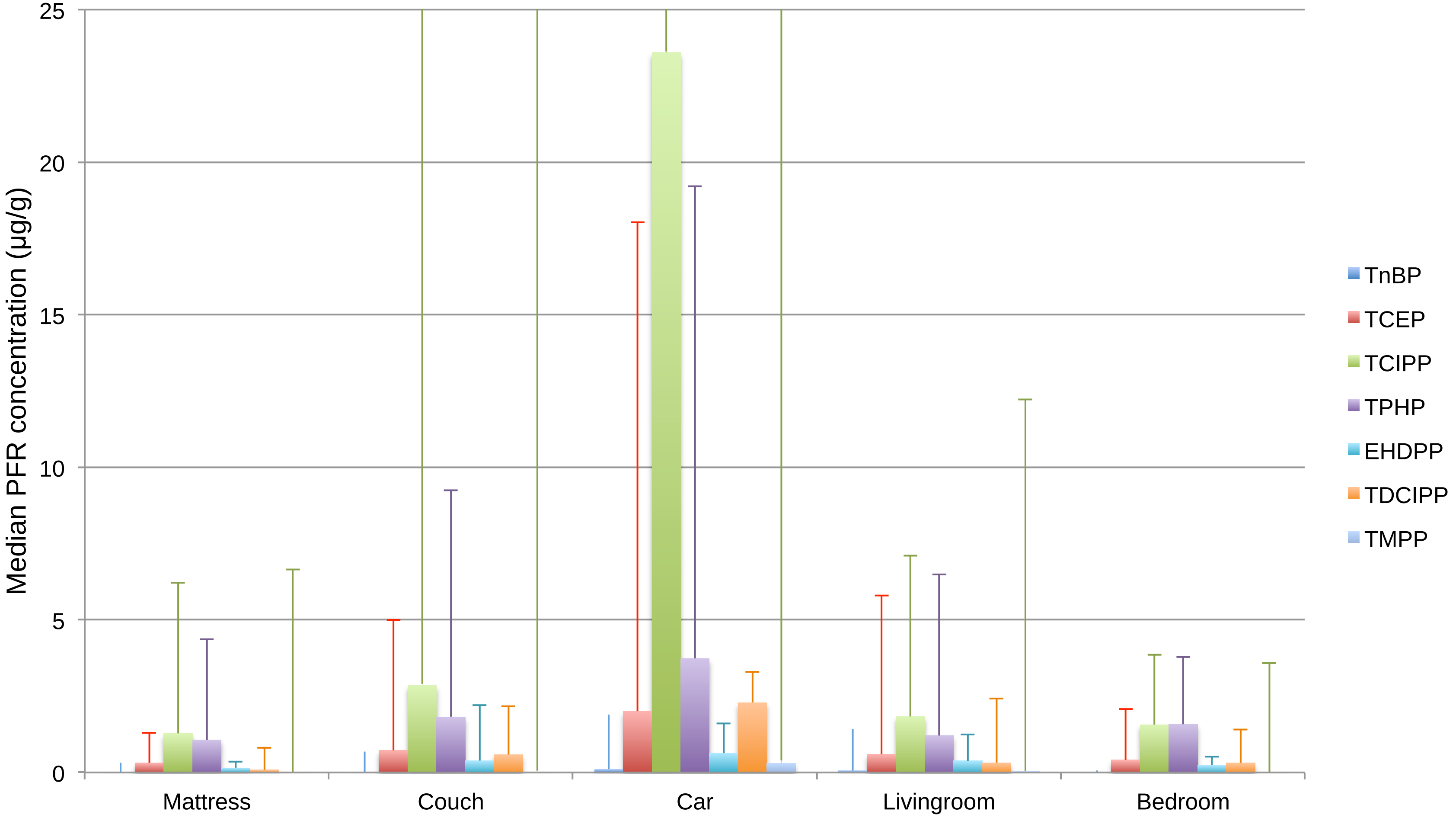


Table 4.13 shows concentrations of each targeted PFR in Australian car dust to exceed significantly those in mattress dust. Moreover, car dust contained significantly higher concentrations of both TCIPP and TDCIPP than those detected in any of the other microenvironment categories studied. In domestic environments, couch dust contained significantly higher concentrations than those found in mattress dust for all PFRs, implying greater PFR use in couches than mattresses.

Table 4.13 *Summary of Statistically Significant (p<0.05) Differences in Concentrations of PFRs in Dust from Different Microenvironment Categories in Australia*

PFR	Microenvironments		
TnBP	Car	>	Mattress
TCEP	Car, Couch, Living room	>	Mattress
	Car	>	Living room
TCIPP	Car, Couch	>	Mattress
	Car	>	Couch, Living room, Bed room
TPHP	Car, Couch	>	Mattress
	Car	>	Living room
EHDPP	Car, Couch	>	Mattress
	Car	>	Living room
TDCIPP	Couch, Car, Living room	>	Mattress
	Car	>	Couch, Living room, Bedroom
TMPP	Car	>	Mattress, Couch, Living room

The only available data on import/use of PFRs for Australia is somewhat dated (2001). There is no evidence that PFRs were produced in Australia itself. As of 2001, TCEP and TCIPP were being imported with that of TDCIPP expected to commence in the near future (NICNAS, 2001). More recent information (May 2013) (NICNAS, 2013) states that the EU classification for TCEP should be adopted, but no mention is made as to whether TCEP's replacement by TCIPP in Australia has occurred or is in progress. As TCEP levels in Australian living rooms (see 4.2.1) were of comparable magnitude to the UK, it suggests that TCEP has now been replaced.

The 2001 NICNAS report states that the majority (85%) of PFRs imported to Australia were used in the production of rigid and flexible foams at typical concentrations of 5-20% depending on the product (NICNAS, 2001). In 2001, around 410 tonnes of TCEP and TCIPP combined were imported to Australia, augmented by a projected 20-40 t of TDCIPP in the future (NICNAS, 2001). It should be noted that these import volumes refer to the chemicals themselves, and do not include PFRs associated with finished goods. Industry estimated at that point, that future imports of TCEP would decrease from 120 to 90 tonnes/year and increase for TCIPP from 290 to 320 tonnes/year, as some users were preferring TCIPP over TCEP, but that combined TCEP and TCIPP use would remain stable (NICNAS, 2001).

Besides that, the elevated TCEP in car dust samples could be a result of the use of V6 in the analysed cars. V6 is known to contain between 4.5-7.5 % TCEP as an impurity. (European Union, 2007) This is consistent with reports that V6 was detected in car samples from the 1990s, suggesting use in the car industry even before TCEP was replaced by TCIPP. (Fang et al., 2013)

4.3.1.1 Matching sample sets

To evaluate if mattresses or couches were a potential source of PFRs, concentrations of PFRs in matching sample sets (e.g. couch dust and living room dust from the same rooms) were analysed via a paired t-test.

A paired t-test revealed that TCIPP concentrations in couch dust were significantly ($p<0.05$) higher compared to their matching living room samples, implying that couches are a source for TCIPP in living rooms. This is no surprise as it is known that TCIPP is applied to furniture foam – and preliminary unpublished data for foam from waste sofas in the UK reports ~80% of samples analysed to contain substantial concentrations of TCIPP (Stubbings, Drage, and Harrad, personal communication). No significant differences were found for the other analysed PFRs in this study.

Comparison of children’s mattress dust samples with their matching bedroom dust samples, revealed significantly ($p<0.05$) higher TDCIPP concentrations in bedroom floor dust compared to mattress dust. Although this result is only based on a very small sample set (n=9, for two bedrooms no matching mattress dust was available as insufficient dust was collected for analysis); it indicates that mattresses are not a direct source of PFRs, consistent with a study from New Zealand (Ali et al., 2012), even though in that study living room floor dust and mattress samples were compared. To our knowledge, no other study has compared PFR concentrations in matched samples of dust from bedroom floors and mattresses.

4.3.1.2 Correlations between PFRs in Australian dust samples

Correlations between log-transformed concentrations of different PFRs were examined. Positive correlations may be indicative of common sources of the two compounds. Interestingly, both couch and bedroom floor dust samples revealed a significant correlation between TCEP and EHDPP, while both mattress and car dust samples showed a significant correlation between TPHP and TDCIPP concentrations. This indicates a common source for those PFRs in the microenvironments concerned. Literature data on PFR concentrations are sparse, which makes comparisons rather difficult. No correlations between PFRs were reported by (Ali et al., 2013) in car dust samples from Kuwait and Pakistan. However, only TPHP was compared to PBDEs and other PBDE replacements, revealing that TPHP did not correlate significantly with the other components of Firemaster 550 in Pakistani dust, and indicating another source of TPHP in cars. Moreover, a study on Spanish car dust (García et al., 2007b) reports data for only two samples and a recently published study on US car dust reported only TDCPP concentrations (Carignan et al., 2013b) or TCEP (Fang et al., 2013).

Table 4.14 *Summary of correlations in Australian dust sample set (embolded correlations were observed in more than one microenvironment)*

Compound 1	Compound 2	Pearson Correlation Coefficient	Microenvironment
Highly significant correlation (p<0.01)			
TCEP	TCIPP	0.629	Living room
TCEP	TPHP	0.429	Couch
Compound 1	Compound 2	Pearson Correlation Coefficient	Microenvironment
TCEP	TDCIPP	0.489	Car
TCIPP	TPHP	0.456	Couch
TPHP	EHDPP	0.491	Couch
TPHP	**TDCIPP**	**0.499**	**Car**
Significant correlation (p<0.05)			
TnBP	TCEP	0.373	Car
TCEP	TCIPP	0.709	Bedroom
TCEP	**EHDPP**	**0.314**	**Couch**
TCEP	**EHDPP**	**0.710**	**Bedroom**
TCEP	TPHP	0.327	Mattress
TCIPP	EHDPP	0.638	Bedroom
TCIPP	TDCIPP	0.294	Mattress
TDCIPP	**TPHP**	**0.262**	**Mattress**

4.3.1.3 Influence of couch age on concentrations of PFRs in Australian couch dust

The average couch age in the Australian sample set was 7 years, with a median of 5 years. No discernible relationship was evident between couch age and concentrations of TCIPP and TCEP in our couch dust samples. For example, the highest concentration of TCEP (27 µg/g) in the Australian couch dust samples was taken from a couch purchased 3 years prior to sampling, some time after TCEP is thought to have been removed from such applications. Likewise, the maximum TCIPP concentration (550 µg/g) was seen in a sample from a couch aged 10 years, while the second highest concentration (210 µg/g) was found in a couch purchased only 2 years ago.

4.3.1.4 Influence of room content on concentrations of PFRs in Australian dust samples

Information about the presence, numbers, and age of putative sources in the Australian living rooms sampled and other potentially influential factors were examined for their influence on the concentrations of PFRs in the corresponding dust samples. Samples for which such information was not available were excluded from such analysis. No significant correlations were found between the age of the TV (all bar one living room contained a TV), the presence of curtains, or the time since the last vacuum clean for all target PFRs. However, a significant correlation ($p<0.05$) between TCIPP concentrations in dust and the presence of carpet was found, such that TCIPP concentrations were higher in rooms containing carpet than in those in rooms with bare floors.

4.3.2 UK

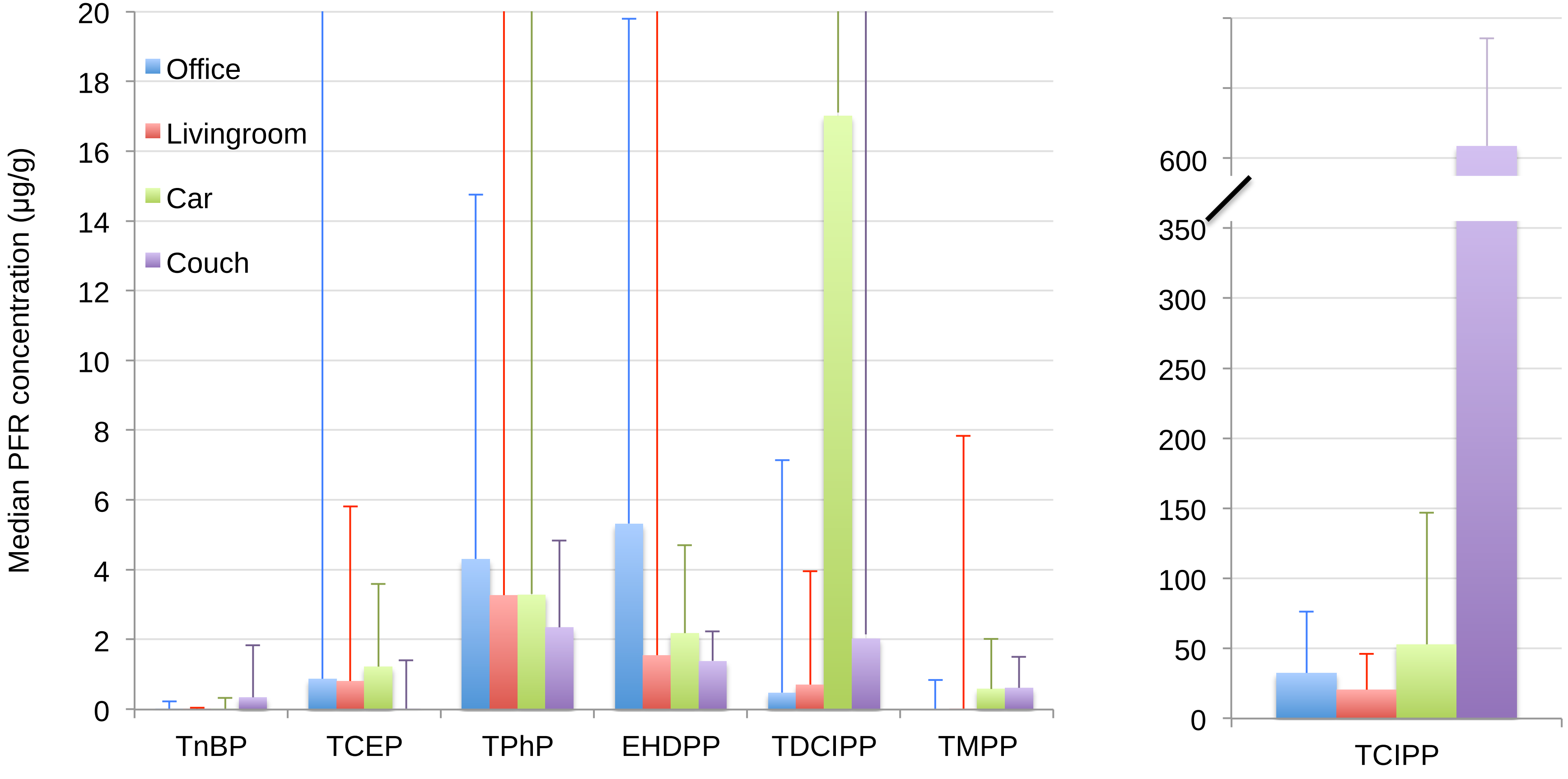
Indoor dust samples were collected from homes (n=32), offices (n=61), cars (n=21) and couches (n=10) within the Birmingham area. As in Australia, the cars selected for study spanned a wide range of ages, manufacturers and models. Concentrations of PFRs in individual samples can be found in Appendix 7, Appendix 9, Appendix 11 and Appendix 13, while summaries are displayed in Table 4.1, Table 4.5, Table 4.8 and Table 4.10. PFRs were present in all samples analysed with TCIPP and TPHP being the two most abundant PFRs in UK dust samples. Median concentrations of PFRs in dust from different microenvironment categories in the UK are shown in Figure 4.5. ΣPFR concentrations were highest in couch dust followed by car dust, which is entirely driven by elevated TCIPP concentrations, with office dust and living room dust samples having comparable ΣPFR concentrations. Figure 4.5 also indicates differences in the extent of contamination between the different microenvironments. ANOVA with Tukey post-hoc test was conducted on log-transformed data and revealed several statistically significant differences ($p<0.01$).

Even though only 10 UK couch dust samples were analysed, these contained significantly higher concentrations of TCIPP compared to office, car and – most relevantly - living room dust. Moreover, TCIPP concentrations in the one matched living room/couch dust sample pair, were higher in the couch dust, and were also the highest reported out of all couch and living room dust samples in this study. This is consistent with the hypothesis that in this living room, the couch may be a significant source. However, it may also be that this room is influenced by another TCIPP source that also influences concentrations in the couch dust.

TDCIPP levels were significantly higher in car dust samples compared to living room and office samples in UK. Usually TCIPP and TDCIPP have similar applications, with TDCIPP finding application only when a higher efficiency is needed to reach a certain standard due to its much higher price (around twice that of TCIPP) (European Union, 2008b).

TCEP levels were significantly higher in office and car samples compared to couch dust samples. As the average UK couch sampled was 13 years, it is very likely that the couches were not treated with TCEP, especially as restrictions were placed on further use of TCEP in polyurethane foams in 1998 (WHO, 1998; Bayerisches Landesamt für Umwelt, 2006). Alternatively, the age of the UK offices sampled are not known, but none of the office buildings studied were classed as new-builds, and thus it is possible that they contain putative TCEP sources. There is the possibility of the TCEP concentrations detected resulting from the application of V6. However, no information is available on the application of V6 in the UK or elsewhere. (European Union, 2007).

Figure 4.5 *Median concentrations of individual PFRs in different microenvironments from the UK, TCIPP and TDCIPP car concentrations are displayed as concentration divided by 2*



As the couch dust samples contained significantly higher concentrations of TCIPP compared to those in dust samples from the other microenvironments analysed, it can be concluded that TCIPP is likely to have been applied to the foam used in the analysed couches.

EHDPP concentrations in office dust were significantly higher than those in couch dust. As the main uses of EHDPP are in PVC, rubber, polyurethanes, and paints (Environment Agency, 2009a) this is not unexpected.

To our knowledge, this is the first study on PFRs in UK indoor dust samples. However, water samples from UK rivers (Cristale et al., 2013b) contain high concentrations of TCIPP, which is consistent with the elevated TCIPP concentrations reported in UK dust samples in this study.

4.3.2.1 Correlation between different PFRs in UK dust samples

Correlations between log-transformed concentrations of different PFRs were examined. Positive correlations may be indicative of common sources of the two compounds. Several significant correlations were observed for the different microenvironments, which are displayed in Table 4.15. A strong correlation ($p<0.01$) was seen in both living room and office samples for EHDPP and TPHP. This is consistent with the fact that commercial EHDPP contains TPHP as an impurity of up to 4 %. (Environment Agency, 2009a) TCIPP and TDCIPP were also strongly correlated in office and car dust. This is somewhat surprising as TCIPP and TDCIPP have similar applications, but their co-application has not to our knowledge been reported. Instead, the observed correlation in car dust suggests that they are used together in cars but in different components e.g. TDCIPP in the seat foam, while TCIPP has been reported to be used in sun-visors. (NICNAS, 2001) A similar explanation may account for the correlation observed in office dust. TCEP and TCIPP concentrations have been shown to correlate in air over the Northern Pacific and Indian Ocean (Möller et al., 2012) a correlation which was seen also in the UK office dust samples.

Table 4.15 *Correlations between log transformed concentrations of individual PFRs in UK dust samples (emboldened correlations were found in more than one microenvironment)*

PFR 1	**PFR 2**	**Pearson Correlation coefficient**	**Microenvironment**	**# >LOQ**
Highly significant correlations (p<0.01)				
TCEP	TCIPP	0.499	Office	56
TCEP	EHDPP	0.478	Office	56
TCEP	TPHP	0.473	Office	56
TCIPP	**TDCIPP**	**0.367**	**Office**	**58**
TCIPP	**TDCIPP**	**0.571**	**Car**	**21**
TCIPP	TPHP	0.408	Office	61
EHDPP	**TPHP**	**0.646**	**Living room**	**31**
EHDPP	**TPHP**	**0.725**	**Office**	**61**
EHDPP	TMPP	0.562	Car	16
Significant correlations (p<0.05)				
TCEP	EHDPP	0.502	Car	20

4.3.2.2 PCA of UK samples

A PCA was conducted for all measured PFRs in office, car, living room and couch samples from the UK. PC1 accounts for 28% of the total variance in the data, with 20 % described by PC2. The rotated component matrix shows the relative contribution of each PFR to each principal component score (Table 4.16). For UK dust samples, PC 1 is positively driven by a high relative abundance of TPHP and EHDPP, and strongly negatively driven by TCIPP. Likewise, PC2 is significantly driven in a positive direction by high relative abundances of TDCIPP, and negatively driven by TCIPP.

Table 4.16 *Rotated component matrix for concentrations of PFRs in UK dust*

Compound	PC1	PC2
TnBP	-0.013	0.475
TCEP	0.064	0.02
TCIPP	-0.855	-0.483
TPHP	0.753	-0.081
EHDPP	0.757	-0.284
TDCIPP	-0.053	0.91
TMPP	0.332	-0.168

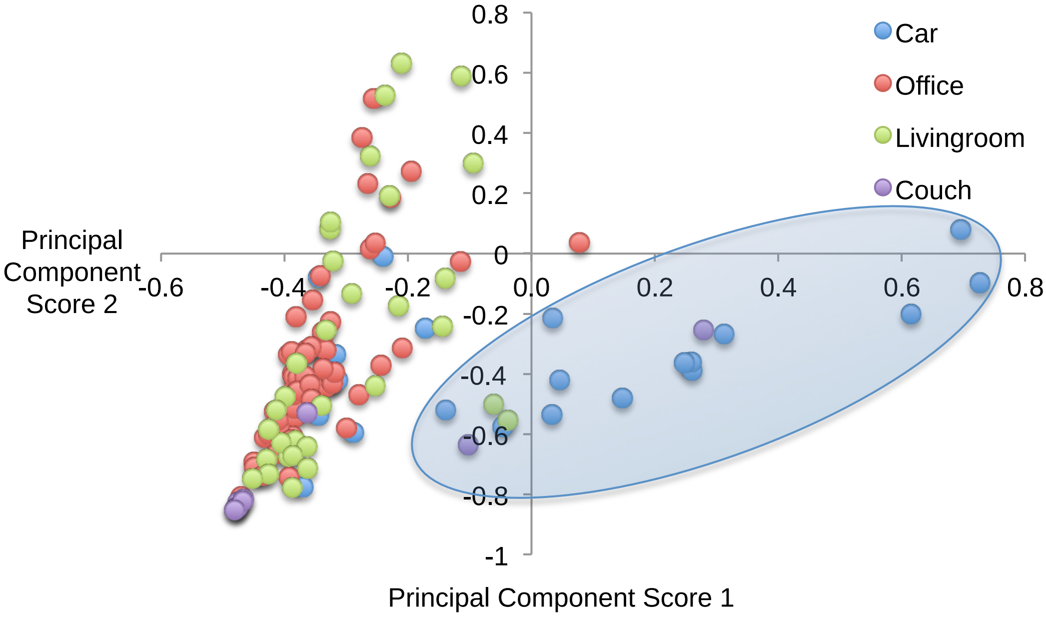


Figure 4.6 *PCA for UK samples*

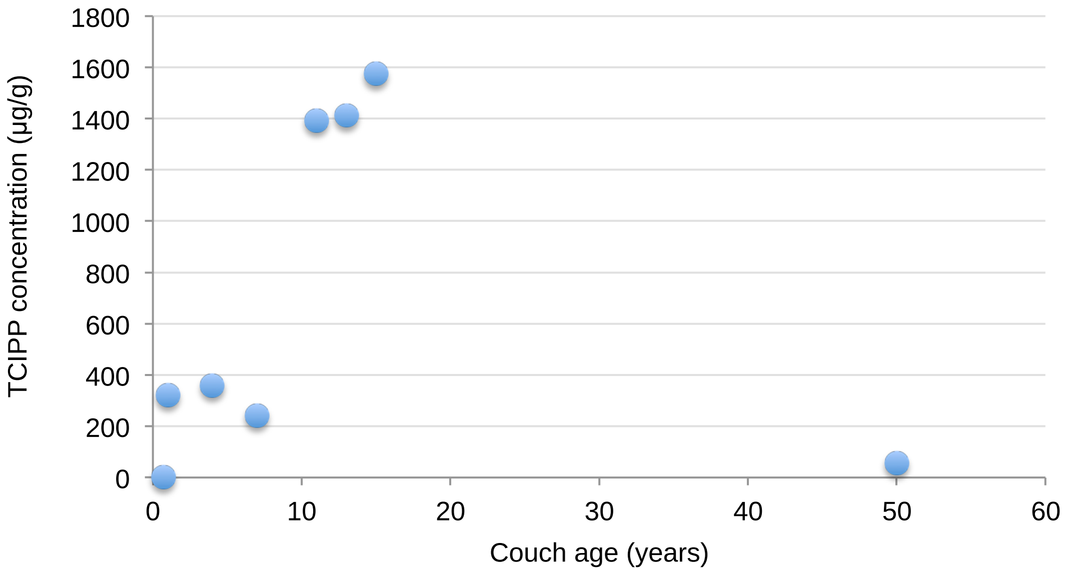
Figure 4.6 shows clear pattern differences between car dust and office/livingroom/couch dust. This is primarily influenced by the high relative abundance of TPHP and TDCIPP in car dust and high relative abundances of TCIPP in the other microenviroments, which results therefor in a tendency of PC2 scores to be more positive driven compared to the other microenvironments. This is a clear indication that different PFRs are applied in vehicles compared to the built environment.

4.3.2.3 Influence of couch age on concentrations of TCIPP in UK couch dust

The average couch age in the UK sample set was 13 years, with a median age of 9 years. For 2 samples the couch age was not known, with one “antique” couch assigned a vague purchase date of “the 1960s”. Notwithstanding the very limited data for UK couch dust samples which precludes firm conclusions, Figure 4.7 shows how concentrations of TCIPP vary with the purchase date of the couch.

As expected, the dust samples procured from the “antique” couch from the 1960s, displayed low TCIPP concentrations. The three couches purchased around 11 years ago showed the highest concentrations, while the lowest concentrations were observed in samples taken from couches purchased most recently. This is exemplified by the detection of the highest concentrations in the dust sampled from the newest couch, which was only 7 months old at the time of sampling. This might suggest that peak TCIPP use in UK couches was about 10-15 years ago with some indication that there is now a shift towards alternatives. But as to our knowledge no recent use and production data is available for the UK, firm conclusions cannot be drawn.

Figure 4.7 *TCIPP concentration in UK couch dust samples versus couch age*



4.3.2.4 Influence of room content on concentrations of PFRs in UK dust samples

Information about the presence, numbers, and age of putative sources in the UK offices and living rooms sampled and other potentially influential factors was examined in the context of the concentrations of PFRs in the corresponding dust samples. To examine the influence of such factors on PFR concentrations in UK dust samples, multiple linear regression analysis was performed on log transformed data. For all multiple linear regression analyses, if a given room content parameter (such as carpet) was either present or absent; where a sample was from a room containing that parameter, it was assigned a value of 1, with samples from rooms where the parameter was not present assigned a value of 0.

As all offices contained carpet, no influence of carpet on PFR concentrations as seen for the Australian living rooms could be determined. Furthermore, all of the offices contained blinds rather than curtains. Even where variation existed in putative sources between offices; no significant correlation ($p<0.05$) between any of the PFRs analysed in this study and the number of PCs, foam chairs and other electrical items was evident for the UK office dust samples. Likewise, no significant positive correlations were detected between concentrations of any target PFRs in UK car dust, and car contents; with a similar absence of significant correlations observed between PFR concentrations in UK living room dust and the numbers of foam chairs and PCs, or the presence of carpets or curtains. In contrast, TCIPP levels were significantly higher in living room dust ($p<0.05$) when TVs were present than when no TV was present. (7 out of 32 living room samples contained no TV). This is somewhat interesting, especially given reports that TVs tend to contain TPHP, TDCIPP and TCP (Saito et al., 2007; Ballesteros-Gómez et al., 2014) but not TCIPP. On the other hand, six out of the seven rooms studied that did not contain a TV were located within a student hall of residence Thus, the low concentrations of TCIPP in these rooms may be attributable to some specific property of the hall buildings studied, rather than simply the absence of a TV.

4.3.3 Germany

German indoor dust samples were collected from living rooms (n=22), offices (n=25), and cars (n=19). Sampling locations were throughout Germany for living room and car samples, while office samples were mainly collected within the greater Stuttgart area. The dust sampling protocol is described in chapter 2. As for Australian and UK samples, the German cars sampled covered a wide variety of manufacturers and ages.

Concentrations of PFRs in individual samples can be found in Appendix 7, Appendix 9 and Appendix 11, while summaries of median concentrations are displayed in Figure 4.8. PFRs were present in all samples analysed with TCIPP and TPHP being the two most abundant PFRs in German samples.

As Figure 4.8 illustrates, ΣPFR concentrations were the highest in car dust followed by office dust, with those in living room dust usually the lowest of the three microenvironment categories. To test whether there were any significant differences in PFR concentrations between German car, home, and office dust, data were log-transformed prior to ANOVA, as PFR concentrations were positively skewed. ANOVA testing with Tukey post-hoc test revealed several statistically significant differences ($p<0.01$).

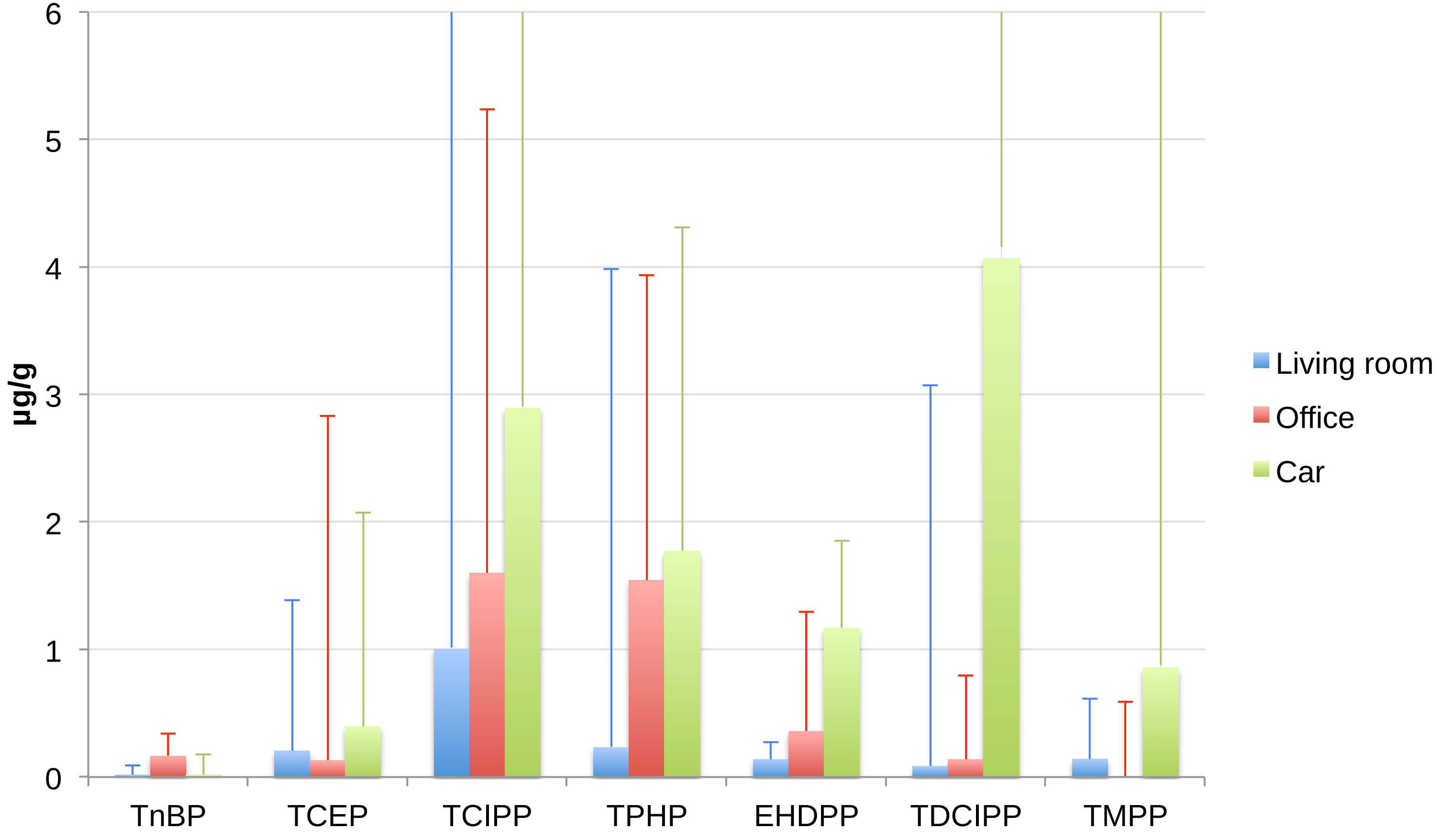
TnBP concentrations were significantly higher in office dust compared to car and living room dust. It has been shown in the literature that TnBP concentrations are related to the building age. (Bergh et al., 2011a) Unfortunately, the building age was unknown for the majority of the German office samples, which makes it impossible to relate the higher TnBP concentrations to the building age. Further, concentrations of both EHDPP and TPhP were significantly lower in living room dust samples, compared to car and office samples. The fact that both these PFRs follow a similar pattern is in line with the fact that they are frequently used in the same formulation. Consistent with the elevated concentrations of TDCIPP in UK car dust, concentrations of TDCIPP were significantly higher in German car dust compared to office and living room dust from the same country. Likewise –

and again in line with our observations for UK dust - concentrations of TMPP were significantly higher in German car dust than in German office dust.

4.3.3.1 Comparison with available data on German indoor dust concentrations

Germany was the only one out of the three main countries targeted in this study, which had available literature data on indoor dust concentrations. Specifically, concentrations of all PFRs except TCIPP determined in the German living rooms in this study, were slightly lower than those detected in a study of 65 Hamburg homes between 1998-2000 (Amt fuer Umweltschutz Hamburg, 2002).

Figure 4.8 *Median concentrations (µg/g) of individual PFRs in different microenvironments from Germany*



The geometric mean concentrations of TCIPP were comparable, while the average TCIPP concentration determined in this study exceeded that in the Hamburg study. This is primarily due to the high concentrations determined in one living room sample in this study. Possible explanations for the higher concentrations of all but TCIPP in the earlier study, include: declines in PFR use, differences in analytical methods, and the dust size fractions analysed. Whereas the earlier study analysed only dust <63 µm diameter, the current study study analysed particles < 500 µm.

To our knowledge there is nothing known on the influence of particulate size on the concentrations of PFRs, but it is plausible that this study's inclusion of larger particles may "dilute" the overall concentration. On the other hand, concentrations in this study were comparable to the geometric mean TCEP and TCIPP concentrations in indoor dust from the western part of Germany. (Ingerowski et al., 2001)

4.3.3.2 Correlation between different PFRs in German dust samples

Correlations between log-transformed concentrations of different PFRs were examined. Positive correlations may indicate common sources of the correlated compounds. Several significant correlations for office and car dust samples were determined which are displayed in Table 4.17.

Table 4.17 *Correlation between log transformed concentrations of individual PFRs in German dust samples*

PFR 1	**PFR 2**	**Pearson Correlation Coefficient**	**Microenvironment**	**#>LOQ**
Highly significant correlation (p<0.01)				
EHDPP	TDCIPP	0.905	Car	6
EHDPP	TPHP	0.918	Car	6
Significant correlation (p<0.05)				
TCEP	TCIPP	0.460	Office	9
EHDPP	TMPP	0.871	Car	6
TDCIPP	TPHP	0.472	Car	18

It needs to be noted though, that the highly significant relationships found for car dust samples, are only based on a very small sample set as the majority of German car dust samples were analysed in Belgium and therefore no EHDPP data was available for those samples. It is however still noteworthy, that as with other sample sets, EHDPP and TPHP are correlated which adds further weight to the hypothesis that they are applied together. No significant correlations were found for German living room dust samples.

4.3.3.3 PCA of German samples

A PCA was conducted for all measured PFRs in office, car, and living room samples from Germany. Samples analysed in Belgium were not included in this pattern comparison as no EHDPP data was available for those samples.

PC1 accounts for 31 % of the total variance in the data, with 19 % described by PC2. The rotated component matrix shows the relative contribution of each PFR to each principal component score (Table 4.18). In this case PC 1 is mainly positively driven by EHDPP and TPHP, while negatively driven by TCIPP. PC 2 is weakly positively driven by TnBP and TCEP, while negatively driven by TDCIPP and TMPP.

Table 4.18 *Rotated Component Matrix for German Dust Samples*

	Component	
	1	**2**
TnBP	0.707	0.441
TCEP	-0.003	0.500
TCIPP	-0.779	0.305
TPHP	0.689	0.014
EHDPP	0.673	0.170
TDCIPP	-0.037	-0.686
TMPP	-0.082	-0.637

As seen in Figure 4.9 no pattern difference between the different microenvironments can be distinguished in the German sample set. This is contrary to what was observed for the UK sample set (Figure 4.6) and is consistent with the hypothesis that PFRs are not widely used in Germany.

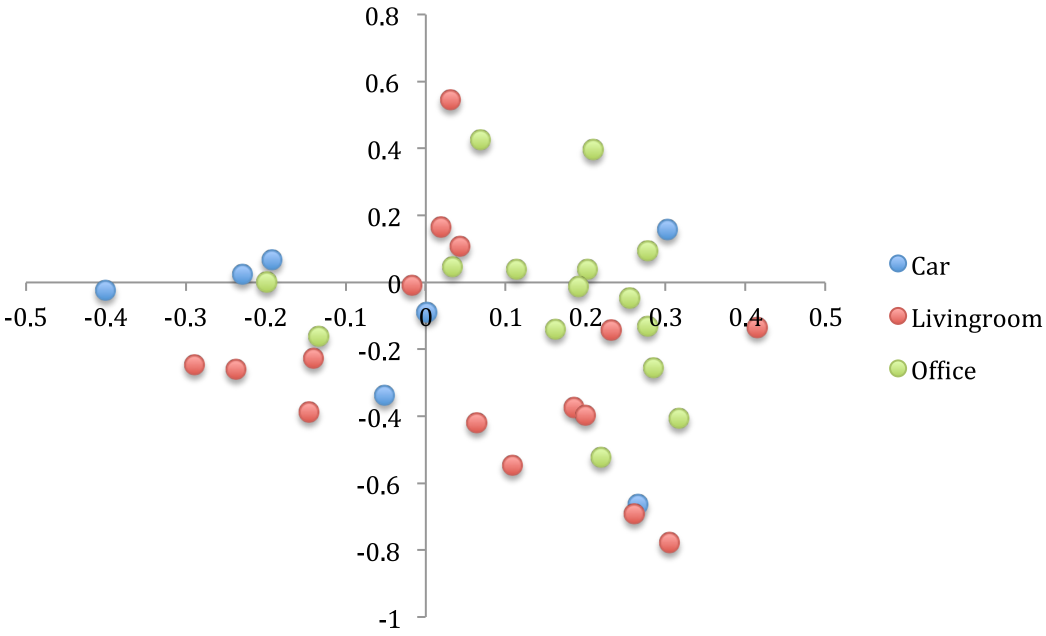


Figure 4.9 *PCA for German samples*

4.3.3.4 Influence of room content on concentrations of PFRs in German dust samples

Information about the presence, numbers, and age of putative sources in the German offices and living rooms sampled, and other potentially influential factors was examined in the context of the concentrations of PFRs in the corresponding dust samples. To examine the influence of room contents on PFR concentration in German dust samples, multiple linear regression analysis was performed on log transformed data. For all multiple linear regression analyses if a given room content parameter (such as carpet) was either present or absent, where a sample was from a room containing that parameter, it was assigned a value of 1, with samples from rooms where the parameter was not present assigned a value of 0.

No significant relationship could be established for the German living room and office dust sample set. This is not surprising, as it was shown earlier that German dust samples showed significantly lower concentrations than the samples collected from Australia and the UK. It needs to be noted though, that there was one sample in which the concentration of TCIPP was two orders of magnitude higher than in the other samples from German living rooms. This room was owned by a somewhat “messy” electronics collector with a large quantity of electronics (>50 different electronic items in various states, e.g. still in use, not in use but still intact, broken and half dismantled) in his living room, which may constitute a substantial source of TCIPP.

4.4 Conclusion

This chapter reveals significant differences in PFR concentrations and patterns between different countries and different microenvironment categories within the same country. TCIPP and TPHP were the two most abundant PFRs in all microenvironments, except cars (in which TDCIPP was the predominant PFR), in all countries. Elevated concentrations of TCIPP in couch dust, suggested couches as a likely source of this PFR in both Australia and the UK. Furthermore, a significant correlation between the presence of carpet in a room and concentrations of TCIPP was detected in Australia. TCIPP concentrations were significantly higher in living room and office dust from the UK compared to samples from these microenvironments in other countries; implying greater TCIPP use in the UK than elsewhere. Overall, concentrations of all PFRs are significantly lower in German dust samples compared to the other countries studied, suggesting low use of PFRs in Germany.

5 CLASSROOM DUST: A MAJOR EXPOSURE PATHWAY TO PFRs FOR CHILDREN?

Concentrations of PFRs in school dust samples from Birmingham, UK and Brisbane, Australia are reported in this chapter. To our knowledge, while there exists one report on PFRs in dust from day care centres in Sweden (Bergh et al., 2011b), these are the first data to our knowledge on PFR concentrations in school classroom dust. Given that classrooms likely contain a large inventory of PFR treated goods and materials, and that exposure of young children to PCBs and BFRs via classroom dust has been shown to be substantial (Harrad et al., 2010a), the hypothesis that this chapter will test is that classroom dust constitutes a similarly important pathway of exposure to PFRs for young children, with a distinct pattern (and concentrations) compared to other indoor microenvironments in the UK and Australia.

5.1 Introduction

Classrooms may be seen as “the office/workplace for children” which makes them relevant for exposure assessment of children (see Chapter 6). Moreover, children’s exposure to PFRs via dust ingestion most likely exceeds that of adults, due to their different behaviour patterns. Children for example, display more frequent hand-to-mouth behaviour while also spending time playing on the floor. Additionally their lower body weight causes higher exposure rates when normalised to their body weight. Furthermore children are growing and the development of their bodies is not complete which puts them at higher risk of adverse effects than adults.

In the UK, archived dust samples collected in 2008 from school and nursery classrooms and previously analysed for PBDEs, PCBs and perfluoroalkyl substances (PFASs) (Harrad et al., 2010a; Goosey and Harrad, 2011) were studied. Additionally, dust samples were collected by collaborators between August 2011 and May 2012, as part of the “Ultrafine Particles from Traffic Emissions and Children’s Health (UPTECH)” project (Toms et al., n.d.). In Australia, at least two samples were taken in each classroom according to the standard procedure in Chapter 2 at the same time from randomly chosen different areas of the same classroom. As sample dust masses were too low in the UPTECH project, at least two room replicate samples were randomly combined to provide usually one sample but occasionally two samples per classroom. For instance, in four schools, sufficient sample mass was available to provide more than one sample per classroom (e.g. sample 1 consisted of sub-samples taken from area 1 and 2 while sample 2 comprised sub-samples from area 3 and 4). Such samples provided a limited indication of within-room variability in PFR concentrations in dust.

Additionally at six schools, low dust loadings meant that the samples obtained from each classroom in a given school were combined to yield just two samples per school. Overall, multiple floor areas in 10 schools and 16 classrooms were sampled and combined as outlined to provide a total of 28 samples for analysis.

5.2 PFR concentrations in Australian Samples

Table 5.1 displays the concentrations of PFRs detected in individual classroom dust samples from Australia, along with descriptive statistics. Concentrations below detection limit were replaced by half the LOQ for all statistical analyses. Internal standard recoveries in Australian classroom dust samples were: 70 % (±8) for d_{27} TBP and 94 % (±11) for d_{15} TPhP. The contamination pattern in Australian samples is primarily dominated by TPhP (median 5.4 µg/g) and EHDPP (median 1.1 µg/g) followed by TCIPP (median 0.70 µg/g) and TDCIPP (median 0.30 µg/g). TnBP, TMPP and TCEP were mainly below the detection limit in these samples.

Table 5.1 *Concentrations and descriptive statistics of PFRs in Australian classroom dust (µg/g)*

Sample ID/ Parameter	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
A S 01 A-1	0.16	<0.06	2.9	4.6	0.81	0.37	0.09	8.9
A S 01 A-2	0.08	0.30	1.2	14	1.2	0.52	0.19	18
A S 01 B-1	0.04	<0.06	0.61	2.5	0.72	0.46	<0.01	4.4
A S 01 B-2	0.06	<0.06	0.45	1.7	0.50	0.27	0.03	3.0
A S 02 A-1	0.07	<0.06	0.64	27	93	0.18	<0.01	120
A S 02 A-2	<0.03	<0.06	0.58	28	100	0.32	<0.01	130
A S 02 B-1	<0.03	<0.06	0.51	19	71	2.8	<0.01	93
A S 02 B-2	0.06	<0.06	0.55	27	110	2.0	<0.01	140
A S 03 A-1	<0.03	<0.06	0.47	0.98	0.71	0.10	0.26	2.6
A S 03 A-2	<0.03	<0.06	0.62	0.44	0.71	0.13	<0.01	2.0
A S 03 B-1	<0.03	<0.06	0.68	0.82	1.1	0.12	<0.01	2.8
A S 03 B-2	0.10	<0.06	0.74	0.76	0.72	0.08	<0.01	2.4
A S 04 A-1	0.09	0.44	0.56	15	2.4	0.61	<0.01	19
A S 04 A-2	0.07	<0.06	0.48	11	2.0	0.22	<0.01	14
A S 04 B-1	0.11	0.39	1.4	10	5.1	0.68	<0.01	18
A S 04 B-2	0.08	<0.06	1.1	14	2.1	0.63	<0.01	18
A S 05 A	0.10	<0.06	2.2	13	0.99	0.14	<0.01	17
A S 05 B	0.09	<0.06	13	0.14	0.05	<0.03	<0.01	13
A S 06 A	0.11	0.53	0.90	1.4	0.70	0.29	0.03	3.9
A S 06 B	0.07	<0.06	0.72	0.47	0.55	0.48	<0.01	2.3
A S 07 A	0.16	0.90	2.9	2.0	3.9	0.49	<0.01	10
A S 07 B	0.07	<0.06	0.48	6.3	0.28	0.05	<0.01	7.2
A S 08 A	0.09	<0.06	16	2.0	0.50	0.30	<0.01	19
A S 08 B	0.04	<0.06	10	10	0.31	0.36	0.06	21
A S 09 A	0.13	0.64	2.0	1.8	2.2	0.51	0.25	7.5
A S 09 B	0.08	0.21	2.0	1.0	1.7	0.21	0.05	5.3
A S 10 A	<0.03	<0.06	0.50	10	56	0.06	<0.01	67
A S 10 B	<0.03	<0.06	0.39	14	66	0.09	<0.01	81
Minimum	<0.03	<0.06	0.39	0.14	0.05	<0.03	<0.01	2.0
5th percentile	<0.03	<0.06	0.46	0.45	0.29	0.05	<0.01	2.4
Median	0.07	<0.06	0.70	5.4	1.1	0.30	<0.01	13
Geometric mean	0.06	<0.06	1.1	4.0	2.3	0.25	<0.01	13
Average	0.07	0.14	2.3	8.6	19	0.45	0.04	30
95th percentile	0.15	0.60	12	27	98	1.5	0.22	130
Maximum	0.16	0.90	16	28	110	2.8	0.26	140
Standard Deviation	0.04	0.23	3.8	8.7	35	0.59	0.07	42
Relative Standard Deviation	59	160	170	100	190	130	190	140

5.2.1 Intra-classroom and intra-school spatial variation in concentrations of PFRs in Australian school classroom dust

Figure 5.1 illustrates the variation in PFR contamination patterns in dust samples for the four Australian schools where two samples were collected from different areas in the same classroom for two classrooms per school. To aid interpretation of Figure 5.1, the sample coding is thus: sample AS 01 A-1 denotes the sample taken from Australian School 1, classroom A, area-mixture 1, sample AS 01 A-2 denotes the sample taken from Australian School 1, classroom A, area-mixture 2, and sample AS 01 B-1 represents the samples taken from Australian School 1, classroom B, area-mixture 1. The data reveal that substantial intra-classroom and intra-school variability exists only in school 1. While Australian school 1 shows a similar pattern for the two sampled areas in Classroom B (samples AS01 B-1 and 2), the two samples from different areas of Classroom A (samples AS01 A-1 and 2) show both a different pattern and absolute PFR concentrations to each other (as well as to classroom B) (Figure 5.2). For example, TCIPP levels in area 1 of classroom A are more than twice as high as those in area 2, while area 2 contains a TPhP concentration of 14 µg/g compared to 4.6 µg/g in area 1. This may indicate that there is a point source for TPhP in the proximity of area 1 of classroom A, which is not present in Classroom B. It was not possible to elucidate the identity of such a putative source.

In contrast, samples from Australian School 2 display a similar pattern in all four classroom samples analysed. In these samples, EHDPP was the dominant PFR contributing around 80% of the total PFR concentration. This school also contained the highest EHDPP concentrations found in all Australian school dust samples and the fact that the levels are equally high in all samples indicate the same source in both classrooms from which the samples were taken. Similar to school 2, school 3 shows a very similar pattern in all 4 samples analysed, with concentrations of TCIPP, EHDPP, and TPHP roughly equal. Likewise, all 4 samples studied from school 4 show a very similar pattern (TPHP > EHDPP > TCIPP> TDCIPP).

Figure 5.1 *Pattern comparison for spatial variations in concentrations of PFRs within classrooms at Australian Schools 1, 2, 3 & 4*

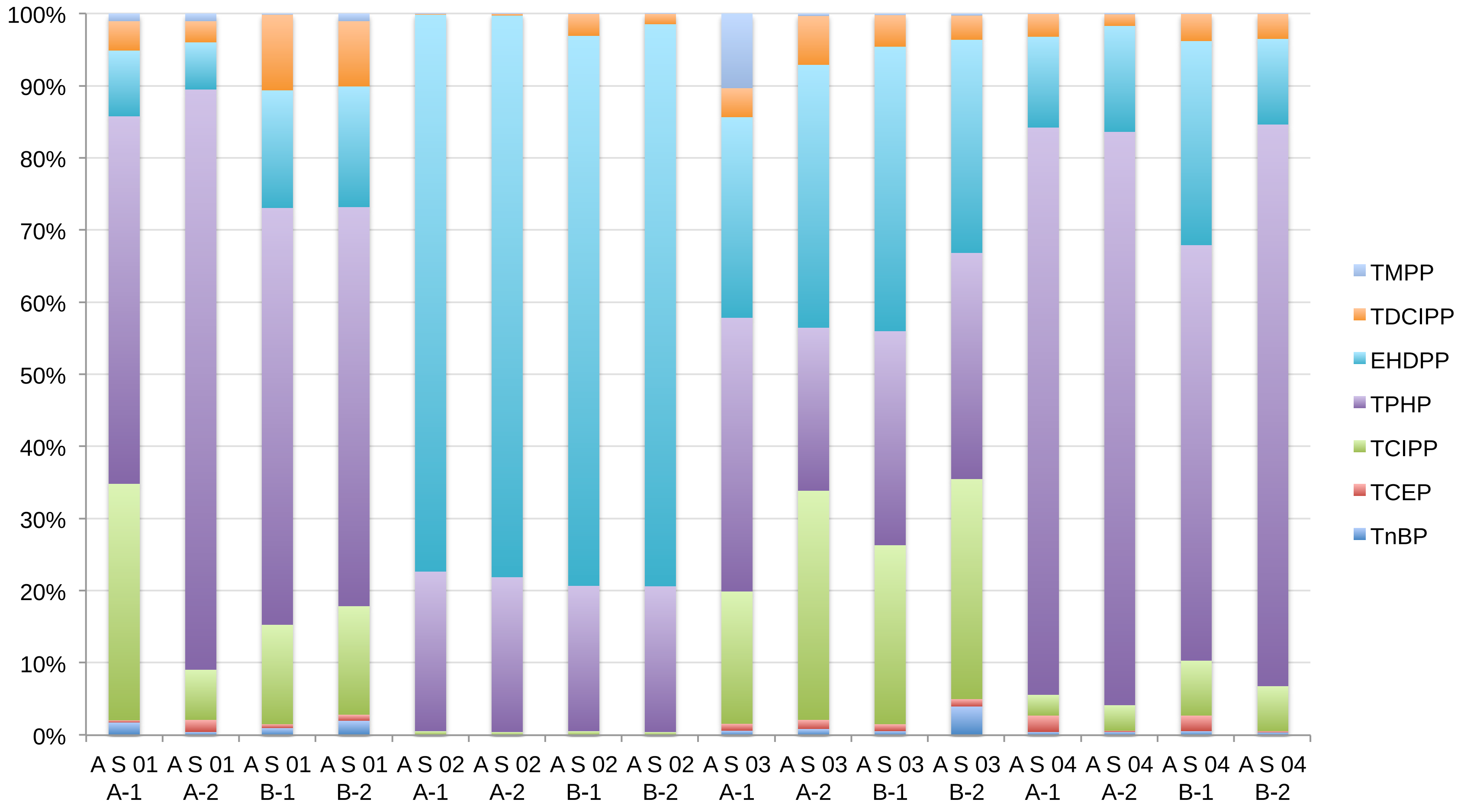
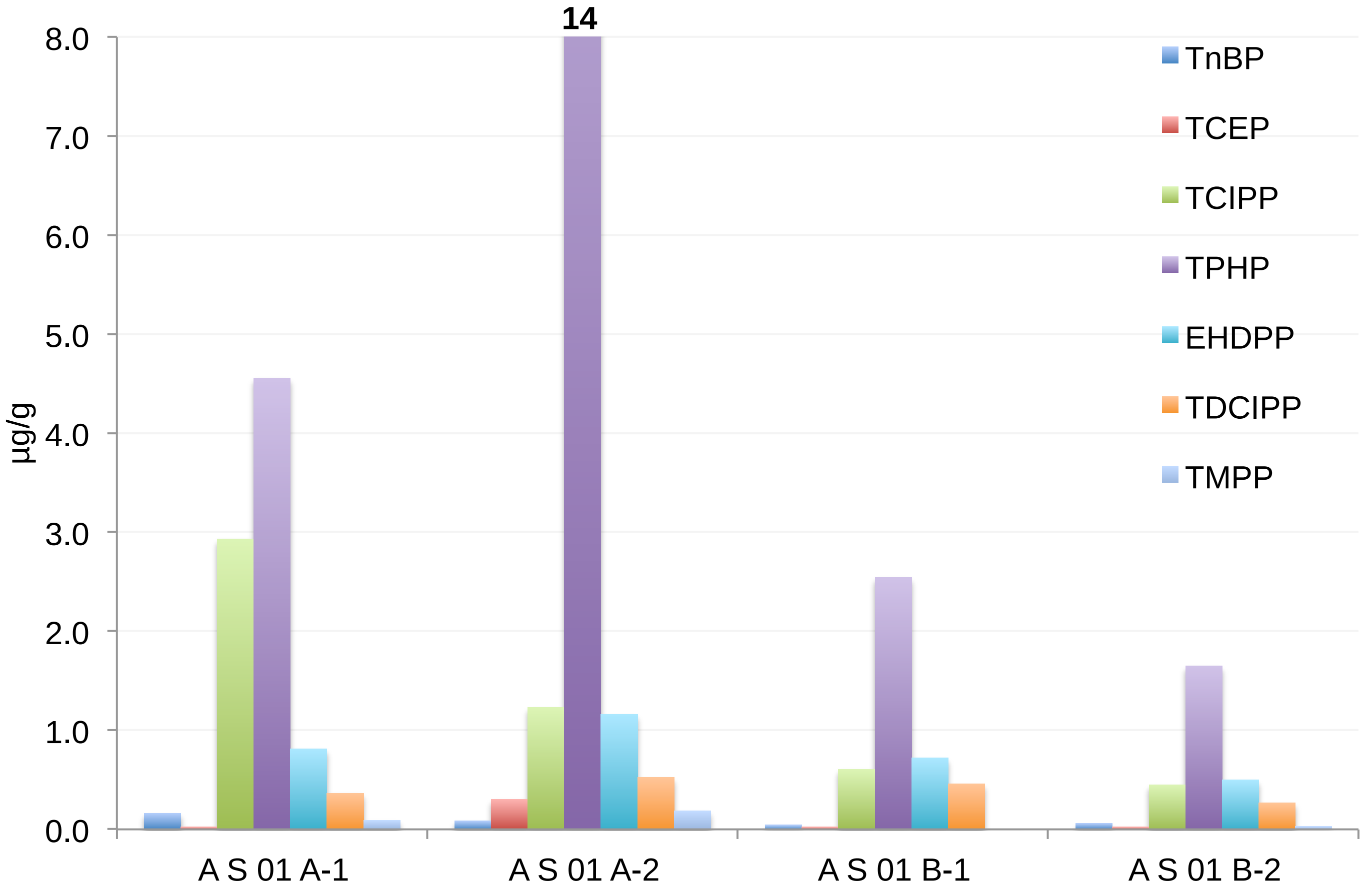


Figure 5.2 *Concentration of PFR concentrations in different dust samples from Australian School 1*



5.2.2 Variability in PFR patterns in Australian school dust samples

A principal component analysis (PCA) was conducted for all measured PFRs in all Australian school dust samples. To eliminate between-sample differences in absolute concentrations, and highlight differences in relative abundance of different PFRs; PCA was conducted using the fractional contribution of each PFR to ΣPFR concentration. Principal component 1 described 32% while principal component 2 accounted for 22% of the total variance in the data. The rotated component matrix shows the relative contribution of each PFR to each principal component score Figure 5.3. A low (negative) score for principal component 1 (PC1) indicated a PFR pattern dominated by EHDPP, while a high score meant high (positive) relative abundances of TnBP, TCEP, TMPP and TDCIPP. Principal component 2 (PC 2) was positively driven by TCIPP and negatively driven by EHDPP.

Table 5.2 *Rotated component matrix score table for Australian school dust samples*

PFR	**Component**	
	1	**2**
TnBP	0.706	0.081
TCEP	0.637	-0.420
TCIPP	-0.250	0.929
TPHP	-0.212	-0.108
EHDPP	-0.446	-0.702
TDCIPP	0.598	-0.145
TMPP	0.630	0.109

Figure 5.3 *Plot of Principal Component 1 versus Principal Component 2 for Australian school dust samples*

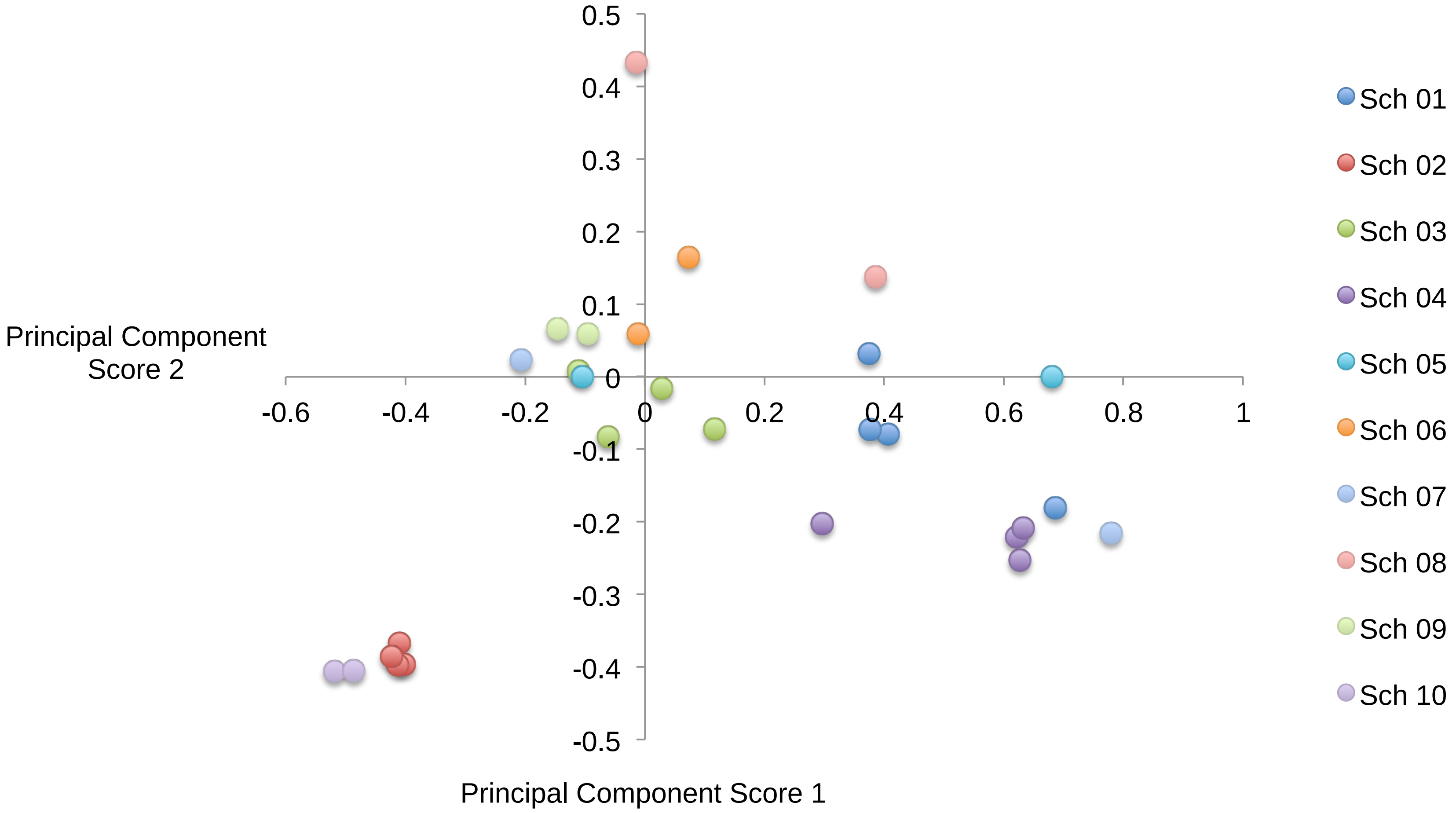


Figure 5.4 shows that the samples from schools 5 and 7 display the greatest intra-school variation in PFR pattern. In school 5, TPhP is dominant in classroom A, while TCIPP dominates the pattern in Classroom B. In school 7, the pattern in classroom B is dominated by TPhP, while in Classroom A EHDPP, TCIPP and TPhP are roughly equally prominent.

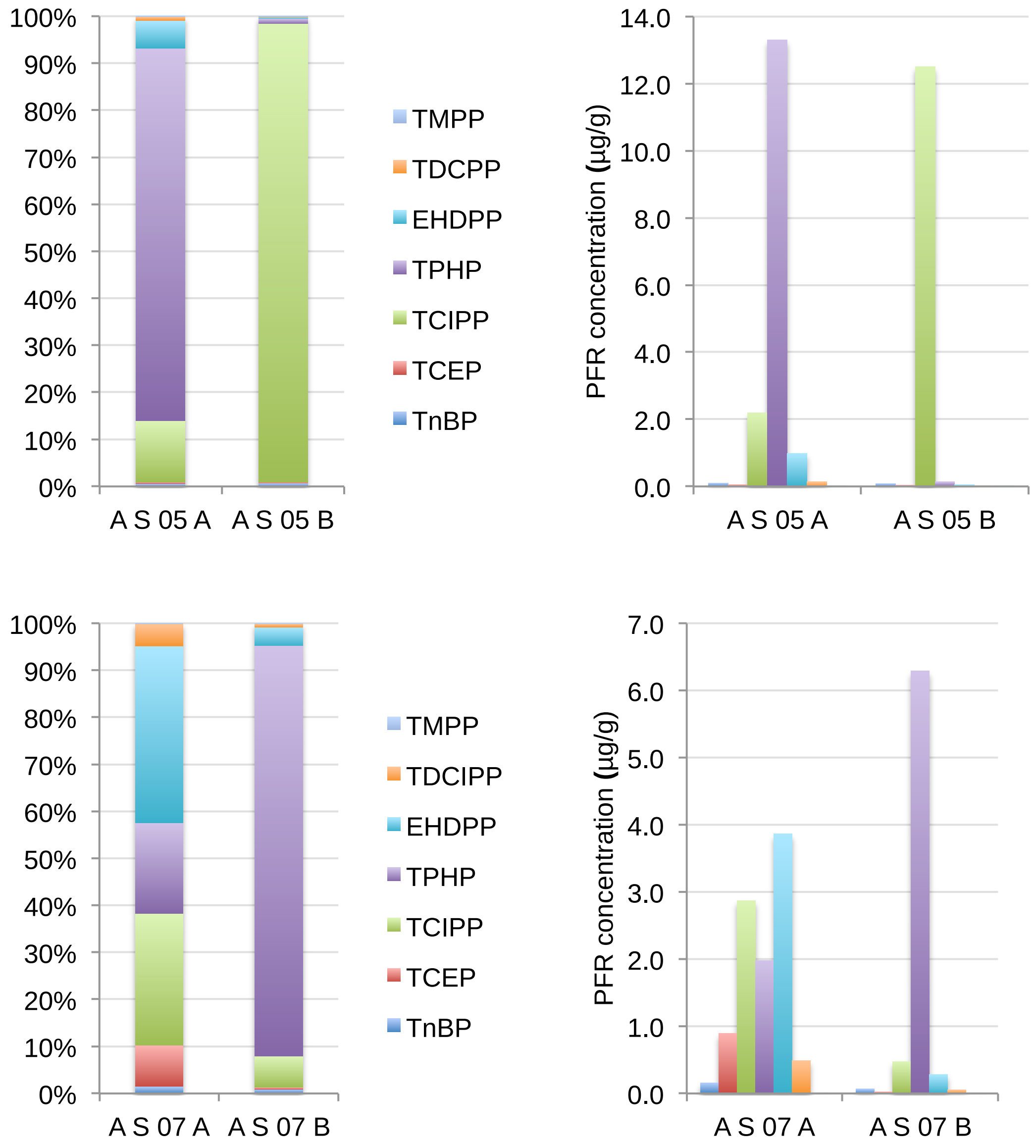


Figure 5.4 *Concentrations and relative abundances of PFRs in dust samples from Schools 5 (top) and 7 (bottom)*

The classrooms from schools 6 and 8 showed intra-school variations in the pattern observed but not to the same extent as observed for schools 5 and 7. (Figure 5.5)

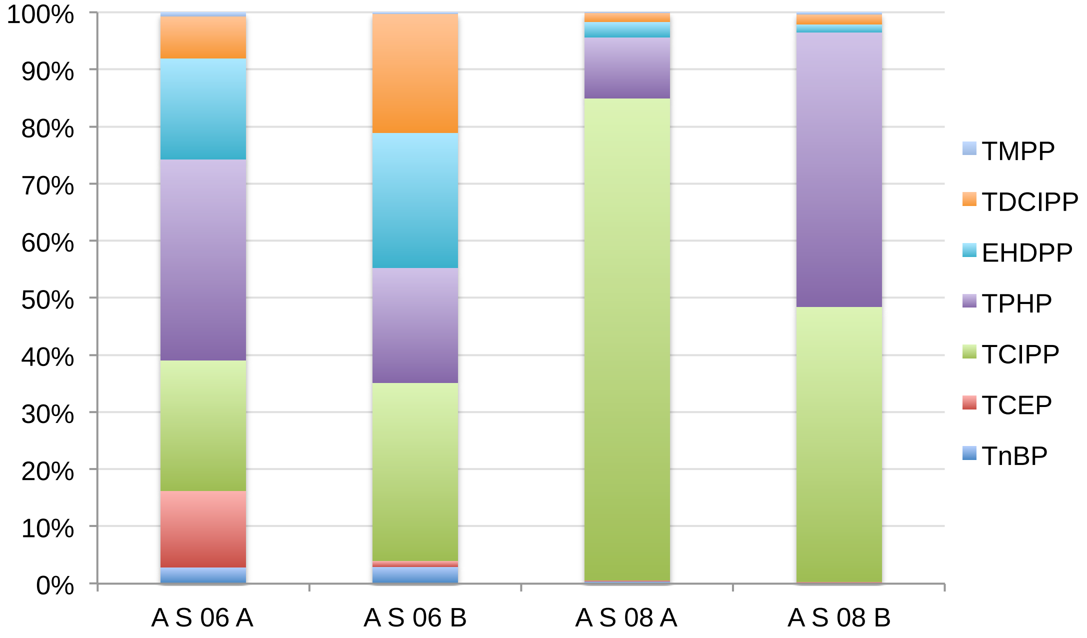


Figure 5.5 *PFR contamination pattern in different dust samples from schools 6 and 8*

In even greater contrast to the intra-school variability observed for schools 5 and 7, Figure 5.6 shows the very similar patterns obtained for different classrooms in schools 9 and 10.

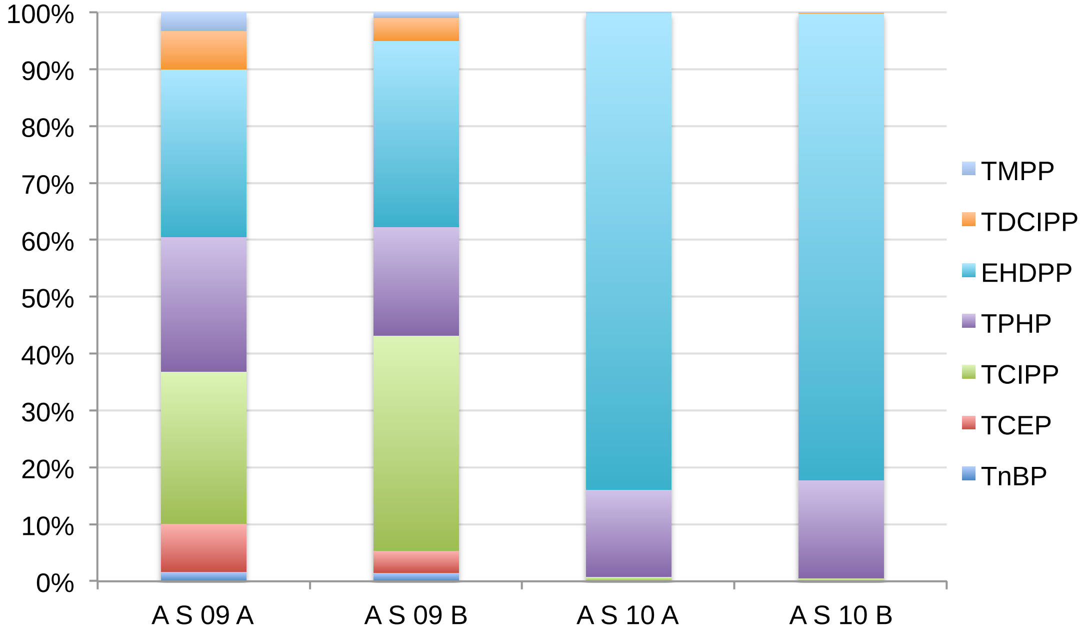


Figure 5.6 *PFR contamination pattern in schools 9 and 10*

Overall, while in some schools, there is minimal variation between the PFR patterns observed in different classrooms, in some schools there is substantial intra-school variability. On first inspection, there is no obvious explanation why such variability exists in Australian schools. Classrooms in the Queensland state school system are remarkably similar from school to school, and thus one would not anticipate substantial variation in the content of putative sources between classrooms. Each classroom contains 24 desks with 24 hard plastic chairs, 1 foam office chair for the teacher, an interactive whiteboard, around five computers and a combination of carpet and vinyl floor covering on an area of around 70 m^2. However, some (but not all) classrooms have soft (PUF) pillows/cushions for sitting on the floor. Moreover, there exists possible variability in the age and exact supplier of the room contents like cushions, carpet, computers, whiteboard. As the FR composition of these can vary with the data and location of manufacture, this may provide some explanation for the observed intra- and inter-school variability.

The two classrooms from school 10 displayed both the lowest intra-school variation and the highest EHDPP concentrations out of all the Australian school dust samples analysed. As part of a refurbishment conducted just before sampling was undertaken, classrooms in school 10 were painted. As EHDPP is used in paints (Environment Agency, 2009a) this is a plausible explanation for the high EHDPP levels found in both classrooms from this school. Likewise, while there is no information on the paint age in School 2; the high EHDPP concentrations in this school suggests a similar paint may have been used.

5.2.3 PFR and PBDE concentrations in Australian school dust samples

Table 5.3 displays the range and median levels of PFRs and PBDEs in the Australian school dust samples. Concentrations of ΣPBDEs were between 0.09 % and 34% of the reported ΣPFR concentrations in the same samples. The significantly higher concentrations of PFRs may indicate that PFRs are replacing PBDEs as the FR of choice in many items requiring flame retardancy. Significantly higher concentrations of PFRs compared to PBDEs in dust have been reported elsewhere (Dodson et al., 2012) despite the fact that the majority of PFRs are more volatile compared to PBDEs (see 1.4), and therefore less prone to partitioning to dust. However, the higher vapour pressures of PFRs renders them more capable of volatilisation from treated goods, and the wider range of applications of PFRs (e.g. as plasticisers) compared to PBDEs, provide likely explanations for the dominance of PFRs over PBDEs in our dust samples.

Table 5.3 *Comparison of PFR and PBDE concentrations in Australian school dust samples (ng/g)*

	Minimum	**Median**	**Maximum**
TnBP	< 30	70	160
TCEP	<60	<60	160
TClPP	390	700	16000
TPhP	140	5400	28000
EHDPP	50	1100	110000
TDClPP	< 3	300	2800
TMPP	< 1	< 1	260
ΣPFR	2000	13000	140000
BDE 17	< 0.36	0.33	2.0
BDE 28	< 0.38	1.0	4.4
BDE 49	< 0.42	1.4	6.1
BDE 47	< 0.50	40	120
BDE 66	< 0.75	1.5	4.6
BDE 100	< 0.75	0.11	110
BDE 99	< 0.83	91	250
BDE 85	< 1.3	0.18	63
BDE 154	< 1.5	5.9	19
BDE 153	< 1.9	12	41
BDE 183	< 2.5	4.7	100
BDE 209	< 10	240	2000
ΣPBDEs	11	470	2200

5.2.4 Correlation between different PFR and PBDE concentrations in Australian school dust samples

Testing for normality of distribution revealed the PFR concentrations in our Australian school dust to display a skewed distribution. The Shapiro-Wilk test showed that concentrations of all PFRs were significantly skewed. Therefore further statistical tests were conducted on log-normalised data.

As PBDEs were analysed in these Australian classroom dust samples in addition to PFRs, correlations between PFRs and PBDEs, as well as between different PFRs could be examined. Positive correlations may be indicative of common sources of the two compounds.

Table 5.4 *Correlation between analysed compounds for Australian samples*

Compound 1	Compound 2	Pearson Correlation
Highly significant correlations (p<0.01)		
TPHP	EHDPP	0.695
BDE209	TDCIPP	0.643
BDE209	EHDPP	0.607
BDE209	TPHP	0.516
Significant correlations (p<0.05)		
TPhP	TDCIPP	0.474
EHDPP	TDCIPP	0.385
BDE47	TPHP	0.390
BDE66	EHDPP	0.425
BDE153	EHDPP	0.426
BDE154	EHDPP	0.442
ΣBDE	ΣPFR	0.409

Table 5.4 lists the significant correlations found between concentrations of a number of PFRs and PBDEs in the Australian school dust sample set. The correlation between EHDPP and TPhP is likely attributable to the fact that commercial EHDPP contains TPhP as an impurity at up to 4 % (Environment Agency, 2009a). Likewise, the correlation between TPhP and BDE 47 may be due to the co-application of TPhP and the PentaBDE mixture in foam (van der

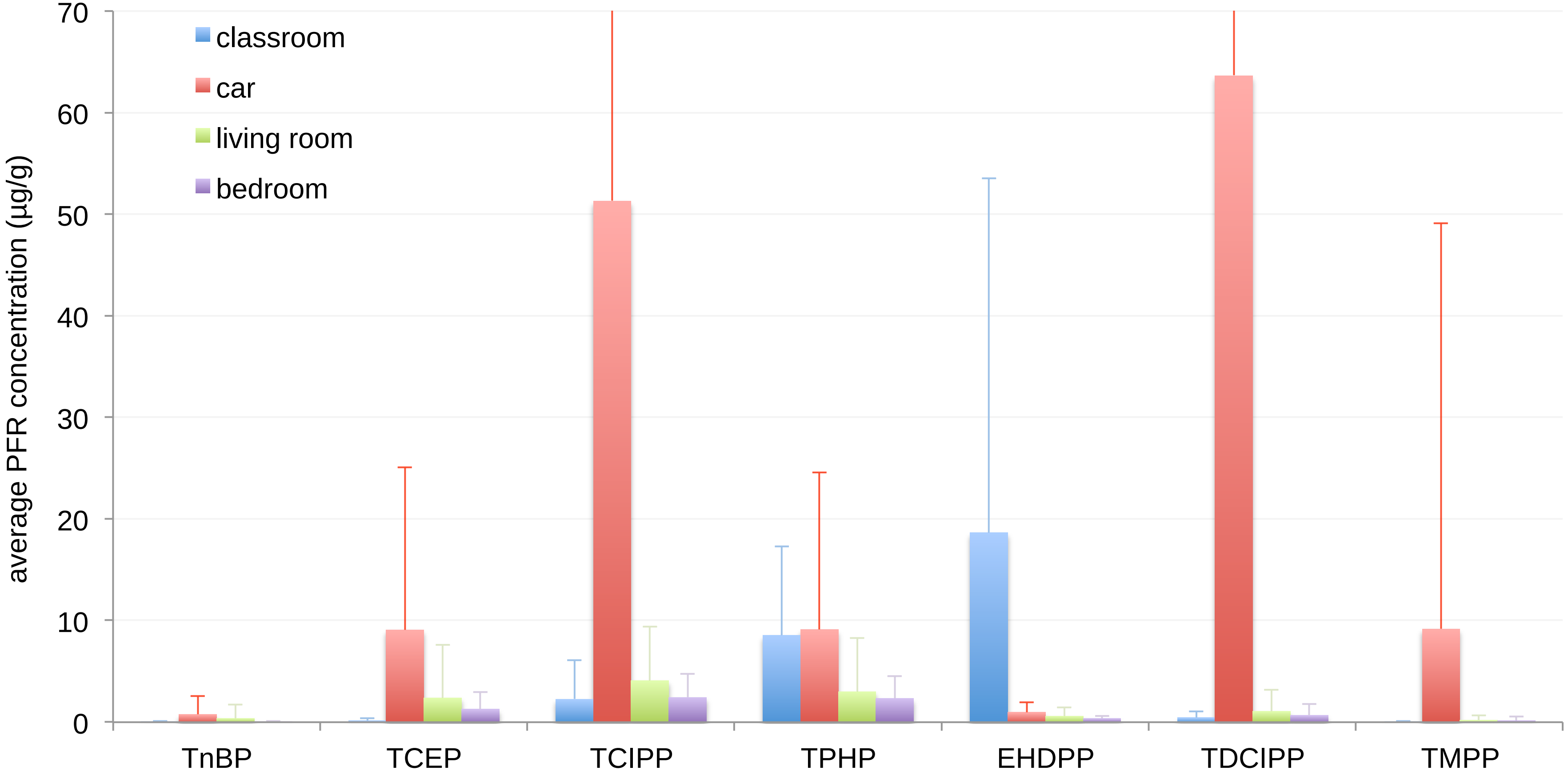
Veen and de Boer, 2012). A similar positive correlation between congeners prevalent in PentaBDE and TPhP was found in dust samples from California (Dodson et al., 2012). To our knowledge, the other correlations detected here have not previously been reported. However, they suggest common applications for several PFRs and PBDEs.

5.2.5 Comparison of classroom PFR concentration to other microenvironments analysed in this study

When classroom concentrations are compared to those in dust from Australian living rooms, bedrooms, and cars differences are revealed. Figure 5.7 displays the average concentrations of those four microenvironments. ANOVA testing with Tukey post-hoc test was performed on log-transformed data. The following significant differences between the means of classrooms and other microenvironments were found.

EHDPP concentrations were significantly ($p<0.05$) greater in the school dust samples compared to the other three microenvironments. TCEP concentrations were significantly ($p<0.05$) lower in school dust samples compared to the other three microenvironments. TCIPP and TDCIPP concentrations were significantly ($p<0.001$) lower in school dust samples compared to car dust samples. Furthermore TPhP concentrations were significantly ($p<0.05$) higher in school dust samples compared to living room samples.

Figure 5.7 *Comparison of average PFR concentration (μg/g) between classroom, car, living room and bedroom samples*



5.3 PFR concentration in UK school classroom dust samples

Table 5.5 displays the concentrations of PFRs detected in individual classroom dust samples from the UK, along with descriptive statistics. Concentrations below detection limit were replaced by half the LOQ for all statistical analyses. Internal standard recoveries were: d_{27}TnBP 76±10% and for d_{15}TPhP 93±6%. The contamination pattern in UK samples is primarily dominated by EHDPP (median 29 µg/g) and TCIPP (median 16 µg/g) followed by TPhP (median 4.1 µg/g). In contrast to the samples from Australia, all 28 UK samples came from different schools.

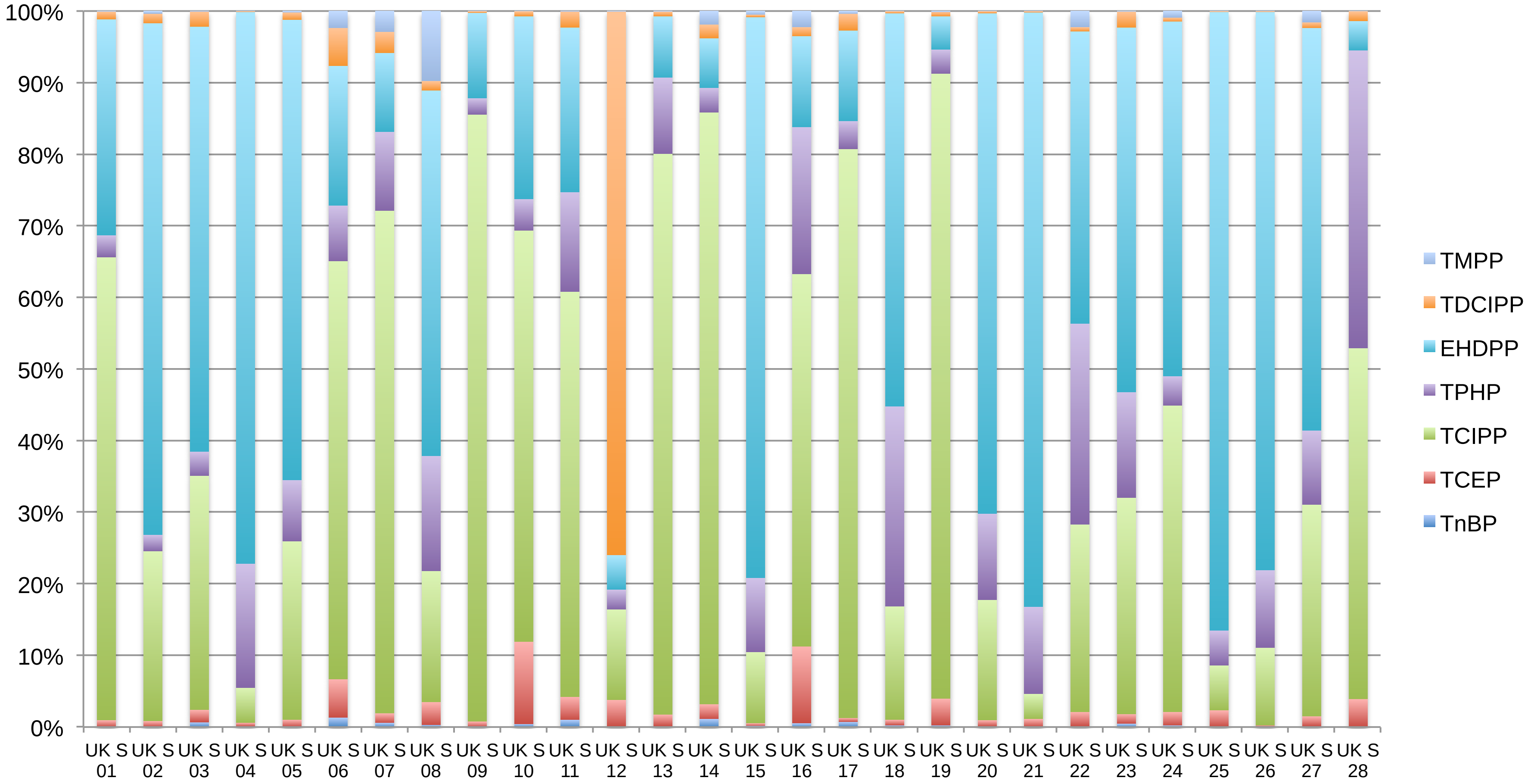
Concentrations of PFRs in UK classroom samples displayed a high relative standard deviation, illustrating the high variability in the data. EHDPP and TCIPP were the compounds displaying the greatest variability while TnBP concentrations were the least variable. Figure 5.8 shows the difference in contamination pattern between individual UK nursery and school dust samples.

The highest ΣPFR concentration detected in both Australian and UK school dust samples was in UK School 26. This was driven primarily by the extremely high concentration of EHDPP (470 µg/g), which was the highest concentration of EHDPP detected in any of the indoor dust samples reported in this thesis. This classroom contained a variety of putative sources including: foam chairs, PCs, TVs, carpet, textiles and was built in 1980. It is not known when the classroom was last painted but highly elevated EHDPP concentration is not inconsistent with a recent renovation with EHDPP-containing paint.

Table 5.5 *Concentrations of PFRs in UK classroom dust (µg/g)*

Sample code	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
UK S 01	0.08	2.1	150	6.8	68	2.47	0.07	220
UK S 02	0.04	0.63	19	1.8	56	1.06	0.25	79
UK S 03	0.33	0.84	16	1.6	28	1.04	<0.01	48
UK S 04	0.17	0.84	7.8	28	120	0.14	<0.01	160
UK S 05	<0.03	0.53	13	4.4	33	0.52	0.09	51
UK S 06	0.36	1.5	16	2.1	5.3	1.44	0.63	27
UK S 07	0.37	0.81	43	6.8	6.8	1.79	1.8	59
UK S 08	0.20	1.9	11	9.5	30	0.77	5.8	53
UK S 09	<0.03	1.9	210	5.5	29	0.51	<0.01	240
UK S 10	0.28	7.0	35	2.7	16	0.41	<0.01	61
UK S 11	0.27	0.87	15	3.8	6.2	0.61	<0.01	27
UK S 12	<0.03	0.50	1.7	0.4	0.6	10	<0.01	13
UK S 13	<0.03	<0.06	8.6	1.2	0.9	0.07	<0.01	11
UK S 14	0.46	0.84	34	1.4	2.8	0.77	0.76	40
UK S 15	0.20	0.40	11	11	86	0.35	0.53	110
UK S 16	0.08	1.7	8.1	3.2	2.0	0.20	0.34	15
UK S 17	0.39	0.28	41	2.0	6.5	1.2	0.19	51
UK S 18	0.34	0.98	20	36	70	0.36	<0.01	130
UK S 19	<0.03	0.24	5.6	0.2	0.3	0.04	<0.01	6.4
UK S 20	0.09	0.84	16	11	66	0.26	<0.01	95
UK S 21	0.06	1.6	5.0	18	120	0.21	<0.01	150
UK S 22	0.05	0.81	10	11	16	0.24	0.89	39
UK S 23	0.09	0.25	5.7	2.8	9.6	0.42	<0.01	19
UK S 24	0.18	1.4	32	3.1	37	0.44	0.65	74
UK S 25	0.04	1.6	4.3	3.3	59	0.08	<0.01	68
UK S 26	0.41	1.3	65	65	470	0.77	<0.01	600
UK S 27	0.13	1.3	28	9.8	53	0.74	1.45	93
UK S 28	0.12	8.3	110	90	8.9	2.91	<0.01	220
Minimum	<0.03	<0.06	1.7	0.22	0.30	0.04	<0.01	6.4
5th percentile	<0.03	0.24	4.5	0.65	0.75	0.07	<0.01	12
Median	0.12	0.86	16	4.1	29	0.51	<0.01	60
Geometric mean	0.11	0.96	18	4.9	17	0.52	0.05	60
Average	0.17	1.48	33	12	50	1.1	0.48	100
95th percentile	0.40	5.3	130	55	120	2.8	1.7	240
Maximum	0.46	8.3	210	90	470	10	5.8	600
Standard Deviation	0.14	1.8	46	20	89	1.9	1.1	120
Relative Standard Deviation	83	130	140	170	180	180	240	120

Figure 5.8 *PFR contamination pattern (concentrations of individual PFRs expressed as a percentage of ΣPFR) in nursery and primary school dust samples from the UK*



5.3.1 PFR and PBDE concentrations in UK school dust samples

As PBDE concentrations were known also known for the analysed UK school dust samples (Harrad et al., 2010a), they were compared to the PFR concentrations obtained in this study. Table 5.6 displays the range and median concentrations of PFRs and PBDEs in the UK school dust samples. Concentrations of ΣPBDEs were between 1 % and 33 % of the reported ΣPFR concentrations in the same samples. It needs to be noted though that in one school dust sample (UK S 12), the concentration of ΣPBDEs (17 µg/g) exceeded that of ΣPFRs (13 µg/g). This is surprising as this classroom contained the highest TDCIPP levels found in the UK sample set. The elevated FR concentrations in this classroom may possibly be attributable to the high number of foam chairs within it (see 5.3.4.)

Table 5.6 *Comparison of PFR and PBDE concentrations in UK school dust samples (ng/g)*

	Minimum	Median	Maximum
TnBP	<30	120	460
TCEP	<60	860	8300
TCIPP	1700	16000	210000
TPhP	220	4100	90000
EHDPP	300	29000	470000
TDCIPP	40	510	10000
TMPP	<10	<10	5800
ΣPFR	6400	60000	600000
BDE 28	<1	<1	25
BDE 47	1.6	27	120
BDE 66	<1	<1	9.7
BDE 100	<1	7.0	50
BDE 99	1.1	38	270
BDE 154	<2	3.8	26
BDE 153	<2	10	310
BDE 183	<2	3.2	48
BDE 197	<3	3.2	35
BDE 203	<3	3.0	50
BDE 196	<3	4.5	42
BDE 209	120	6000	88000
ΣPBDEs	130	6300	89000

5.3.2 Correlation between concentrations of different PFRs and PBDEs in UK school dust samples

The Shapiro-Wilk test showed that concentrations of all PFRs were not normally distributed but significantly positively skewed. Therefore further statistical tests were conducted on log-normalised data. Table 5.7 displays the significant correlations detected between PFRs, as well as between PFRs and PBDEs in UK classroom dust samples. Positive correlations may be indicative of common sources of the two compounds.

Table 5.7 *Correlation between concentrations of individual PFRs and PBDEs in UK school dust*

Compound 1	Compound 2	Pearson Correlation Coefficient
Highly significant correlations (p<0.01)		
TCEP	TPHP	0.497
EHDPP	TPhP	0.729
BDE 100	TCIPP	0.494
BDE 209	EHDPP	0.534
BDE 209	TPhP	0.508
ΣBDE	ΣPFR	0.581
Significant correlations (p<0.05)		
TCEP	TCIPP	0.475
TCIPP	TPHP	0.395
BDE 47	TCIPP	0.452
BDE 47	TDCIPP	0.443
BDE 47	TCEP	0.457
BDE 100	TDCIPP	0.466
BDE 100	TCEP	0.431
BDE 99	TCIPP	0.471
BDE 99	TDCIPP	0.474
BDE 99	TCEP	0.473

As with the Australian school dust samples, several significant correlations were found in the UK sample set. As EHDPP and TPHP correlated highly significantly with a Pearson correlation coefficient of 0.729, it is likely that a substantial source of TPHP in the analysed samples was as a result of its co-application with EHDPP (Environment Agency, 2009a). Penta-BDE (47, 99 and 100) congeners were significantly correlated with TCEP, TCIPP and TDCIPP in the UK sample set. This is interesting as all of these three PFRs have the same application and are/were used interchangeably including as Penta-BDE alternatives. Differences to the Australian samples are discussed in 5.2.4.

5.3.3 Influence of building age on PFR concentrations in UK school dust

In light of its reported influence on PFR concentrations in air from Swedish buildings (Bergh et al., 2011a), the influence of building age on PFR concentrations in UK school dust was tested using one-way ANOVA with tukey post-hoc test on log-transformed data. Note that this analysis was not conducted for Australian samples as information about the building age was not available for the sample set. Buildings were separated into five age ranges: pre 1960 (n=7), 1960 – 1979 (n=4), 1980-1989 (n=7), 1990-1999 (n=5), 2000-2008 (n=5) to reflect as far as possible the age ranges used in the Swedish study (Bergh et al., 2011a) Results indicated significant differences ($p<0.05$) between concentrations of TnBP in the different building ages. Pre-1960 buildings had the highest average concentrations (0.27 µg/g), followed by 1960-1979 (0.22 µg/g), 1980-1989 (0.20 µg/g), 1990-1999 (0.07 µg/g) and 2000-2008 (0.06 µg/g). This observation that the TnBP concentration in dust decreases with building age is consistent with that reported for TnBP in air from Swedish apartments (Bergh et al., 2011a). No significant differences were observed for all of the other analysed PFRs according to the building age, which is in line with the study in Sweden (Bergh et al., 2011a).

5.3.4 Influence of room contents on concentrations of PFRs in UK school dust

To examine the influence of room contents on PFR concentration in UK classroom dust, multiple linear regression analysis was performed on log transformed data and resulted in several significant regressions. For all multiple linear regression analyses if a given room content parameter (such as carpet) was either present or absent; where a sample was from a room containing that parameter, it was assigned a value of 1, with samples from rooms where the parameter was not present assigned a value of 0.

A significant relationship was established for the concentrations of TCIPP in relation to classroom contents of putative sources:

logTCIPP = 0.32 (number of PCs) + 0.305 (number of TVs) (r^2= 0.323; $p<0.05$)

The greatest influence on the concentration of TCIPP in a room is the number of PCs with a beta value of 0.488 and a significance of $p<0.01$. This is not surprising as TCIPP is known to have been used in electronics (Kemmlein et al., 2003) and a chamber study showed that TCIPP is emitted from computer equipment (Kemmlein et al., 2003) The second highest influence on the TCIPP concentration was the number of TVs with a beta value of 0.356 and a significance of $p<0.05$. The relationships for foam chairs and flooring were not significant.

Interestingly a similar significant relationship was also established for TDCIPP at a lower significance level:

Log TDCIPP: 0.027 (number of foam chairs) +0.294 (number of TVs) (r^2= 0.194, $p<0.1$)

The greatest influence on the TDCIPP concentration was exerted by the number of foam chairs in one room. This variable itself had a significance level of $p<0.05$ and a beta value of 0.342. It is known that TDCIPP is primarily used in foam products. In the study by (Kemmlein et al., 2003) emission rates of TDCIPP from foam products were below the detection limit.

Table 5.8 *Questionnaire results used for multiple linear regression analysis between concentrations and putative sources of PFRs in UK classrooms*

Sample id	# of PCs	# of foam chairs	carpet present[a]	# of TVs
UK S 01	1	1	1	2
UK S 02	1	1	1	1
UK S 03	6	4	0	0
UK S 04	2	0	0	0
UK S 05	0	0	0	0
UK S 06	0	2	0	0
UK S 07	3	3	1	0
UK S 08	2	0	0	1
UK S 09	39	31	1	0
UK S 10	1	3	1	0
UK S 11	1	7	0	1
UK S 12	0	18	0	0
UK S 13	0	0	0	0
UK S 14	1	1	2	0
UK S 15	5	1	0	0
UK S 16	2	1	1	1
UK S 17	2	2	0	0
UK S 18	0	0	1	1
UK S 19	4	0	1	0
UK S 20	0	0	1	0
UK S 21	1	0	0	0
UK S 22	0	0	1	0
UK S 23	3	6	1	1
UK S 24	2	2	1	0
UK S 25	1	1	0	0
UK S 26	5	5	1	1
UK S 27	2	3	1	0
UK S 28	1	0	0	1

[a] 1 = yes; 0 = no

However, it was shown in the same study that TCIPP emission rates of foam products were measurable (Kemmlein et al., 2003) These seemingly conflicting findings may simply reflect either a temporal change from TCIPP to TDCIPP as a preferred FR in furniture foam, or a difference in the preferred FR used in Germany compared to the UK. Additionally, the TDCIPP content

was positively correlated with the amount of TVs in the room (beta value 0.317; $p<0.1$). As a similar positive correlation with TVs was also seen for TCIPP, it appears that both TCIPP and TDCIPP are used in TVs. No significant relationship between the number of PCs and the presence/absence of carpet could be established for TDCIPP.
No significant relationships ($p<0.05$) between room contents and concentrations of TnBP, TCEP, EHDPP and ΣPFRs were established.

To our knowledge this is the first time that the PC content in a room has shown to be significantly correlated with the TCIPP contamination in dust. Furthermore it is to our knowledge the first time that the number of foam chairs in a microenvironment has been shown to influence concentrations of TDCIPP.

5.3.5 Comparison of classroom samples with other microenvironments analysed in this study

When classroom samples are compared to those from UK home, cars and offices, differences are revealed. Figure 5.7 displays the average concentrations of those four microenvironments. ANOVA testing with Tukey post-hoc test was transformed on log-transformed data. Significant differences between the means of classrooms and other microenvironments were revealed. EHDPP concentrations were significantly ($p<0.001$) greater in the school dust samples compared to the other three microenvironments. Interestingly this was also found for the Australian school dust samples. This means that in general schools have a typical source of EHDPP, which is not found in all of the other microenvironments to that extent.

On the other hand concentrations of TCIPP were significantly ($p<0.05$) greater in office and car dust compared to the school dust samples. While TDCIPP levels were significantly ($p<0.001$) higher in car dust samples compared to the school dust samples. The TnBP results were excluded from this comparison as there were too few detectable concentrations in the whole dataset, which would have indicated false significant correlations. No other significant differences between PFR concentrations between the school dust samples and other microenvironments were found.

5.4 Comparison of concentrations and relative abundances of PFRs in dust from schools and nursery classrooms in Australia and UK

5.4.1 Comparison of PFR concentrations between Australia and UK school dust samples

To evaluate if PFR concentrations in Australian classroom dust samples were significantly different to those in the corresponding UK samples, a t-test comparison was performed on log-transformed data. This revealed that concentrations of TnBP, TCEP, TCIPP, EHDPP, TDCIPP, TMPP and ΣPFR were significantly higher ($p<0.05$) in UK compared to Australian samples.

Note that the data reported in this chapter are used in Chapter 6 to conduct an exposure and risk assessment for children.

5.4.2 Comparison of PFR patterns between Australia and UK school dust samples

To compare PFR patterns in UK and Australian school dust samples, PCA was conducted for all measured PFRs in all school dust samples from both countries. (Figure 5.9) Principal component 1 accounted for 28% and principal component 2, 21% of the total variance in the data. The rotated component matrix shows the relative contribution of each PFR to each principal component (Figure 5.10). This indicates that PC1 is driven in a negative direction by high relative abundances of EHDPP, and in a positive direction by high relative abundance of TnBP. PC 2 is positively driven by TCIPP and negatively driven by TPhP.

Figure 5.9 *Comparison of average PFR concentrations (µg/g) between UK classroom, car, living room and office dust samples*

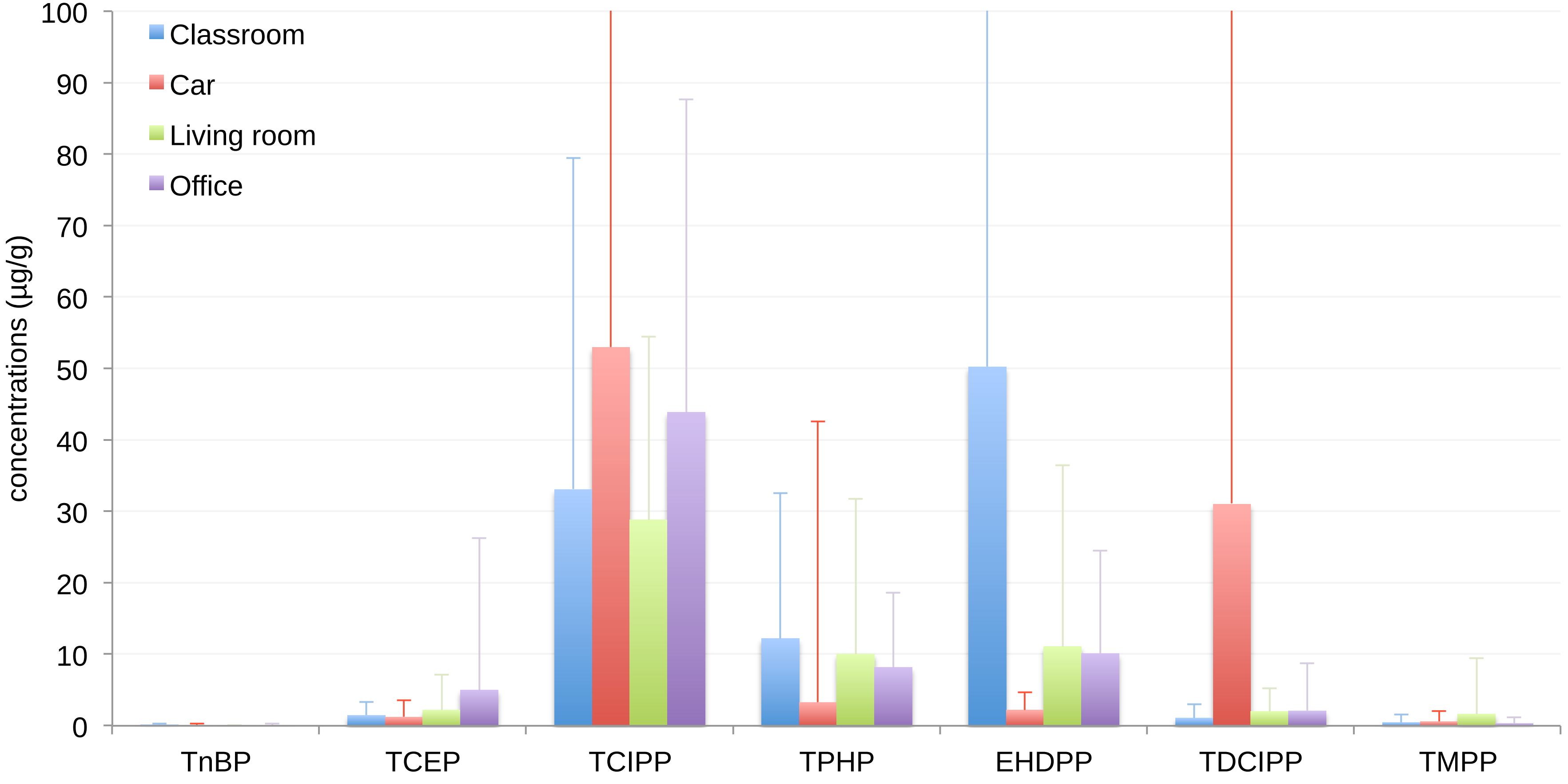


Table 5.9 *Rotated component matrix score table*

	Component	
	1	**2**
TnBP	0.713	-0.018
TCEP	0.465	0.387
TCIPP	0.265	0.858
TPhP	0.459	-0.799
EHDPP	-0.855	-0.181
TDCIPP	0.350	-0.043
TMPP	0.152	0.114

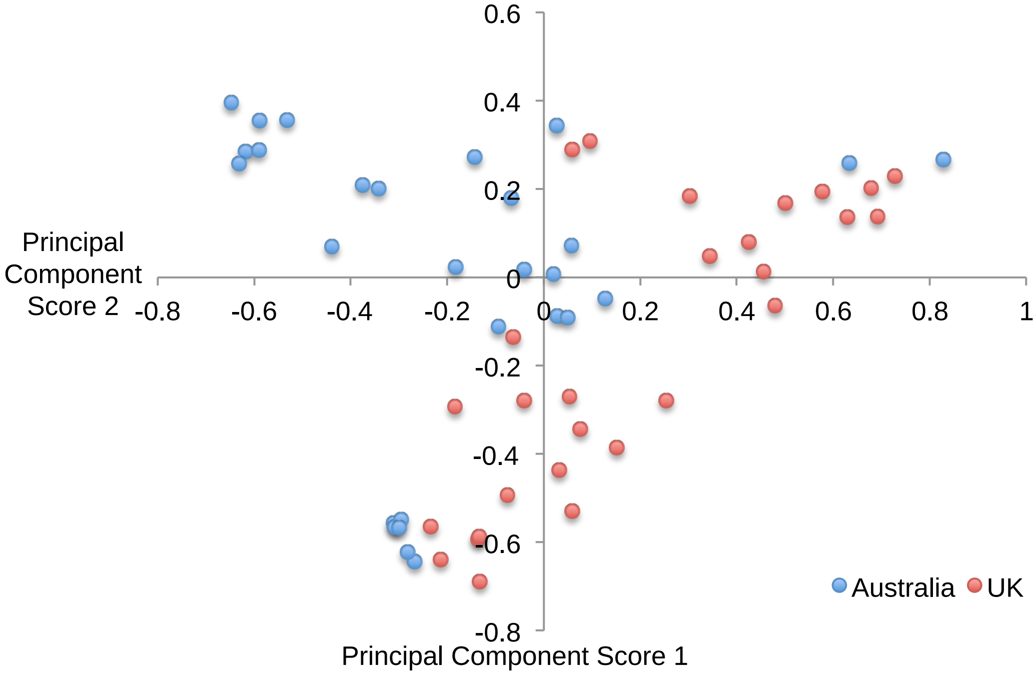


Figure 5.10 *PCA plot of PC1 versus PC2 for Australian and UK school dust samples*

Figure 5.10 shows clearly that there is a PFR pattern difference between Australian and UK school dust samples. This is not surprising as TCIPP contributes on average 21% ΣPFR in Australian compared to 40% ΣPFR in UK samples. Likewise, TPhP comprised on average 40% ΣPFR in Australian samples compared to only 11% ΣPFR in UK samples. Combined, these pattern differences are manifested in the generally higher PC2 scores for UK samples. These pattern differences likely reflect differences in the PFRs used in the two countries.

Figure 5.11 displays the relative abundance of different PFR in both UK and Australian classroom dust samples. It indicates that the greatest contributions arise from TCIPP, EHDPP and TPHP in both countries, followed by TDCIPP and TCEP, with very small contributions from TMPP and TnBP.

5.4.3 Comparison of PFR and PBDE correlations between Australia and UK school dust samples

Despite the international differences in PFR use patterns inferred by the PCA above, there are indications of common PFR sources. For example, in both the UK and Australian sample sets, EHDPP and TPHP were highly significantly correlated both with each other and with BDE-209. In contrast, the positive correlation between TPhP and PBDE congeners prevalent in the PentaBDE mixture that was seen in the Australian sample set and in an earlier US study (Dodson et al., 2012) was not detected in the UK samples. Moreover, the significant correlations between concentrations of TCEP, TCIPP and TDCIPP and PentaBDE congeners (PBDEs- 47, 99 and 100) that were detected for the UK samples, were not observed in Australia.

5.5 Comparison with available literature data

Comparison with literature data in classroom dust is very difficult due to the fact that the literature database currently consists of just one preliminary study on PFRs in 10 samples of dust from child day care centres in Sweden (Bergh et al., 2011b). Table 5.10 compares the median concentrations detected in this study with those found in the Swedish survey. To test if statistically significant differences exist between the Australian, Swedish, and UK data, an ANOVA-test with Tukey post-hoc was performed on log-transformed data.

Figure 5.11 *Average contribution to ΣPFR in classroom samples (%), error bars represent standard deviation*

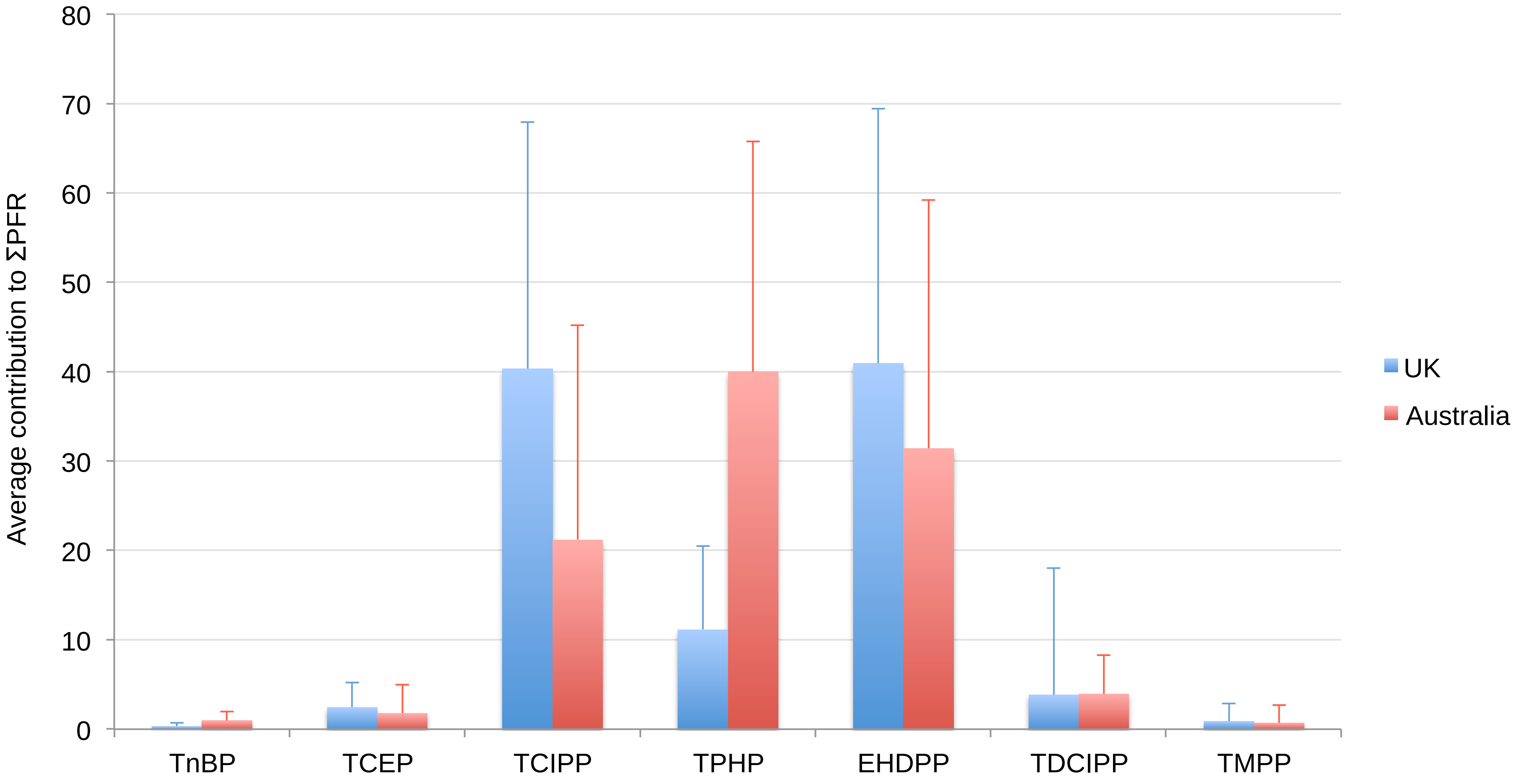


Table 5.10 *Median Concentrations of PFRs in dust from UK and Australian Classrooms and Swedish Child Day Care Centres (µg/g)*

	TnBP	TCEP	TCIPP	TPhP	EHDPP	TDCIPP	TMPP
Australia	0.07	<0.06	0.7	5.4	1.1	0.3	<0.01
Sweden	1.2	30	3.1	1.9	0.8	9.1	0.4
UK	0.12	0.98	16	4.1	29	0.44	<0.01

As significant differences between Australian and UK school dust samples are displayed in 5.4.1, only differences compared to the Swedish samples are discussed at this point. Significant differences (p<0.01) are displayed in Table 5.11.

Table 5.11 *Significant differences (p<0.01) between PFR concentrations in dust from UK and Australian Classrooms and Swedish Child Day Care Centres*

Compound	Significant difference		
TnBP	Sweden	>	UK, Australia
TCEP	Sweden	>	UK, Australia
TCIPP	UK	>	Sweden
	Sweden	>	Australia
EHDPP	UK	>	Sweden
TDCIPP	Sweden	>	UK, Australia
TMPP	Sweden	>	Australia

Table 5.11 shows clearly that there are significant differences between the concentrations of some PFRs in the Swedish dust samples compared to those reported in this study. TPhP is the only compound analysed in this study for which no significant difference was found between the datasets. TCEP and TDCIPP were present at significantly higher concentrations in the Swedish compared to the Australian and UK samples. As the building age of the Swedish day care centres studied is not known, it is not possible to evaluate whether the buildings sampled in Sweden were of an age that would be associated with a higher likelihood of containing TCEP in their roofing insulation material.

A possible explanation for the difference in PFR concentrations detected in the Swedish study and this one, could lie with the different sampling method used to collect the Swedish day care centre samples. In the Swedish study, dust was collected from elevated surfaces, e.g. on tops of bookshelves, cupboards, desks, window casings and doors at least 0.8 m above the floor. Furthermore extracting the whole sample of a cellulose filter results in a different particle size range, with a trend toward the smaller particles. Those are much lighter and much more likely to be transported through air circulation within the room. The Swedish study does not state the exact dimensions of the cellulose filter used which means that the “cut-off” point is not known, but the sample socks used to collect Australian and UK samples collection have a cut-off of <25 µm. Additionally to that, as a result of post-sampling sieving, the upper particle size “cut-off” point for the samples in this study is 500 µm. By comparison, there is no such “cut-off” point for the Swedish samples as they are not sieved. While such potential influences of the sampling method are acknowledged however, and merit further investigation in the future; they are not wholly consistent with the lack of systematic differences between studies in concentrations of TPhP and the lower concentrations in the Swedish samples of EHDPP and TCIPP.

To determine if the significant differences in absolute concentrations in samples from different countries are accompanied by significant differences in PFR pattern, a PCA was conducted for all measured PFRs in the 3 datasets. Principal component 1 accounted for 28% and principal component 2, 20% of the total variance in the data. The rotated component matrix shows the relative contribution of each PFR to each principal component (Figure 5.12). This indicates that PC1 is driven in a positive direction by high relative abundances of TCEP, TMPP, TnBP, and TDCIPP, and in a negative direction by a high abundance of EHDPP. PC 2 is positively driven by TCIPP and negatively driven by EHDPP. This is manifested in markedly higher PC1 scores for most Swedish samples, while PC2 is more effective at distinguishing UK and Australian samples.

Table 5.12 *Rotated component matrix score table for comparison of Australian, Swedish and UK school dust PFR pattern*

PFR	**Component**	
	1	**2**
TnBP	0.706	0.081
TCEP	0.637	-0.420
TCIPP	-0.250	0.929
TPhP	-0.212	-0.108
EHDPP	-0.446	-0.702
TDCIPP	0.598	-0.145
TMPP	0.630	0.109

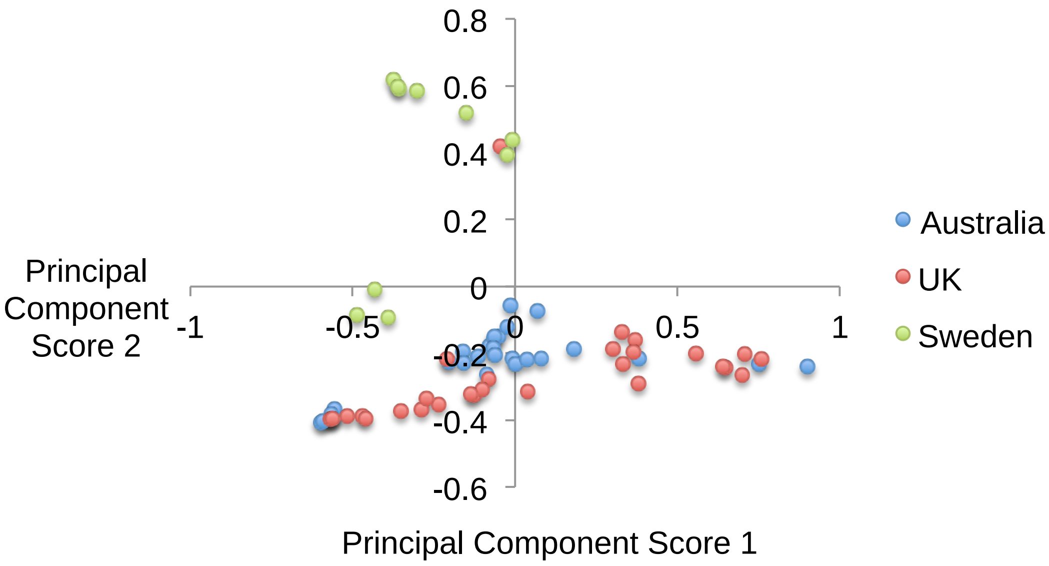


Figure 5.12 *PCA for Australian, UK school dust and Swedish day care centre literature data*

5.6 Conclusion

This chapter reveals significant differences in both absolute concentrations and relative abundances of PFRs in floor dust from Australian and UK classrooms, with further differences detected when data from this study were compared to an earlier study of dust from elevated surfaces in Swedish child daycare centres. With the exception of TPhP, dust from UK classrooms showed significantly higher concentrations of PFRs compared to dust from Australian classrooms. Concentrations of ΣPFRs in Australian and UK school dust samples exceeded significantly those of ΣPBDEs in the same samples.

One UK school showed the highest EHDPP concentration detected in all dust samples analysed in this thesis. For both Australian and UK schools, concentrations of TPhP and EHDPP levels correlated significantly, indicating a common source of these PFRs. Furthermore, both Australian and UK schools showed significant higher EHDPP concentrations than other microenvironments studied. With respect to temporal variation, concentrations of TnBP in UK school dust were significantly higher in older buildings. With respect to the influence of putative sources in UK classrooms; concentrations of TCIPP were significantly positively correlated with the number of PCs in the room, while a similar – albeit less significant – correlation was observed between the number of foam chairs in the room and concentrations of TDCIPP.

6 EXPOSURE TO PFRs VIA INGESTION OF INDOOR DUST

Biomonitoring studies have shown both the presence of PFRs in human milk (Sundkvist et al., 2010) and of PFR metabolites in human urine. (Schindler and Förster, 2009; Schindler et al., 2014; Carignan et al., 2013b) This demonstrates that human exposure to PFRs is occurring. Dust has been reported previously as an important pathway of human exposure to flame retardants. (Abdallah and Harrad, 2009; Harrad et al., 2010a). Therefore we investigated the extent of PFR exposure through dust ingestion for humans. Evidence of a positive trend between TDCIPP concentrations in office dust and the metabolite BDCPP in urine samples of office occupants was found in the US (Carignan et al., 2013b). Furthermore, differences in TnBP and TPhP metabolite urine concentrations (higher levels post shift) were found for aircraft maintenance technicians (Schindler et al., 2014), and in an initial study 6 out of 12 airplane passengers displayed detectable concentrations of *o*-TMPP in their urine after completing a flight (Liyasova et al., 2011). Additionally, PFRs were detected in pooled human milk samples from Sweden (Sundkvist et al., 2010), and PFR metabolites were detected in urine of the general population in Germany (Schindler and Förster, 2009).

This chapter also examines which microenvironment category contributes the most to human exposure. As seen in Chapter 4, concentrations of PFRs in dust varied significantly between different microenvironments, raising the possibility that different population sectors might be more exposed to PFRs than others. It has been shown for PBDEs that the majority of overall dust exposure occurs in the home (Harrad et al., 2010a), while classrooms have been shown to be a major contributor to the PFOS exposure of children. (Goosey and Harrad, 2011)

This chapter uses data on PFR concentrations in dust samples to generate estimates of human exposure via ingestion of indoor dust. The risk to human health is evaluated by comparing exposure estimates derived under three plausible scenarios, with the appropriate health based limit value (HBLV). The HBLV values used in this study are given in Table 6.1.

Table 6.1 *HBLV for individual PFRs analysed in this study (ng/kg bodyweight (bw) per day)*

PFR	HBLV	Reference
TnBP	24,000 [a)]	(Ali et al., 2012)
TCEP	22,000 [a)]	(Ali et al., 2012)
TCIPP	80,000 [a)]	(Ali et al., 2012)
TPHP	70,000 [a)]	(Ali et al., 2012)
EHDPP	6,000,000[b)]	(Environment Agency, 2009a)
TDCIPP	15,000 [a)]	(Ali et al., 2012)
TMPP	13,000 [a)]	(Ali et al., 2012)

a) Chronic no observed adverse effect level (NOAEL) divided by a factor of 1000

b) NOAEL for liver enzyme perturbations

6.1 Exposure pathways and assessment

Exposure via dust ingestion is evaluated for two groups: a) adults, and b) children. Ingestion of dust is assumed proportional to the time spent in different microenvironment categories (Harrad et al., 2008a). Dust ingestion for toddlers is considered to occur primarily through deliberate hand-to-mouth contact, or by eating food, which has accumulated dust having been dropped on the floor. Adult ingestion of dust is thought to occur via direct hand-to-mouth behaviour or via eating food with unwashed hands thereby effecting oral dust transfer. (Wilson et al., 2013)

Human exposure via dust ingestion was estimated using three different exposure scenarios:

a) low-end exposure where the human receptor is assumed to ingest dust contaminated at the 5th percentile concentration in each microenvironment category considered at the average rate (2.6 mg and 41 mg per day for adults and toddlers respectively (Wilson et al., 2013));

(b) "typical" exposure, where dust contaminated at the median concentration is assumed to be ingested at the average rate; and

(c) high-end exposure in which dust contaminated at the 95th percentile concentration is assumed to be ingested at the high rate (8.6 mg and 140 mg per day for adults and toddlers respectively (Wilson et al., 2013)).

It should be noted that the dust ingestion rates cited here do not include dust intake via object-to-mouth behaviour as this pathway was regarded as too uncertain (Wilson et al., 2013). It was assumed in that study that 50% of the dust-bearing surfaces with which the person has contact are soft surfaces, while the other 50% are hard surfaces. This is because soft surfaces like couches, carpets, and mattresses, are likely to have a greater dust loading than hard surfaces, e.g. hardwood floors, countertops, tables, and window seals.

It has been highlighted elsewhere (Harrad et al., 2010b), that human rates for dust ingestion are a major area of uncertainty, as there are very few primary data studies on this issue, with most data extrapolated directly from studies of soil ingestion. In this context, the ingestion rates used in this study differ from those used in many previous studies. (Harrad et al., 2010a; Abdallah and Harrad, 2009; Goosey and Harrad, 2011; Ali et al., 2013) We have chosen these dust ingestion rates, as they are amongst the most recent available, were derived specifically for dust (rather than soil) ingestion, and consider factors such as: particle loading to indoor surfaces, the fraction transferred to the hands, hand surface area, the fraction of hand surface area that may be mouthed or in contact with food, the frequency of hand-to-mouth events, the amount dissolved by saliva and the duration of exposure to the dust.

Figure 6.1 shows the algorithm used to calculate dust ingestion rates in the (Wilson et al., 2013) study.

DUST INGESTION RATE

$$\mathrm{DIG} = \mathrm{DSL} \times \mathrm{FTSS} \times \mathrm{SA}_{\mathrm{HAND}} \times \mathrm{FSA}_{\mathrm{FINGERS}} \times \mathrm{FQ} \times \mathrm{SE} \times \mathrm{ET}$$

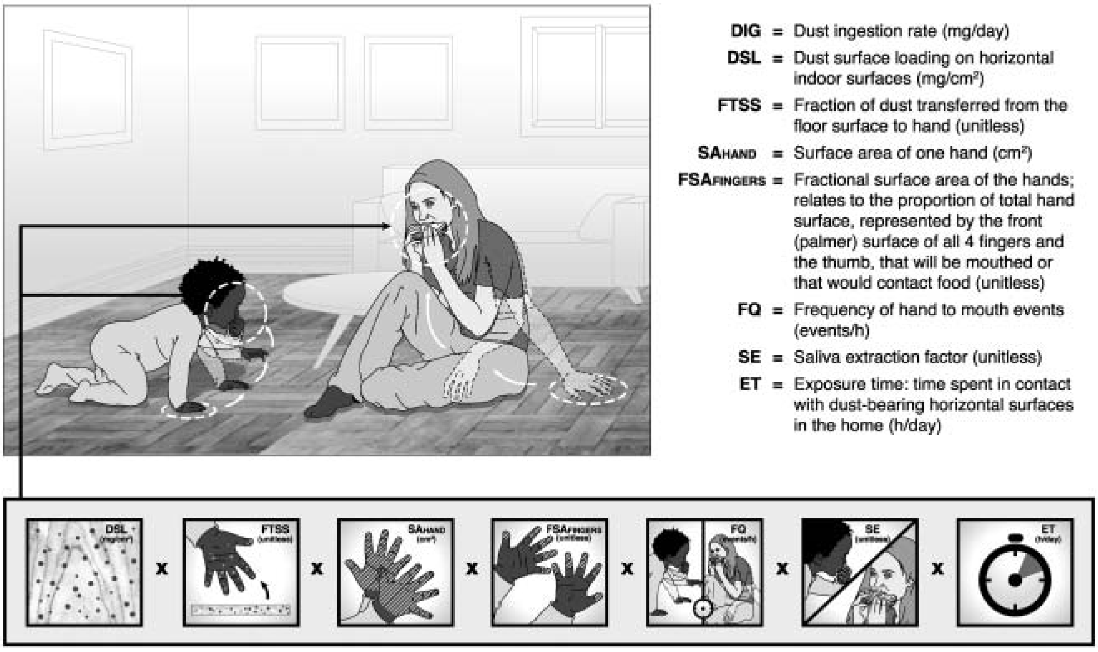


Figure 6.1 *Conceptual diagram showing estimation of dust ingestion rates (Wilson et al., 2013)*

As well as the considerable uncertainty in our exposure estimates associated with dust ingestion rates, additional uncertainty is introduced though factors such as our use of fixed periods of time spent in different microenvironment categories. Clearly these figures will be subject to substantial variation between individuals. It is also unclear as to the extent to which the individual microenvironments sampled in this study are representative of the PFR contamination encountered by the population as a whole. Further uncertainty may be associated with inter-individual variation in hand-washing frequency, given recent indications that higher frequency of hand-washing may decrease the concentrations of BDCPP (a TDCIPP metabolite) in urine. (Carignan et al., 2013b)

Supplementary to this, we have assumed 100% absorption of PFRs from dust. This is necessary in the absence of any empirical data to the contrary, but it is likely that actual bioavailability across the gastro-intestinal tract will be

– perhaps substantially – lower than 100%, given recent indications from in vitro gut bioaccessibility studies of BFR uptake from dust (Abdallah et al., 2012).

With respect to time–activity patterns; adults were assumed to spend 4.2% in cars, 23.8% in offices and the rest of the day at home (Harrad et al., 2008a). Children were assumed to spend 20.1 % of their time in classrooms, 4.2 % in cars and the rest of the day at home (75.7%) (Harrad et al., 2010a).

For comparison with HBLVs, we normalised exposure estimates to bodyweight using 20 kg as the estimated bodyweight of a UK 6 year old child (Harrad et al., 2010a), with an assumed adult body weight of 70 kg.

6.2 Results

In the UK, exposure assessment was conducted for both adults and children as PFR data were available for a wide suite of microenvironment categories. In contrast, no data were available for PFR concentrations in German classrooms, and hence only adult exposure was estimated in Germany. For the Australian population, exposure was estimated for children and adults. However, as no data were available on PFR concentrations in Australian offices, the latter exposure estimate was based only on house and car PFR concentrations, assuming 4.2% of time spent in cars and the rest at home. The resultant estimates of exposure to PFRs via dust ingestion can be found in Table 6.2.

The results indicate that under the average exposure scenario, UK adult exposure ranges from <0.01 to 0.92 ng/kg bw day for individual PFRs, for German adults from <0.01 to 0.05 ng/kg bw day, and for Australian adults from <0.01 to 0.07 ng/kg bw day.

Table 6.2 *Estimates of human exposure to PFR via dust ingestion in ng/kg bw per day*

	TnBP	**TCEP**	**TCIPP**	**TPHP**	**EHDPP**	**TDCIPP**	**TMPP**	**ΣPFR**
ADULT								
				UK				
low	<0.01	<0.01	0.22	0.03	0.02	<0.01	<0.01	0.28
average	<0.01	0.03	0.92	0.13	0.09	0.07	<0.01	1.3
high	0.02	1.3	13	5.6	5.10	3.1	0.19	28
				Germany				
low	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	0.03
average	<0.01	0.01	0.05	0.02	0.01	0.01	0.01	0.10
high	0.04	0.25	1.9	0.38	0.11	3.0	0.85	6.5
				Australia				
low	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	0.03
average	<0.01	0.02	0.07	0.04	0.01	0.01	<0.01	0.16
high	0.12	2.1	2.7	0.97	0.22	2.6	0.28	8.9
CHILD								
				UK				
low	<0.01	0.29	10	1.3	0.86	0.27	<0.01	13
average	0.08	1.7	43	7.0	14	4.0	0.08	70
high	1.3	45	740	360	420	170	11	1740
				Australia				
low	0.03	0.05	0.76	0.67	0.14	0.07	0.20	2
average	0.13	1.1	5.2	4.4	1.1	0.82	0.37	13
high	5.9	96	150	84	150	140	31	654

Table 6.2 shows that there are international variations in PFR exposure, reflecting such variations in PFR concentrations in dust. For UK children under the average exposure scenario, individual PFR exposures range from 0.08 to 43 ng/kg bw day, with those for Australian children ranging from 0.13 to 5.2 ng/kg bw day. Substantial variation is evident in exposures to different PFRs, but overall children appear considerably more exposed to PFRs than adults, especially after normalisation to body weight.

6.3 Relative contribution of different microenvironments to overall exposure to PFRs via dust ingestion

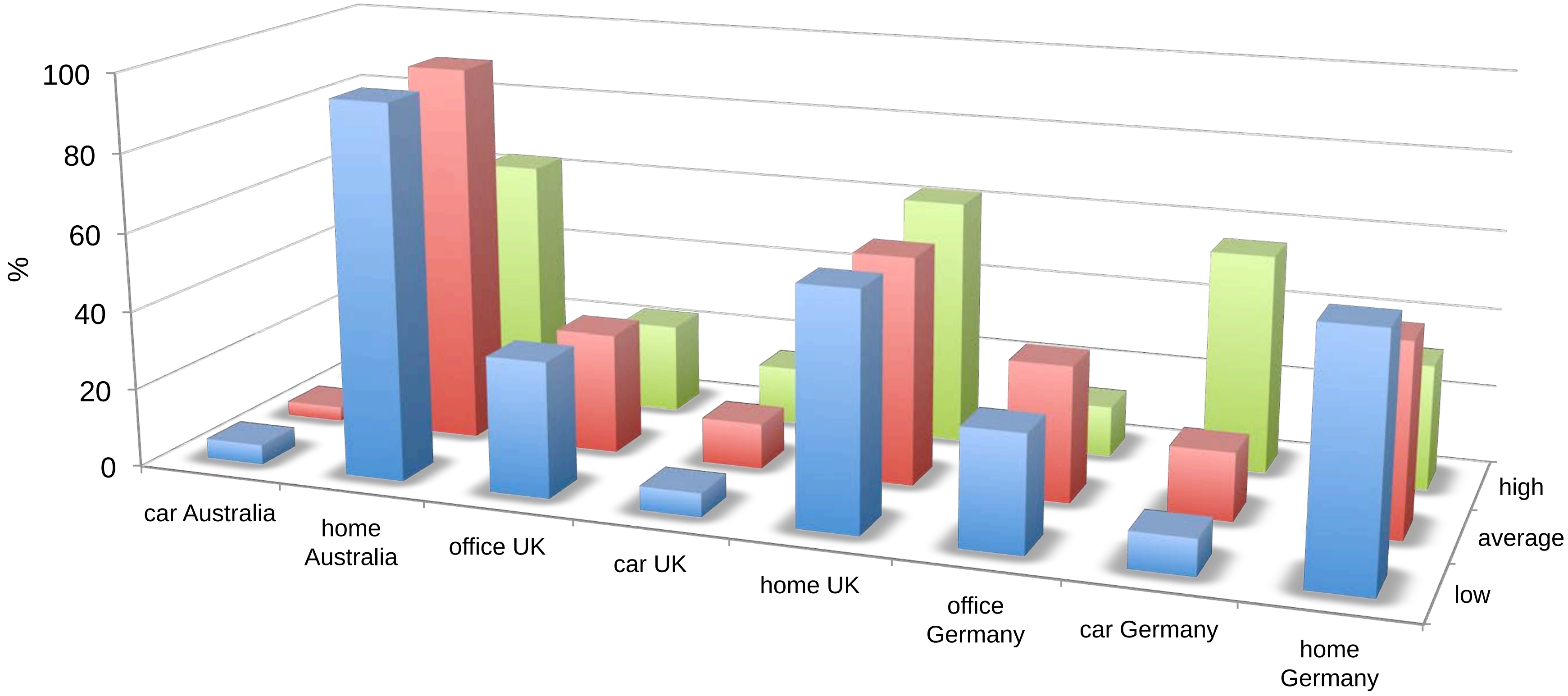
6.3.1 Adult exposure

Figure 6.2 displays the contribution made by cars, homes, and offices to the exposure to PFRs via dust ingestion for Australian, British and German adults. The contribution made by office exposures could not be calculated for Australia. Clearly, these estimated contributions are subject to uncertainty related to variations in individual lifestyle, and the extent to which our data are representative of PFR contamination of dust from different microenvironments. Figure 6.2 illustrates that the most important microenvironment for human exposure to PFRs via dust ingestion is the domestic environment, broadly in line with the proportion of time spent at home. The one exception to this dominance of domestic exposure, is under the high-end scenario for German adults; under such conditions exposure in vehicles dominates.

6.3.1.1 UK adult exposure

The contribution of each microenvironment category to overall exposure to individual PFRs was calculated. Figure 6.3 illustrates such contributions for the UK average exposure scenario. While as expected, living room dust makes the highest contribution to exposure to TCEP, TCIPP, and TPHP; it is Interesting that the highest exposure to TDCIPP and TMPP arises from the car environment. Furthermore, the exposure to EHDPP is more or less equal in the office and home environment.

Figure 6.2 *Percentage of total exposure to SPFRs via dust ingestion according to the environment for the different exposure scenarios for adults from Australia, Germany and the UK*



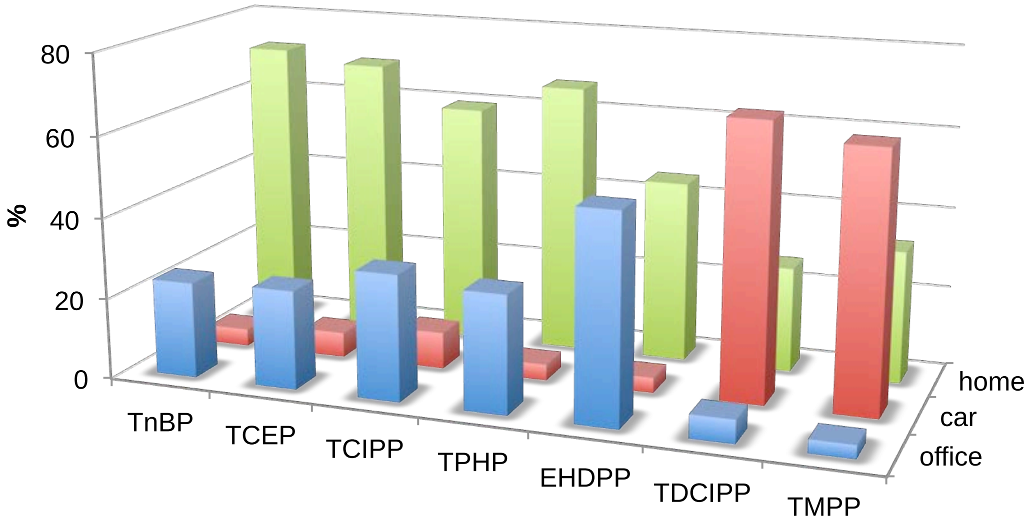


Figure 6.3 *Percentage of total exposure* to a given PFR *via dust ingestion of UK adults under average conditions*

6.3.1.2 German adult exposure

Looking at the average exposure scenario for Germany, it is evident that the highest exposure to TnBP and TPHP occurs in the office environment, with cars providing the majority of exposure to TDCIPP (Figure 6.4).

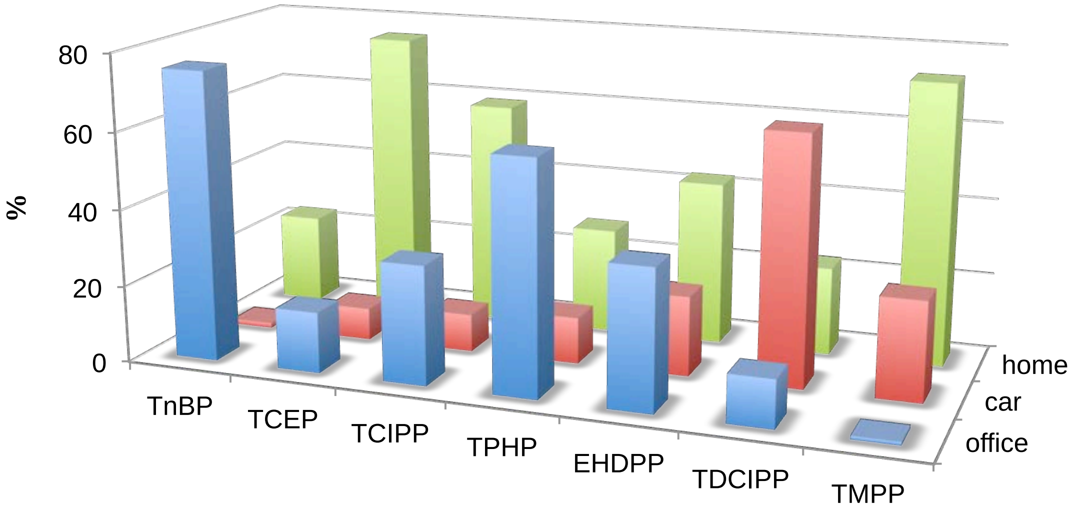


Figure 6.4 *Percentage of total exposure* to a given PFR *via dust ingestion of German adults under average conditions*

6.3.1.3 *Australian adult exposure*

The picture looks somewhat different for Australian adults. Under the average exposure scenario, exposure in the home environment is dominant for all PFRs. This is different to the other countries studied, but is likely at least in part due to the fact that no office data were available for Australia (Figure 6.5).

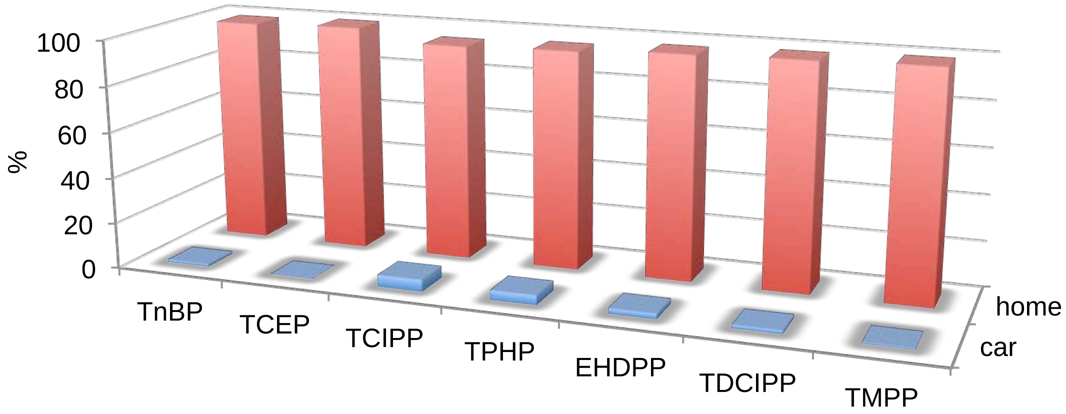


Figure 6.5 *Percentage of total exposure* to a given PFR *via dust ingestion of Australian adults under average conditions*

6.3.1.4 *High end exposure for adults from Australia, Germany and UK*

Interestingly, a pattern shift is evident under the high exposure scenario. To illustrate, while under the average exposure scenario, offices are the main contributor to UK adult exposure to EHDPP; under the high-end exposure scenario, exposure in the home is about four times higher than from the office environment (Figure 6.6). Likewise, while under the average exposure scenario, German adults are exposed to EHDPP broadly equally via homes and offices; under the high-end exposure scenario, exposure occurs primarily in offices (Figure 6.7).

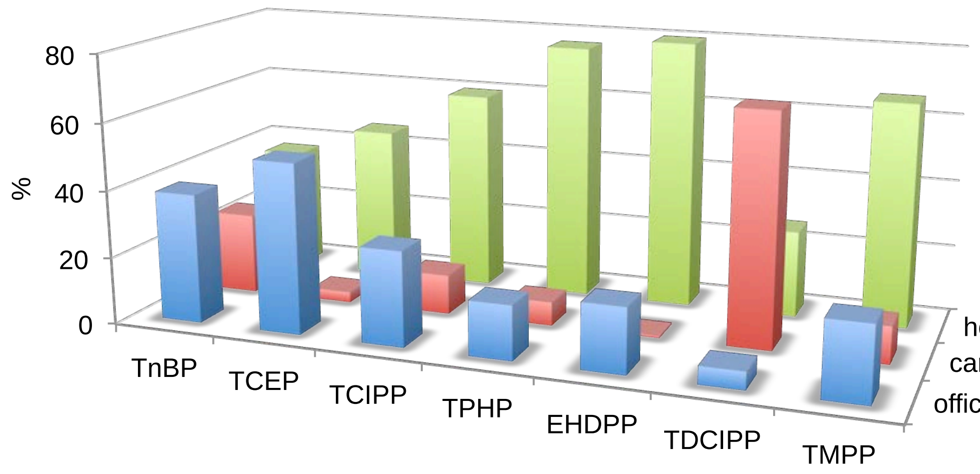


Figure 6.6 *Percentage of total exposure* to a given PFR *via dust ingestion of UK adults under high end exposure scenario*

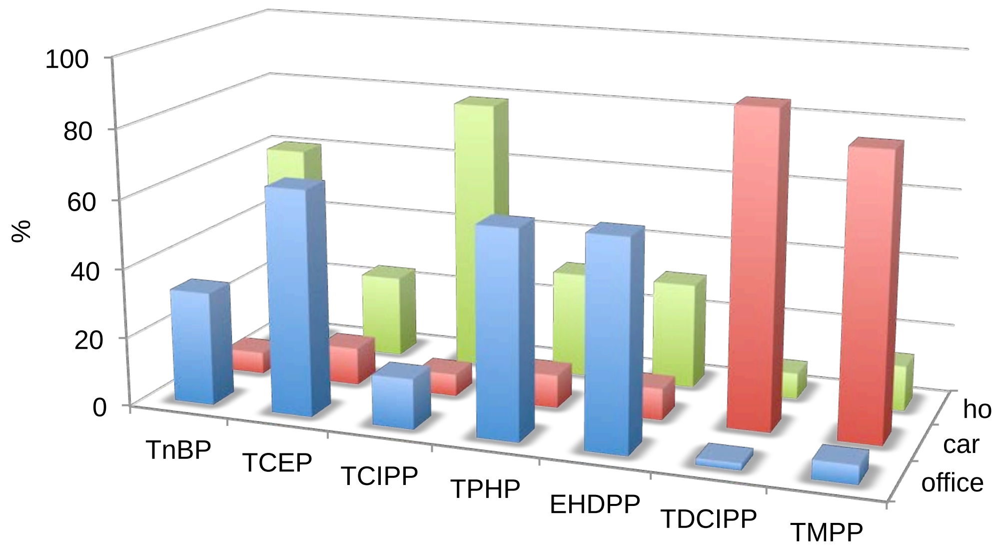


Figure 6.7 *Percentage of total exposure* to a given PFR *via dust ingestion of German adults under high end exposure scenario*

Interestingly, when looking at the high end exposure scenario for Australian adults, the overall contribution to human exposure to TDCIPP and TMPP via ingestion of car dust rises to 70 and 68% respectively.

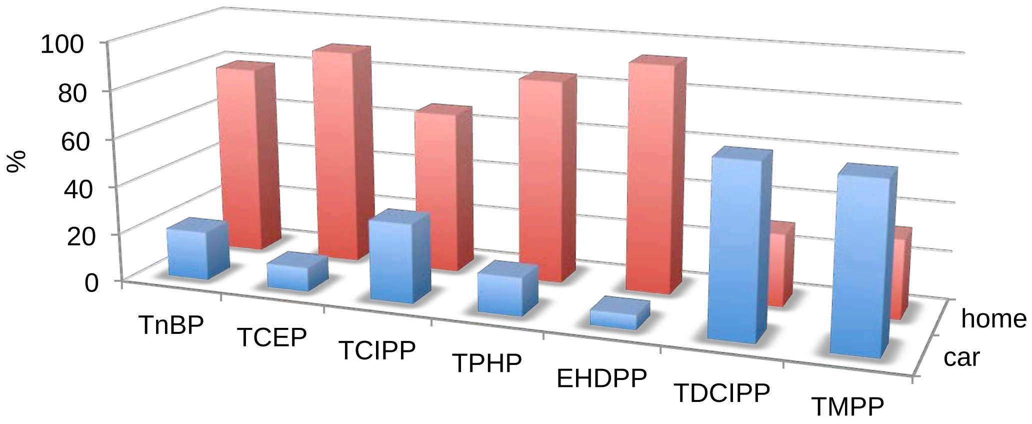


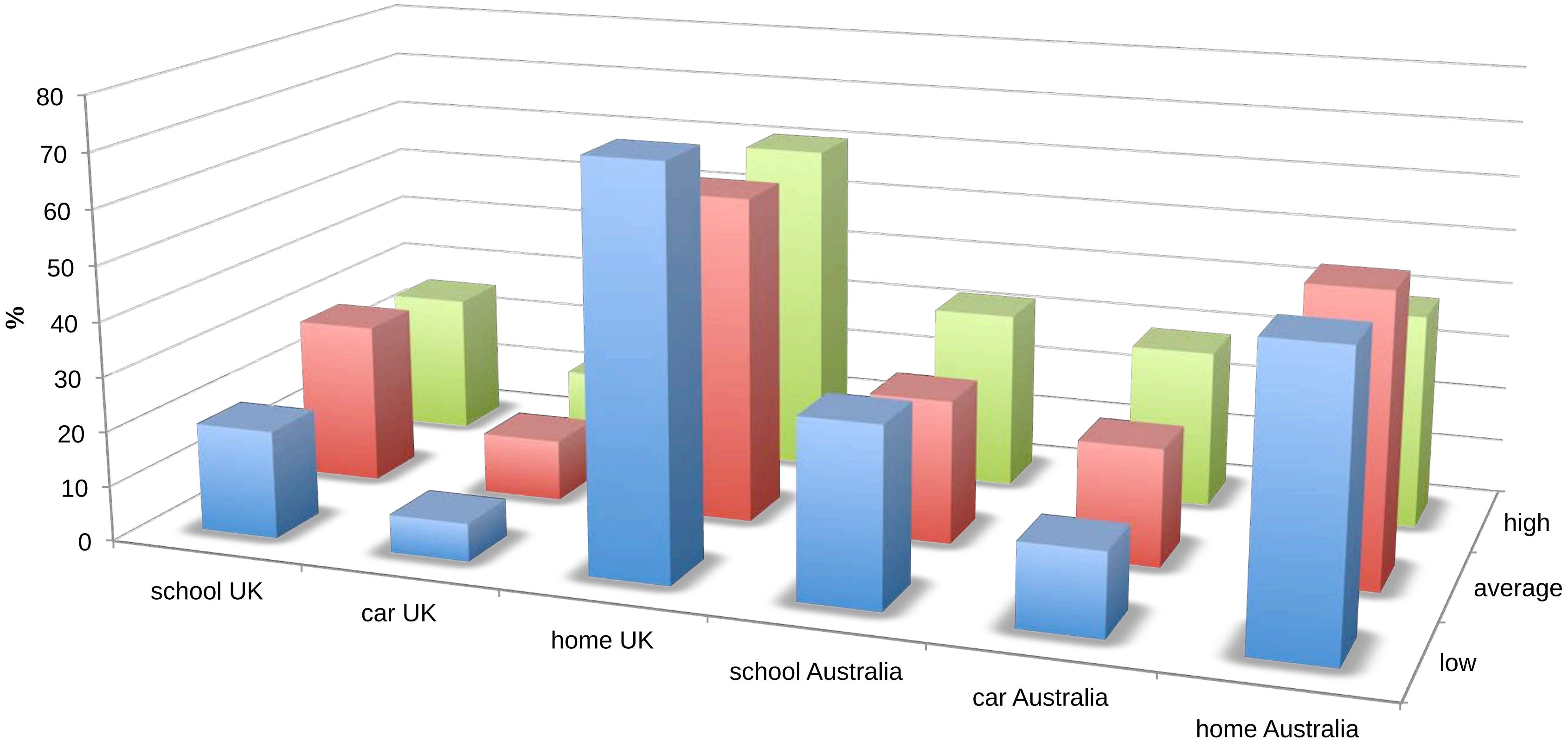
Figure 6.8 *Percentage of total exposure* to a given PFR *via dust ingestion of Australian adults under high end exposure scenario*

6.3.2 Child exposure

Figure 6.9 displays the contribution of cars, classrooms, and homes to overall exposure of children to PFRs via ingestion of indoor dust in Australia and the UK. Exposure scenarios were calculated as stated in 6.2.

Figure 6.9 shows the home is the microenvironment making the greatest contribution (60% of overall exposure) to the exposure of children to PFRs via dust ingestion in the UK. This is primarily due to the amount of time children spend at home.

Figure 6.9 *Percentage of total exposure to ΣPFRs via dust ingestion according to microenvironment for the different exposure scenarios for children from Australia and the UK*



Interestingly the data from Australia shows a different picture. Under the average exposure scenario, just over 50% of the PFR intake is provided by the home environment ,while under the high end exposure scenario all three microenvironments contribute nearly equally to the overall exposure.

6.3.2.1 UK Child exposure

The percentage contribution of cars, classrooms, and homes to overall exposure of UK children to individual PFRs was analysed for the average exposure scenario and displayed in Figure 6.10.

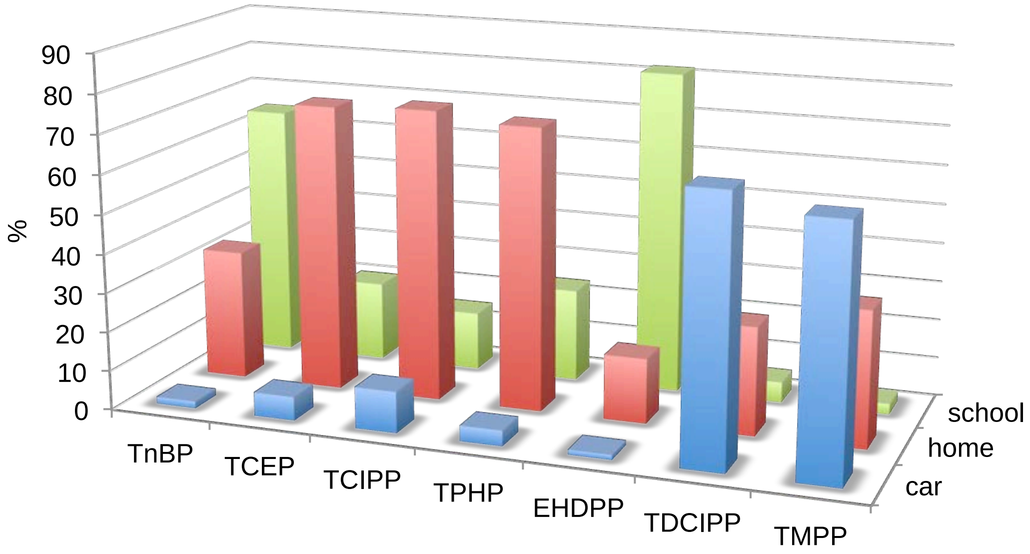


Figure 6.10 *Percentage of total exposure of British children via dust ingestion to individual PFRs under average exposure scenario*

Under the average exposure scenario, the classroom environment is the principal contributor to British children's exposure via dust ingestion to TnBP and EHDPP. By comparison, the majority of exposure to TCEP, TCIPP and TPHP occurs at home, while cars are the dominant exposure venue for British children with respect to TDCIPP and TMPP. In contrast, under the high exposure scenario, the home environment is the principal contributor to exposure for most PFRs. The exceptions to this are: (a) TDCIPP, for which cars remain the principal exposure venue, and (b) TnBP for which classroom exposure exceeds slightly that in homes.

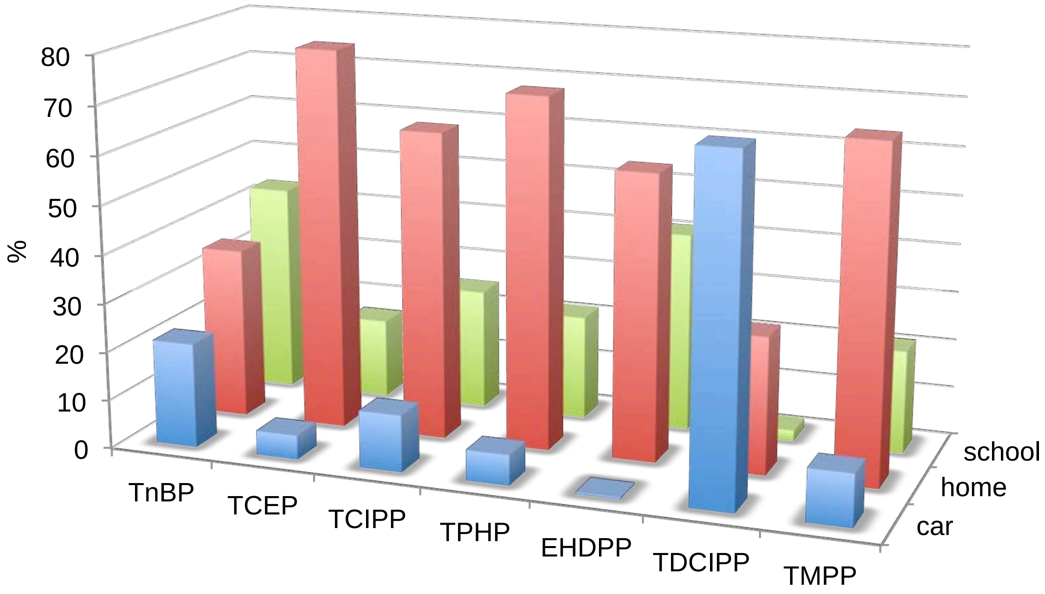


Figure 6.11 *Percentage of total exposure to individual PFRs of British children via dust ingestion under high end exposure scenario*

6.3.2.2 Australian child exposure

For Australian children, the home environment is the major contributor to exposure under the average exposure scenario for all PFRs. The exceptions to this are: (a) TMPP, for which 78% of overall exposure occurs in classrooms and (b) TPHP for which classrooms and homes contribute roughly equally. (Figure 6.12)

Under the high end exposure scenario (Figure 6.13), classrooms contribute 93% of EHDPP exposure, while cars contribute 73% of TDCIPP exposure. In summary, this means that under the high end exposure scenario, cars provide the majority of exposure to TDCIPP, even though relatively little time is spent in this environment. This is due to the significantly higher concentrations of TDCIPP in car dust compared to dust from other microenvironments.

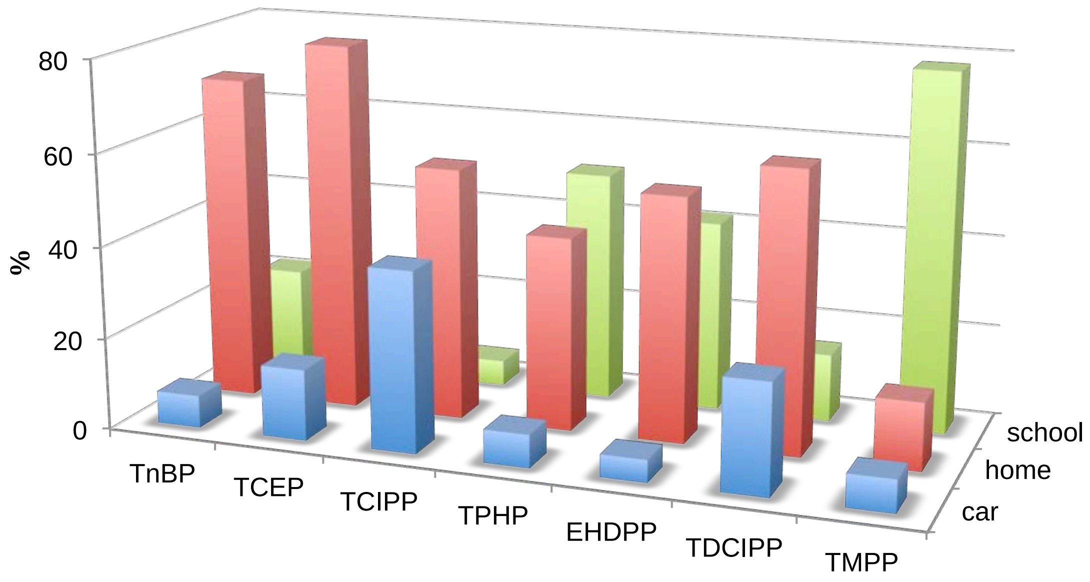


Figure 6.12 *Percentage of total exposure to individual PFRs of Australian children via dust ingestion under average exposure scenario*

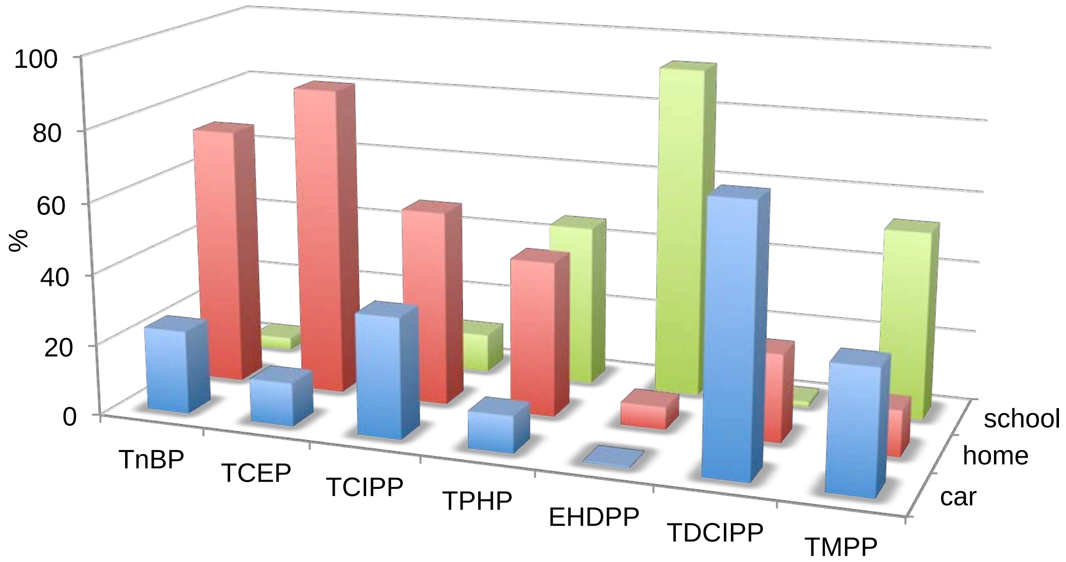


Figure 6.13 *Percentage of total exposure to individual PFRs of Australian children via dust ingestion under high end exposure scenario*

Exposure to TCIPP is substantial for both adults and children under all exposure scenarios with homes the major contributory microenvironment.

Finally, in contrast to adults, who are in general not substantially exposed to EHDPP, it can represent the PFR providing the second highest exposure for children under the high end exposure scenario.

6.4 Comparison of Exposure Estimates with Health Based Limit Values (HBLVs)

Reassuringly, the exposure estimates reported in 6.2 for both adults and children are several orders of magnitude below the relevant HBLVs. However, the high end exposure scenario estimates obtained for children from dust ingestion alone is only around 100 times lower than the HBLVs calculated by (Ali et al., 2012). For younger children, there will likely be a further erosion of the margin of safety given they will have a lower body weight than 20 kg. Moreover, the HBLV values cited are based on relatively old toxicological studies and may therefore be revised downward in future (Ali et al., 2012).

6.5 Importance of dust ingestion compared to other exposure pathways for PFRs

6.5.1 Inhalation exposure

(Marklund et al., 2005a) estimated that based on a daily air inhalation rate of 19.2 m^3 and an assumption that 87.5% of time is spent indoors, a Swedish adult weighing 70 kg would be exposed to 0.1-180 ng/kg day TCEP via inhalation compared to 0.3-96 ng kg day via ingestion of dust. They also showed that in general, ingestion of dust contributed more substantially to overall exposure than inhalation. In particular, they determined that dust ingestion was more important than inhalation as a pathway of exposure for children in all studied environments. However, they estimated that in three of their tested microenvironments, inhalation made a greater contribution than dust ingestion to overall adult exposure to PFRs.

To our knowledge there are no data available on atmospheric concentrations of PFRs within the UK. Provision of such data would be especially interesting for TCIPP, which we hypothesise will be present at high concentrations in UK air, given the high levels detected in dust samples in this study.

Indoor air samples taken from a sport outfitters and an office in Norway were dominated by TPHP with concentrations up to 47 µg/m^3. This is three orders of magnitude higher than those of TCIPP - the second most abundant PFR detected in the same study – for which the maximum concentration was 49 ng/m^3. Even though those results are from a very limited data set (only 4 samples) it is not known why they showed such a high concentration of TPHP. (Green et al., 2008) This is interesting, especially as a comparison study from Japan showed TDCIPP and TPHP levels to be higher in dust compared to the air samples, with TDCIPP levels in Japanese indoor air were ranged from below detection limit to 61.4 ng/m^3 (Kanazawa et al., 2010) To our knowledge, no data on concentrations of PFRs in Norwegian indoor dust are available, which could corroborate those extraordinarily high TPHP levels.

A German study from 2001 (Ingerowski et al., 2001) estimated human adult exposure to TCEP and TCIPP in Germany via indoor air inhalation to range from 0.2 – 2 ug/ day. Appling a respiratory volume of 10 m^3/day for children yields a TCEP and TCIPP intake via indoor air inhalation of 0.1 – 1 ug/day. Those levels are somewhat higher than it would be expected with the German data generated in this study, especially as the estimated intake via dust ingestion was calculated in the Ingerowski study to be between 0.01-5 ug/day. (Ingerowski et al., 2001) When normalised to body weight this would result in a exposure of up to 71 ng/kg bw, which is over an order of magnitude higher than the high end exposure estimate for dust ingestion for German adults in our study.

A study of human exposure via inhalation of indoor air of the more volatile PFRs (TnBP TCEP and TCIPP) using recently published data on indoor air contamination within Swedish buildings (Bergh et al., 2011a) reported a median air concentration of 29 ng/m^3 for these 3 PFRs combined. Taking a daily respiratory volume of 20 m^3/day for adults and 10 m^3/day for children into account, results in an exposure through inhalation of 580 ng/day and 290 ng/day respectively for TnBP, TCEP and TCIPP combined. Median concentrations of TPHP and EHDPP were below detection limits. Overall, this leads to the conclusion that for the more volatile PFRs (TnBP, TCEP and TCIPP) inhalation is likely of some importance as an exposure pathway, especially for adults for whom dust ingestion is less important than for children.

6.5.2 Dietary exposure

There are currently very few data available on human dietary exposure to PFRs. In North America, TCEP and TCIPP were below the detection limit in the majority of the samples analysed for food basket studies conducted in the US between 1991 and 2003 (U.S. FDA, 2006). In Europe, (Sundkvist et al., 2010) estimated that a Swedish adult consuming 3 portions of 125 g of fish per week would be exposed to 20 ng ΣPFR /kg bw/day. This is equal to the high end exposure scenario estimate calculated for dust ingestion in our study for UK adults. It must be noted though that the Swedish study does not provide dietary exposure data for individual PFRs and includes TBEOP in the assessment, which is excluded from our dust exposure assessment. Additionally, UK consumption of lacustrine fresh water fish is likely far lower than for the Swedish population, meaning that UK exposure to PFRs via this pathway is likely commensurately lower. Furthermore a Swedish study did not find detectable concentrations of PFR in fish samples collected from the supermarket shelf. (Campone and Piccinelli, 2010) This is supported by the observation of (Sundkvist et al., 2010) that fish is seen as a minor source of PFR exposure compared to the intake via dust ingestion and inhalation for the Swedish population. Breast milk samples were also analysed in this Swedish study. Based on the PFR concentrations found, a 5 kg baby consuming 1 L of breast milk a day would be exposed to 64 ng ΣPFR/kg/day, which is less than our estimates of exposure via dust ingestion for a 6 year old UK child. While measurements of PFRs in UK human milk are required to confirm this; it therefore appears human exposure to PFRs via the consumption of human milk is of minor significance compared to that received via inhalation and dust ingestion.

EHDPP was found in 32 out of 40 candy caramel samples in market basket studies from 1991 to 2003 in the US ((U.S. FDA, 2006) with a mean concentration of 2.5 µg/g. It was also detected in half of the analysed margarine samples at a mean concentration of 1.2 µg/g. Such elevated concentrations may be due to the fact that EHDPP is used as a plasticiser in PVC food packaging in the US (SGP, 2012). By comparison, there is no information on the application of EHDPP within food packaging in Europe (Environment Agency, 2009a). Based on a US FDA market basket study from 1986-1991, the mean daily dietary intake of EHDPP was an estimated 1.2 µg/kg body weight for a 2 year old and 0.41 µg/kg body weight for a 14-16 year old (Gunderson, 1995 cited in SGP, 2012). This FDA dietary exposure estimate exceeds our estimates of exposure via dust ingestion for a 6-year old child in Australia and the UK under the average exposure scenario. However, a 1986 UK food study could not detect EHDPP in any of the samples analysed (Gilbert, 1986 cited in Environment Agency, 2009). While analysis of current UK diet samples are required to confirm this; this suggests UK adult exposure to EHDPP via the diet may be lower than for Americans, and that exposure via dust ingestion may exceed that received via the diet for non-US residents.

TPHP was found in 24 out of 40 candy caramel samples in US market basket studies from 1991 to 2003 (U.S. FDA, 2006) at an average concentration of 0.045 µg/g. It was also detected in 15 out of 44 margarine samples at an average concentration of 0.041 µg/g. Since these concentrations are about 2 orders of magnitude lower than the EHDPP concentrations detected in the same food groups, it seems reasonable to hypothesise that the origin of the TPHP is as an impurity of the EHDPP used as a plasticiser in food packaging.

Only one food group (cracked wheat bread) was analysed for TMPP in the 1991 to 2003 US market basket studies (U.S. FDA, 2006). TMPP was detected in only one out of 44 samples at a level of 2 ng/g. To our knowledge, these are the only data available on concentrations of TMPP in foodstuffs, but they suggest strongly that diet is not a significant pathway of exposure to TMPP.

6.5.3 Drinking water

(Stackelberg et al., 2007) reported TCEP to be present at up to 0.05 µg/L in American drinking water, with maximum concentrations of TDCIPP, TnBP being 0.07 µg/L and 0.18 µg/L respectively, while TPHP was below the detection limit. (Kim et al., 2007) detected TCEP in surface water near the intake points for the water supply, which were then reduced below the detection limit in the drinking water. Another American study (Benotti et al., 2009) detected TCEP concentrations of up to 0.02 µg/L in tap water.

(Benotti et al., 2009) detected TCIPP at a median concentration of 240 ng/L in tap water across the US, even though only 6 out of 15 samples were above the detection limit. Additionally, TCIPP was the most abundant PFR in river and groundwater samples from Germany (Stepien et al., 2013), suggesting potential for human exposure if such water was used as a source of drinking water.

TnBP was detected in all 28 tap water samples from Spain with concentrations ranging from 11-148 ng/L (median 32 ng/L), while TCIPP was detected at a median concentration of 40 ng/L. (Rodil et al., 2012)

Furthermore, a very recently published study in China reported mean concentrations of TPHP and TCIPP in tap water to be 40 ng/L and 33 ng/L respectively. (Li et al., 2014) Furthermore, they detected TPHP and TCIPP in bottled water, even though the concentrations found were between 10-25% of those detected in tap water. However, that study also reported that boiling the tap water increased TPHP and TCIPP levels by about 6 ng/L. As this is inconsistent with the high vapour pressure of TPHP and TCIPP, the higher levels might result from contamination via the kettle.

To summarise, overall, the very limited data available to date suggest that while drinking water is a potential source for human exposure to PFRs if not treated correctly; it is unlikely to represent a more significant pathway than dust ingestion.

6.5.4 Dermal exposure

Very few data are available on dermal exposure to PFRs. Total PFR levels in hand wash samples ranged between 3.5 and 34 µg/g individual for workers in a furniture workshop and circuit board factory (Mäkinen et al., 2009). In addition to this, (Cooper and Stapleton, 2011) detected TPHP and TDCIPP levels of up to 0.2 and 2 µg per individual respectively in hand wipes after leisure activities. Overall, the very limited data suggests that dermal exposure is a potential source for human exposure to PFRs especially for occupationally-exposed individuals. However, for a definitive comparison of the contribution of dermal exposure with that from dust ingestion, more data is needed about the former pathway, particularly related to dermal absorption.

6.6 Conclusions

For the target PFRs analysed in this study, there exist substantial international variations in human exposure via dust ingestion. Such exposure occurs primarily in the domestic environment for most PFRs, although exposure to TDCIPP occurs primarily in cars. Furthermore, children are substantially exposed to EHDPP via ingestion of classroom dust. Reassuringly, the exposure levels calculated in this study are at least 2 orders of magnitude below HBLVs reported in the literature. A cautionary note is sounded for TCIPP however, as the margin of safety between exposure and the HBLV was lower than for other PFRs, and this may be further eroded once inhalation and other exposure pathways are taken into account. More generally, one must also bear in mind that existing HBLVs are based on relatively old toxicological data and may be reduced as new data emerges, with likely further erosion of the current margins of safety. Finally, comparison of our estimates of exposure via dust ingestion with the limited data available on exposure via other pathways, suggests that dust ingestion is likely a significant pathway of exposure to many – if not all – PFRs.

CONCLUSIONS

7.1. Conclusions

This study has provided insights into the contamination of indoor dust from living rooms, offices, bedrooms, cars and schools with PFRs and the associated potential for exposure for both adults and children.

Use of PFRs dates back to the 1960s. They are used in different applications, primarily dependent on the side chain. Chlorinated alkyl phosphates such as TCIPP and TDCIPP are used as flame retardants in e.g. foam products like couches and car seats, which can lead to exposure especially when the product gets abraded over time. The second biggest group with respect to production volume are non-halogenated aryl phosphates like TPHP, which are used as both flame retardants and plasticisers. Finally, alkyl phosphates like TnBP are primarily used as plasticisers, but which also offer flame retardant properties.

This versatility of PFRs has resulted in widespread use and it is thus not surprising that concentrations of PFRs have been reported in different matrices like dust, air, water, rain/snow, waste water treatment plants, soil, human milk, and fish. Moreover, reports of PFRs in remote arctic air and ice are concerning, as they imply a capacity for long-range atmospheric transport.

The last two decades have seen progressive introduction of restrictions on the use of PFRs. For example, TCEP production has ceased in Europe and North America, even though there are still some indications that production continues within Asia. Furthermore, the application of TDCIPP in the transport industry is scheduled to end in 2015.

This study indicates that PFRs have a ubiquitous presence within several different categories of indoor microenvironments from several different countries and that this presence makes a substantial contribution to human exposure. Measurable concentrations of PFRs were found in every sample analysed in this study. The aims of this project have been addressed as outlined below.

7.1.1. Hypothesis I: Vapour pressure of PFRs can be determined via the gas chromatography retention time (GC-RT) method

Vapour pressures and enthalpies of vaporisation were determined for selected PFRs via the GC-RT method. The resulting log $p_{298}(\mathrm{Pa})_{\mathrm{RT}}$ values agreed well with values predicted by the EPISUITE software (log $p_{298}(\mathrm{Pa})_{\mathrm{EpiSuite}}$) and with the mean of literature values (log $p_{298}(\mathrm{Pa})_{\mathrm{lit}}$). A bias toward higher values by GC-RT, as might be expected from chromatography of polar compounds on a nonpolar stationary phase, was not seen overall, although this is suggested for the chlorinated compounds TCEP, TCIPP and TDCIPP. It was also shown that the SPARC prediction software seriously underestimated p, especially for the less volatile compounds.

Application of the Junge-Pankow (J-P) adsorption model using p_{288} values indicates that most PFRs - except TCEP and TCIPP - are expected to be predominantly particulate-bound in urban air, but more equally distributed between the particulate and gas phases in background air. Data from field studies in both urban air (Salamova et al., 2014) and marine air over the North Sea (Möller et al., 2012, 2011), indicates even higher proportions to be associated with the particulate phase. This suggests stronger sorption of PFRs to aerosols or to air sampling filters than predicted by the J-P model.

7.1.2. Hypothesis II: Global variation in PFR use leads to a significant variation in the degree of contamination of indoor dust with PFRs as well as a country specific PFR pattern

PFRs were analysed in indoor dust samples from various microenvironments from Australia, Germany, Kazakhstan, Canada and the UK. PFRs were present in all samples analysed, which underlines the importance of this study.

PFRs were determined in living room dust samples from Australia, Canada, Germany, Kazakhstan, and the UK. Concentrations of TCIPP were significantly ($p<0.05$) higher in dust from UK living rooms compared to those from other countries. Furthermore, samples from Germany contained concentrations of PFRs that were lower than those from other countries. In particular, concentrations of TCEP and TPHP were significantly lower ($p<0.05$) in German dust compared to that from other countries; while concentrations of TDCIPP in German dust were significantly lower than in dust from the UK, Australia, and Canada.

Principal component analysis showed differences in PFR pattern between living room dust samples from different countries. Three different clusters were determined. The UK samples showed predominantly negative PC1 scores, due to a high relative abundance of TCIPP. Dust samples from Kazakhstan displayed positive PC1 scores, as a result of the high relative abundance of TPHP in such samples. The third cluster – which exhibited some overlap with clusters 1 and 2 - encompassed samples from Australia, which showed primarily negative PC2 scores, driven by a high relative abundance of TDCIPP, TCEP, and TCIPP. German and Canadian samples did not fall into a single cluster, likely due to the comparatively small number of samples analysed from those countries.

PFRs were analysed in office dust samples from Kazakhstan, Germany, and the UK. Concentrations of TCIPP, EHDPP, and TDCIPP were significantly higher ($p<0.05$) in UK office dust samples compared to those from Germany, with UK offices also displaying significantly higher concentrations of TCIPP and EHDPP compared to those from Kazakhstan. The high relative abundance of TCIPP in UK dust was reflected in PCA where UK samples fell into a distinct cluster.

Several key observations arise from comparison of PFR concentrations in car dust samples from Australia, Germany and the UK. Firstly, concentrations of TCIPP were significantly higher in UK and Australian samples compared to Germany. Secondly, EHDPP was more abundant in samples from the UK compared to Australia. Thirdly, TDCIPP concentrations were significantly higher in UK samples compared to those in samples from Australia and Germany.

Such international differences in absolute concentrations and relative abundance of different PFRs, illustrates the necessity of country specific exposure assessment, as an extrapolation from one country to another may result in inaccurate exposure assessment.

7.1.3. Hypothesis III: Indoor dust contamination varies between different microenvironments within the same country

PFR concentrations were determined in different microenvironments in samples from Australia, Germany, and the UK.

TDCIPP concentrations in car dust samples were significantly ($p<0.05$) higher in all three countries studied (Australia, Germany, and the UK) compared to other microenvironments in these countries. This leads to the conclusion that the principal use of TDCIPP is in the car industry. Even though TCIPP and TDCIPP have similar applications, use of TDCIPP is preferred only when a higher efficiency is needed to reach a specific flame retardancy standard, due to its much higher price (around twice that of TCIPP) (European Union, 2008b). However, no correlation was seen between the extent of car use or age and TDCIPP concentration.

In German samples, significantly higher TnBP concentrations were found in office dust compared to the car and living room dust; while concentrations of both EHDPP and TPHP were significantly lower in living room samples compared to the other two microenvironments studied.

The differences in PFR concentrations between different microenvironment categories underlines the fact that analysis of various microenvironments is needed to perform a better assessment of human exposure.

7.1.4. Hypothesis IV: Couches represent a source of PFRs within living rooms

Couch dust samples from Australia and the UK were collected to provide an insight into the role of couches as PFR sources in living rooms. To our knowledge, this is the first report of PFRs in couch dust. Since only 10 UK couch dust samples were collected, findings for the UK are viewed as indicative only. Except for TCEP, concentrations of all other PFRs were significantly higher in UK than Australian couch dust samples. A paired t-test comparing concentrations of PFRs in matched Australian couch and living room floor dust revealed concentrations in couch dust to be significantly higher ($p<0.05$). This suggests that couches are a source of PFRs within the living rooms, consistent with the reported use of TCIPP in foam used in furniture upholstery. The elevated concentrations in couch dust also have potential implications for human exposure assessment, as such assessments have hitherto usually been founded on concentrations in floor dust.

7.1.5. Hypothesis V: Classroom dust has a distinctive PFR signature, which varies from that found in other microenvironments, is distinctive to a given country, and that PFR concentrations in classroom dust exceed significantly those of PBDEs

PFR concentrations in school dust samples were analysed to verify whether EHDPP concentrations were significantly greater in both Australian ($p<0.05$) and UK ($p<0.001$) school dust samples compared to those from other microenvironments in the same countries. Such significant elevation of EHDPP contamination suggests strongly the existence of a specific EHDPP source within the school environment. Analysis of information on EHDPP applications suggests the likely source is its use in paint.

Significant differences in both absolute concentrations and relative abundance of individual PFRs in floor dust from Australian and UK classrooms were detected. Further differences were revealed when the data acquired in this study was compared with that from an earlier study of dust from elevated surfaces in Swedish child day-care centres. With the exception of TPhP, dust from UK classrooms showed significantly higher concentrations of PFRs compared to dust from Australian classrooms. Concentrations of SPFRs in Australian and UK school dust samples exceeded significantly those of SPBDEs in the same samples. One UK school showed the highest EHDPP concentration detected in all dust samples analysed in this thesis. For both Australian and UK schools, concentrations of TPhP and EHDPP correlated significantly, indicating a common source of these PFRs.

In line with a study from Swedish apartments (Bergh et al., 2011a), concentrations of TnBP in UK school dust were significantly higher in older than newer buildings. Building age exerted no significant influence on concentrations of any of the other PFRs targeted, which is also in line with the study in Sweden (Bergh et al., 2011a). As the building age of Australian schools was not known, the existence of a similar relationship with PFR contamination could not be studied.

With respect to the influence of putative sources in UK classrooms; concentrations of TCIPP were significantly positively correlated with the number of PCs in the room, while a similar – albeit less significant – correlation was observed between the number of foam chairs in the room and concentrations of TDCIPP. To our knowledge, these are the first reports of correlations between putative sources of PFRs and their concentrations in indoor dust.

7.1.6. Hypothesis VI: The presence of PFRs in the indoor environment results in significant human exposure

Estimates of exposure via dust ingestion were generated for the populations of Australia, Germany, and the UK. Three different exposure scenarios (low, average, and high) were examined for both adults and children. These estimates suggest dust ingestion contributes significantly to human exposure of PFRs. Reassuringly however, our exposure estimates were for all PFRs substantially below currently available HBLVs. For example, our high end exposure estimate for UK children via dust ingestion was just under 1 % of the

HLBV for TCIPP, thereby suggesting that such exposure is unlikely to exert adverse effects. However, caution is advised, given the additional contribution from other exposure pathways such as inhalation and diet, and the fact that our exposure estimate was normalised to the 20 kg body weight of a 6 year old child, rather than lighter toddlers who may also ingest dust at a higher rate. Furthermore, current HLBV values for TCIPP and other PFRs are based on comparatively old toxicological data, and future studies may result in reductions of HBLVs.

Likely due to the high proportion of time spent at home, the majority of human exposure to PFRs via dust ingestion occurs in the domestic environment. A notable exception is for TDCIPP, where the highly elevated concentrations in cars, means that vehicle dust provides the majority of exposure to this PFR. Additionally, a significant proportion of the exposure of children to EHDPP occurs via ingestion of classroom dust.

7.2. Recommendations for future work

Since PFRs are still being manufactured and used they will continue to be present in the environment for the foreseeable future. Despite this, and the recent shift in scientific focus from PBDE towards PFRs, substantial research gaps in our knowledge of PFRs remain, especially related to their environmental behaviour, toxicity and human exposure. Suggested research to fill some of the most important such gaps includes:

- Further experimental measurements of PFR vapour pressures, especially as the values obtained in this study are based on the assumption that non-polar compounds display similar behaviour to polar PFRs, which might not be the case.
- Determination of concentrations of PFRs in indoor air. This is important for TCEP and TCIPP in particular, given their comparatively vapour pressures.
- Measurements of human dietary exposure to PFRs.
- Research into the human toxicology, uptake, and metabolism of PFRs.

- Determination of dermal exposure, as this has been shown to occur for some PFRs for workers in “high-risk” occupations e.g. waste electronics dismantling facilities.
- Studies of emissions of PFRs from waste furniture/electronic waste into the environment during disposal.
- Evaluation of the impact of different dust sampling strategies (e.g. floor dust vs. elevated surface dust) on PFR concentrations in indoor dust.
- Studies of the pathways via which PFRs transfer from their sources to indoor dust, and
- Evaluation of sources of PFRs within schools, with a particular focus on elucidating the cause of the elevated concentrations of EHDPP in classroom dust.

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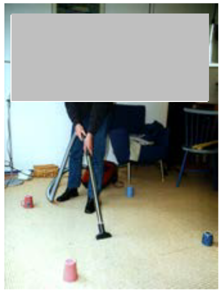
Appendix 1 *Dust sampling protocol*

1. In the plastic bag you will find: A twist tie and a sample 'sock' for dust collection. <u>Please keep the bag closed until sampling and minimise touching the socks.</u>

4. Measure out a square of <u>**1 m^2**</u> in (or close to) the **sitting area** on *carpeted floor*. In case of *bare smooth floor* sample<u> **4 m^2**</u>. Mark the corners of the measured square meter(s). Small pieces of furniture may be moved, but do not move large objects such as sofas, book cases etc.

2. Use the 'sock' marked 'living room floor' (or ‘rug’; see below). Slide the opening of the 'sock' over the furniture attachment (small vacuum foot) of the vacuum cleaner.

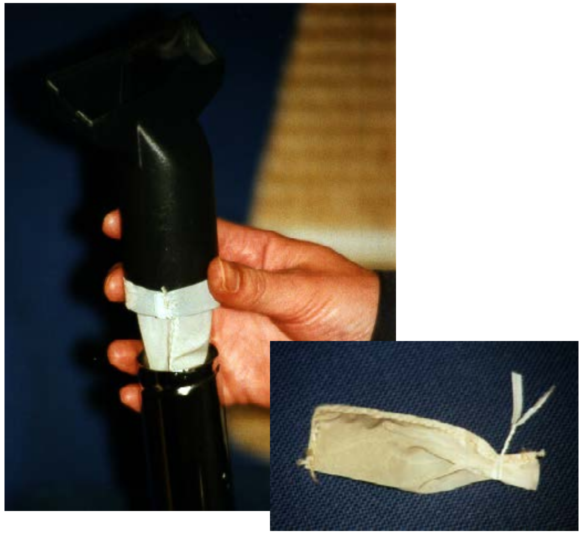


[redacted]

5 wall-to-wall carpet

5. Vacuum the square (**1 m^2** in case of **wall to wall carpet** and <u>**4 m^2** </u>in case of **bare smooth floors**<u>) </u>evenly and thoroughly for exactly **2 minutes (**or **4 minutes** in case of **smooth floor)**. The dust will collect inside the 'sock'. TURN THE FOOT UP AND THEN SWITCH OFF THE VACUUM CLEANER (to avoid dust falling out).

3. Trap the 'sock' <u>firmly</u> into place. The 'sock' should always overlap onto the attachment.

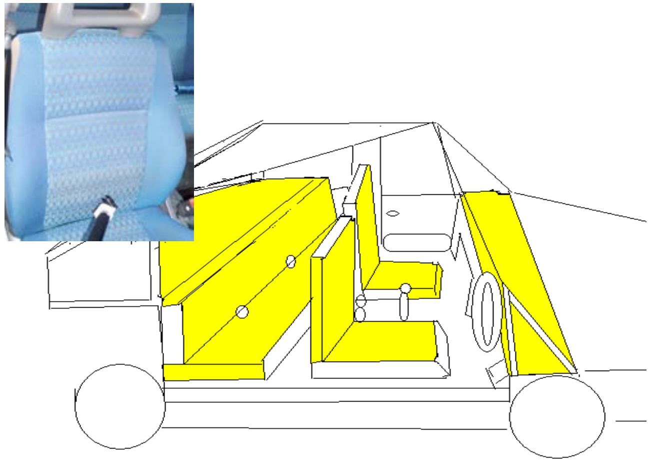


6. Carefully remove the 'sock'. Tie the top with the twist tie. Place the 'sock' into the plastic bag and close it tightly. Complete the information questionnaire, and return as advised.

1. The package includes one nylon sock, 1 tie and 1 plastic sealable bag.

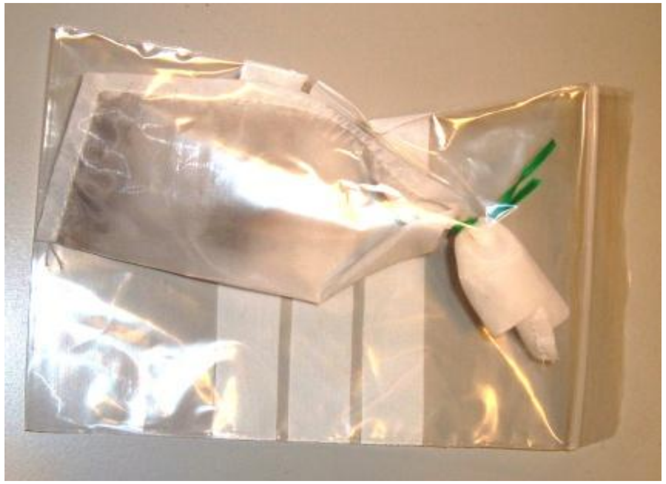
2. Place the nylon sock, over the tubing on the head of the vacuum cleaner.

3. Insert sock into tubing, making sure there is about 1cm of sock around the outside of the nozzle.



4. Vacuum for two minutes the seats (front and rear), parcel shelf and dashboard (the areas highlighted on the diagram).

5. Turn vacuum head up and switch off vacuum cleaner. Remove bag and seal with tie.



6. Place sock and questionnaire in plastic bag and seal.

Appendix 2

COUCH QUESTIONNAIRE

Sample ID (for researcher use only)

Date

Please indicate if you would like to be informed about the sample results. If yes please include an email address:

○ yes, email address:____ ○ no

Type of cover material:

○ fabric ○ synthetic leather ○ leather

How old is the couch:

if less than 1 year: _______ months

if more than 1 year: _______ years

Approximate time since last vacuumed/ wet washed:

____

____

Usual couch cleaning interval:

every ____ months /____year(s)/ never

Approximate time (hours per week) spent on the couch by

family adults:___________________ children: ___________________

Please add any further information you feel may be relevant

Appendix 3

MATTRESS QUESTIONNAIRE

Sample ID (for researcher use only)

Date

Please indicate if you would like to be informed about the sample results. If yes please include an email address:

O yes, email address:____ O no

Type of mattress:

O foam rubber O latex O inner spring O other

How old is the mattress:

if less than 1 year: _______ months

if more than 1 year: _______ years

Is this mattress in an adult’s or a child’s bedroom:

O adult O child

Do you use a mattress protector:

O yes O no

if yes, how old is your mattress protector:

Approximate time since last vacuumed/ wet washed mattress:

____

Usual mattress cleaning interval:

every ____ months /____year(s)/ never

Appendix 4

CHILDRENS' BEDROOM QUESTIONNAIRE

Sample ID (for researcher use only)

Date

Please indicate if you would like to be informed about the sample results. If yes please include an email address:

O yes, email address:____ O no

Construction year of the building (if known):

Approximate time since last vacuumed:

(please leave at least 2 days between date of last vacuum and taking sample collection)

Room specifications:

Room ventilation: O natural O air conditioned

Numbers of beds (plus year of manufacture/purchase if known):

Number of mattresses (plus year of manufacture/purchase if known):

Number of foam containing chairs/sofas (plus year of manufacture/purchase if known):

Number of TVs (plus year of manufacture/purchase if known):

Number of other items of electrical equipment (DVD player, computer, playstation etc.) (plus year of manufacture/purchase if known):

Is the room carpeted? (If so, what is the year of manufacture/purchase if known):

Do the windows have curtains or fabric blinds (as opposed to venetian blinds)? (If so, what is the year of manufacture/purchase if known):

Approximately how frequently do you vacuum this room?

Please add any further information you feel may be relevant (continue overleaf)

Appendix 5

CAR SAMPLE QUESTIONNAIRE

Sample ID (for researcher use only)
Date
Please indicate if you would like to be informed about the sample results. If yes please include an email address:
○ yes, email address:____ ○ no
Car manufacturer and model:____
Year of manufacture:
No. of seats:
Car ventilation: ○ natural ○ air conditioned
Type of seat cover: ○ fabric ○ leather
Electronics inside the car (please tick box if appropriate)
Stereo: ○
Speakers: ○
DVD player: ○
Navigation device: ○
other electronic equipment which is usually in the car during usage (e.g. smartphone, Ipod):
____
Approximate time since last vacuumed:
____
Usual car cleaning interval:
every ____ months /____year(s)
yearly driven mileage:
____
total mileage:
____
Manufacturer, model number and date of manufacturing (if known) of child seat(s) (If more than one please give details of each)

Approximate time (hours per week) spent in the car by
family adults: ____________________
children:_________________________________

Appendix 6

LIVINGROOM QUESTIONNAIRE

Sample ID (for researcher use only)
Date
Please indicate if you would like to be informed about the sample results. If yes please include an email address:
○ yes, email address:____ ○ no
Construction year of the building (if known):
Approximate time since last vacuumed:
(please leave at least 2 days between date of last vacuum and taking sample collection)
Room specifications:
Room ventilation: ○ natural ○ air condition

Number of foam containing chairs (plus year of manufacture/purchase if known):

Number of foam containing sofas (plus year of manufacture/purchase if known):

Number of TVs (plus year of manufacture/purchase if known):

Number of other items of electrical equipment (printer, home cinema, video, DVD player, microwaves etc.) (plus year of manufacture/purchase if known):

Is the room carpeted? (If so, what is the year of manufacture/purchase if known):

Do the windows have curtains (as opposed to blinds)? (If so, what is the year of manufacture/purchase if known):

Approximately how frequently do you vacuum this room

Appendix 7 *Individual concentrations of Living room samples analysed in this study*

Canada

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Liv 01	<0.03	1.2	1.7	37	0.67	1.9	0.07	42
Liv 02	0.13	0.65	0.85	18	0.17	0.19	<0.01	20
Liv 03	<0.03	0.96	3.1	32	0.20	3.2	<0.01	40
Liv 04	0.13	2.7	24	14	0.73	3.0	<0.01	44
Liv 05	<0.03	0.56	1.8	12	0.54	0.91	0.67	17
Liv 06	0.28	1.3	1.0	1.7	0.32	0.32	0.07	5.0
Liv 07	0.39	0.28	0.44	0.81	0.14	1.5	0.07	3.6
Liv 08	0.14	0.25	1.1	0.69	0.40	0.46	<0.01	3.0
Liv 09	1.16	0.74	0.70	1.0	0.45	1.7	<0.01	5.8
Liv 10	<0.03	1.8	2.1	0.35	0.50	0.42	<0.01	5.2
Liv 11	<0.03	0.19	0.12	0.02	0.01	0.03	<0.01	0.4
Liv 12	<0.03	37	54	1.5	0.39	1.2	<0.01	94
Liv 13	0.13	0.53	0.65	0.69	0.61	0.38	<0.01	3.0
Liv 14	0.13	0.46	1.3	2.1	0.16	1.6	0.04	5.8

Kazakhstan

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Liv 01	0.22	1.3	1.8	8.5	0.27	0.11	<0.01	12
Liv 02	<0.03	1.0	1.1	2.1	0.22	2.0	<0.01	6.4
Liv 03	0.11	2.2	1.0	3.8	0.19	0.06	<0.01	7.3
Liv 04	0.11	0.95	0.88	3.5	0.63	<0.03	<0.01	6.1
Liv 05	0.11	1.4	2.9	9.2	0.32	0.07	1.00	15
Liv 06	0.23	2.8	1.5	5.8	1.2	0.19	1.13	13
Liv 07	0.11	1.9	0.42	2.7	0.16	0.51	<0.01	5.8
Liv 08	0.21	6.8	0.52	1.2	0.06	0.50	<0.01	9.2
Liv 09	0.10	0.62	0.57	3.8	0.30	0.10	<0.01	5.5

Australia

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Liv 01	<0.03	1.1	23	1.3	0.33	0.11	0.06	26
Liv 02	0.08	0.31	1.1	3.8	0.18	0.19	0.08	5.8
Liv 03	0.05	<0.06	1.7	0.88	0.12	1.3	<0.01	4.0
Liv 04	<0.03	<0.06	0.32	0.31	0.40	<0.03	<0.01	1.0
Liv 05	0.08	<0.06	0.36	2.7	0.96	6.83	<0.01	11
Liv 06	<0.03	0.47	2.0	3.1	0.26	0.96	<0.01	6.7
Liv 07	0.20	0.30	1.3	0.34	0.10	1.2	<0.01	3.4
Liv 08	0.52	2.1	4.1	1.9	0.51	0.29	0.52	9.9
Liv 09	<0.03	16	5.6	0.38	0.33	0.83	<0.01	23
Liv 10	0.11	8.0	5.8	4.9	0.77	0.25	0.11	20
Liv 11	<0.03	19	16	31	0.60	0.12	0.23	67
Liv 12	0.07	<0.06	1.6	0.36	<0.01	0.15	<0.01	2.2
Liv 13	<0.03	1.7	1.8	1.7	0.25	0.64	0.02	6.1
Liv 14	0.06	0.36	2.4	2.0	0.57	0.13	0.22	5.7
Liv 15	0.23	0.59	1.2	4.8	0.64	0.26	0.23	8.0
Liv 16	0.30	0.36	0.90	4.7	0.41	0.80	<0.01	7.5
Liv 17	0.12	1.3	2.1	0.76	1.83	0.13	0.01	6.2
Liv 18	0.06	0.30	4.7	0.75	0.75	2.1	0.52	9.1
Liv 19	<0.03	0.60	1.3	6.5	0.40	0.49	0.03	9.3
Liv 20	<0.03	<0.06	0.33	0.46	0.19	0.28	<0.01	1.3
Liv 21	<0.03	<0.06	0.51	2.0	0.27	0.15	<0.01	2.9
Liv 22	0.51	1.0	5.1	3.2	1.79	0.24	<0.01	12
Liv 23	8.43	1.5	12	1.1	0.57	0.11	<0.01	23
Liv 24	0.06	0.34	0.46	1.4	<0.01	0.62	0.06	3.0
Liv 25	0.15	6.3	1.2	0.54	0.28	1.3	0.01	9.7
Liv 26	0.82	0.38	1.0	0.42	0.40	0.73	0.82	4.6
Liv 27	<0.03	0.39	1.9	16	0.69	7.1	0.77	27
Liv 28	0.11	<0.06	0.24	0.24	0.19	0.60	0.11	1.5
Liv 29	<0.03	0.29	4.7	4.4	0.02	0.10	<0.01	9.5
Liv 30	0.09	<0.06	3.5	0.72	1.35	0.29	<0.01	6.0
Liv 31	2.98	1.0	1.7	0.99	5.12	0.10	2.98	15
Liv 32	0.06	0.89	1.1	2.15	1.76	0.09	0.06	6.1
Liv 33	0.06	0.41	0.53	6.9	<0.01	1.4	0.06	9.4
Liv 34	<0.03	2.6	2.3	0.81	0.24	1.0	0.03	7.1
Liv 35	0.14	1.3	3.0	0.76	0.42	2.0	0.14	7.8
Liv 36	0.04	1.8	3.3	0.27	0.11	0.35	0.04	5.9
Liv 37	0.51	1.2	0.98	0.31	0.12	10	0.51	14
Liv 38	0.04	0.69	9.0	3.2	0.82	0.84	0.04	15
Liv 39	0.06	24	11	6.0	0.29	0.06	<0.01	41
Liv 40	0.08	0.29	1.7	0.93	0.19	0.25	0.08	3.5
Liv 41	<0.03	0.69	11	0.78	0.36	0.05	0.02	13
Liv 42	0.05	2.7	20	1.1	1.1	0.50	0.05	26

Germany

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Liv 01	<0.03	0.68	340	0.16	0.09	0.11	<0.01	340
Liv 02	<0.03	<0.06	4.1	0.21	0.13	0.09	0.97	5.5
Liv 03	0.09	5.7	1.7	0.21	0.08	0.01	0.18	7.9
Liv 04	<0.03	<0.06	1.0	0.07	0.13	0.74	1.3	3.2
Liv 05	<0.03	0.27	16	0.26	0.26	0.72	<0.01	17
Liv 06	<0.03	<0.06	2.3	0.70	0.11	0.05	0.15	3.3
Liv 07	<0.03	<0.06	0.92	0.22	0.15	0.07	0.96	2.3
Liv 08	<0.03	0.36	0.81	0.38	0.16	0.07	<0.01	1.8
Liv 09	<0.03	0.35	1.6	0.12	0.04	2.66	<0.01	4.8
Liv 10	0.04	<0.06	0.33	0.38	0.32	0.05	0.20	1.3
Liv 11	<0.03	0.55	0.53	0.44	0.21	0.01	0.81	2.6
Liv 12	<0.03	<0.06	4.3	0.92	<0.01	0.21	1.2	6.6
Liv 13	0.06	0.33	1.8	0.25	0.12	0.28	<0.01	2.9
Liv 14	0.11	0.57	17	0.63	0.26	14	1.3	34
Liv 15	<0.03	0.37	1.6	18	0.56	0.08	0.48	21
Liv 16	0.05	<0.06	0.50	0.54	0.25	0.24	<0.01	1.6
Liv 17	<0.03	0.14	0.37	1.33	a)	0.07	<0.01	1.9
Liv 18	0.25	0.19	0.70	0.19	a)	0.05	0.07	1.4
Liv 19	<0.03	0.28	0.96	0.18	a)	0.05	0.09	1.6
Liv 20	0.25	0.20	0.94	0.22	a)	0.05	0.13	1.8
Liv 21	0.11	0.20	0.83	0.18	a)	0.09	0.24	1.6
Liv 22	0.15	0.21	0.64	0.18	a)	0.11	0.03	1.3

a) sample analysed in Belgium, EHDPP was not targeted in Belgium therefor no concentration available

UK

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Liv 01	<0.03	0.44	100	1.1	0.39	7.0	<0.01	110
Liv 02	<0.03	5.4	38	0.75	1.1	0.67	<0.01	46
Liv 03	0.09	0.03	24	3.7	29	1.2	0.14	58
Liv 04	0.07	28	18	0.72	1.4	1.6	0.27	50
Liv 05	<0.03	0.60	32	12	6.0	0.85	0.91	53
Liv 06	0.07	1.5	18	0.68	1.2	0.62	0.36	23
Liv 07	0.07	<0.06	6.6	0.49	0.31	0.15	0.26	7.9
Liv 08	0.06	0.59	24	1.1	3.2	0.11	0.46	30
Liv 09	<0.03	8.3	21	1.5	1.5	2.0	0.37	35
Liv 10	0.09	0.61	20	0.84	0.87	0.16	0.35	23
Liv 11	0.07	3.9	27	5.4	16	2.3	<0.01	54
Liv 12	<0.03	0.40	29	0.77	0.45	14	<0.01	45
Liv 13	<0.03	0.18	9.8	0.77	0.34	0.66	<0.01	12
Liv 14	<0.03	0.58	19	2.8	1.3	1.3	0.77	26
Liv 15	0.05	0.51	24	2.0	0.65	11	0.13	38
Liv 16	<0.03	2.5	4.2	2.2	0.18	0.20	<0.01	9.3
Liv 17	<0.03	0.34	3.7	8.50	15	0.16	<0.01	28
Liv 18	<0.03	0.24	16	2.9	2.1	0.09	<0.01	22
Liv 19	<0.03	0.92	9.1	11	15	0.06	<0.01	36
Liv 20	<0.03	1.8	7.0	71	131	0.13	44	260
Liv 21	<0.03	2.0	7.7	3.7	3.0	2.4	<0.01	19
Liv 22	<0.03	0.55	11	110	0.82	0.75	0.30	120
Liv 23	<0.03	1.8	79	8.6	11	0.27	<0.01	100
Liv 24	0.09	0.97	5.7	11	6.7	3.3	1.6	29
Liv 25	<0.03	0.92	12	4.7	7.9	0.15	<0.01	26
Liv 26	<0.03	0.26	14	11	16	2.3	<0.01	43
Liv 27	<0.03	0.45	43	4.0	0.47	2.1	<0.01	50
Liv 28	0.05	1.9	47	0.74	0.84	0.85	1.28	53
Liv 29	<0.03	1.5	43	6.1	12	0.62	0.25	64
Liv 30	0.09	1.1	41	0.57	1.6	0.16	0.03	44
Liv 31	<0.03	0.71	65	29	67	0.12	<0.01	160
Liv 32	<0.03	1.1	100	5.0	0.43	7.9	<0.01	110

Appendix 8 *Descriptive Statistical Summary of Concentrations (µg/g) of PFRs in Living Room Dust Samples from Australia, Canada, Germany, Kazakhstan, and the UK (µg/g)*

TnBP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.03	<0.03	<0.03	<0.03	<0.03
5th percentile	<0.03	<0.03	<0.03	<0.03	<0.03
Median	0.06	0.13	<0.03	0.11	<0.03
Geometric mean	0.08	0.07	0.04	0.11	0.03
Average	0.39	0.19	0.06	0.14	0.04
95th percentile	0.81	0.66	0.24	0.22	0.09
Maximum	8.4	1.2	0.25	0.23	0.09
Standard Deviation	1.36	0.30	0.07	0.07	0.03
Relative Standard Deviation	350	160	120	51	77
TCEP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.06	0.19	<0.06	0.62	<0.06
5th percentile	<0.06	0.23	<0.06	0.75	<0.06
Median	0.60	0.69	0.21	1.4	0.81
Geometric mean	0.54	0.90	0.16	1.6	0.82
Average	2.4	3.5	0.48	2.1	2.2
95th percentile	16	15	0.68	5.2	6.7
Maximum	24	37	5.7	6.8	28
Standard Deviation	5.2	9.6	1.2	1.9	5.0
Relative Standard Deviation	220	280	250	90	230
TCIPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	0.24	0.12	0.33	0.42	3.7
5th percentile	0.34	0.33	0.37	0.46	5.0
Median	1.8	1.2	1.0	1.0	21
Geometric mean	2.1	1.6	1.75	1.0	20
Average	4.1	6.6	18	1.2	29
95th percentile	15	34	17	2.5	88
Maximum	23	54	340	2.9	100
Standard Deviation	5.3	15	71.1	0.80	26
Relative Standard Deviation	130	230	400	67	89

TPHP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	0.24	0.02	0.07	1.2	0.49
5th percentile	0.31	0.24	0.12	1.5	0.63
Median	1.2	1.6	0.23	3.8	3.3
Geometric mean	1.5	2.2	0.34	3.8	3.3
Average	3.0	8.7	1.2	4.5	10
95th percentile	6.9	34	1.3	8.9	48
Maximum	31	37	18	9.2	110
Standard Deviation	5.3	12	3.8	2.8	22
Relative Standard Deviation	180	140	320	62	220

EHDPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.01	0.01	<0.01	0.06	0.18
5th percentile	<0.01	0.09	0.03	0.10	0.33
Median	0.38	0.39	0.14	0.27	1.6
Geometric mean	0.27	0.26	0.12	0.27	2.6
Average	0.61	0.38	0.18	0.38	11
95th percentile	1.8	0.69	0.38	1.0	46
Maximum	5.1	0.73	0.56	1.2	130
Standard Deviation	0.85	0.22	0.13	0.36	25
Relative Standard Deviation	140	58	75	96	230

TDCIPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.03	0.03	<0.03	<0.03	0.06
5th percentile	0.06	0.13	0.02	0.03	0.10
Median	0.32	1.1	0.08	0.11	0.71
Geometric mean	0.40	0.72	0.13	0.16	0.71
Average	1.1	1.2	0.90	0.39	2.0
95th percentile	6.6	3.0	2.6	1.4	9.1
Maximum	11	3.2	14	2.0	14
Standard Deviation	2.1	1.0	3.0	0.62	3.2
Relative Standard Deviation	190	84	330	160	160

TMPP	Australia	Canada	Germany	Kazakhstan	UK
Minimum	<0.01	<0.01	<0.01	<0.01	<0.01
5th percentile	<0.01	<0.01	<0.01	<0.01	<0.01
Median	0.04	<0.01	0.14	<0.01	0.02
Geometric mean	0.03	0.02	0.09	0.02	0.05
Average	0.19	0.07	0.37	0.24	1.6
95th percentile	0.76	0.28	1.3	1.1	1.4
Maximum	3.0	0.67	1.3	1.1	44
Standard Deviation	0.49	0.18	0.47	0.47	7.8
Relative Standard Deviation	260	250	130	190	480

ΣPFR	Australia	Canada	Germany	Kazakhstan	UK
Minimum	1.1	0.38	1.3	5.5	7.9
5th percentile	1.6	2.1	1.3	5.6	11
Median	7.9	5.8	2.7	7.3	44
Geometric mean	8.1	9.1	4.3	8.4	41
Average	12	21	21	8.9	56
95th percentile	27	62	33	14	140
Maximum	67	94	340	15	260
Standard Deviation	12	26	71	3.6	51
Relative Standard Deviation	100	130	340	40	91

Appendix 9 *Individual concentrations of Car dust samples analysed in this study*

Australia

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Car 01	0.32	30	13	1.8	0.28	44	34	120
Car 02	0.15	0.92	240	7.8	1.8	3.6	<0.01	250
Car 03	4.05	32	3.5	1.9	0.34	2.5	0.49	45
Car 04	<0.03	1.6	170	7.9	1.6	0.94	<0.01	180
Car 05	1.59	0.16	120	0.33	0.33	0.12	<0.01	120
Car 06	0.36	2.2	98	5.8	0.21	16	0.31	120
Car 07	<0.03	<0.06	11	7.9	0.63	1.0	1.40	22
Car 08	0.24	0.44	1.4	1.5	1.4	1.7	<0.01	6.7
Car 09	0.23	0.66	4.6	1.8	0.25	1.7	0.48	9.8
Car 10	<0.03	1.2	87	16	0.21	0.06	240	350
Car 11	0.19	0.7	15	24	0.37	426	<0.01	470
Car 12	5.38	0.46	20	12	1.00	1.1	2.3	42
Car 13	0.35	24	72	2.5	0.77	46	<0.01	150
Car 14	4.64	38	29	3.5	1.1	100	0.68	180
Car 15	<0.03	4.3	79	5.0	0.76	0.43	0.34	90
Car 16	<0.03	2.9	8.0	6.2	0.54	3.1	0.54	21
Car 17	0.14	1.1	24	2.2	1.9	0.13	10	39
Car 18	8.44	62	48	3.6	2.3	1.12	0.43	130
Car 19	<0.03	0.03	14	1.5	0.41	0.10	0.06	16
Car 20	<0.03	0.61	89	14	2.6	40	<0.01	150
Car 21	0.08	29	140	6.3	0.64	140	<0.01	320
Car 22	<0.03	7.0	84	28	0.31	740	<0.01	850
Car 23	0.41	1.2	2.4	4.6	0.71	0.12	0.59	10
Car 24	0.04	0.67	13	3.9	0.26	3.0	0.34	21
Car 25	0.48	1.1	4.3	1.4	4.8	2.3	1.2	16
Car 26	0.11	<0.06	0.31	1.2	0.37	0.36	0.18	2.6
Car 27	<0.03	0.31	6.4	2.8	0.85	8.5	0.13	19
Car 28	0.09	3.3	32	2.4	0.36	0.67	<0.01	39
Car 29	0.35	60	6.7	2.7	0.51	10	57	140
Car 30	0.34	24	13	21	0.86	340	0.52	400
Car 31	1.58	4.5	31	48	0.45	110	<0.01	200
Car 32	0.04	2.4	33	2.0	0.24	1.7	<0.01	39
Car 33	<0.03	4.3	62	1.6	0.18	0.92	<0.01	69
Car 34	0.06	2.4	75	2.1	0.41	5.3	0.22	86
Car 35	<0.03	1.2	3.6	3.8	0.36	0.24	<0.01	9.1
Car 36	0.26	2.0	2.7	1.0	2.8	81	0.47	90
Car 37	0.04	0.64	31	3.7	1.1	0.99	0.94	39
Car 38	0.07	4.9	17	85	2.5	350	0.97	460
Car 39	<0.03	2.3	310	7.6	1.5	1.5	<0.01	320

Germany

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Car 01	0.06	0.32	2.6	2.0	0.94	12	0.35	18
Car 02	0.07	0.26	3.9	1.4	1.9	2.1	0.33	10
Car 03	<0.03	0.62	0.29	0.33	0.01	<0.03	<0.01	1.3
Car 04	<0.03	0.40	1.8	1.7	1.2	1.2	3.9	10
Car 05	0.05	<0.06	0.82	0.89	0.55	1.1	0.71	4.1
Car 06	0.06	0.45	15	2.5	1.2	1.2	9.0	29
Car 07	<0.03	5.2	101	2.1	1.9	4.1	0.66	110
Car 08	<0.03	0.13	3.4	11	a)	620	<0.01	640
Car 09	<0.03	0.58	2.7	6.6	a)	10	<0.01	20
Car 10	<0.03	<0.06	1.4	2.8	a)	0.67	2.0	6.8
Car 11	<0.03	0.41	3.9	0.86	a)	150	130	290
Car 12	0.16	<0.06	3.7	1.8	a)	13	3.0	22
Car 13	0.63	5.8	4.0	0.93	a)	<0.03	<0.01	11
Car 14	<0.03	0.15	2.1	0.50	a)	29	1.5	33
Car 15	<0.03	2.32	2.9	0.9	a)	0.78	0.61	7.4
Car 16	<0.03	0.14	2.9	3.2	a)	1.5	1.3	9.0
Car 17	0.41	0.10	3.7	1.1	a)	190	1.1	200
Car 18	<0.03	0.92	4.3	3.1	a)	45	150	200
Car 19	<0.03	0.71	2.0	3.6	a)	520	0.86	520

a) sample analysed in Belgium, EHDPP was not targeted in Belgium therefor no concentration available

UK

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Car 01	<0.03	<0.06	10	1.2	0.98	16	0.78	30
Car 02	<0.03	0.62	72	6.4	3.3	24	0.42	110
Car 03	0.25	1.5	48	5.3	1.5	31	0.95	89
Car 04	<0.03	0.72	170	8.2	1.1	200	1.8	390
Car 05	<0.03	0.97	91	4.8	2.2	350	<0.01	460
Car 06	0.08	1.8	50	1.8	3.7	7.3	0.59	65
Car 07	<0.03	8.7	73	7.0	2.0	3.2	5.6	100
Car 08	0.07	0.83	18	2.6	2.3	1.5	1.2	26
Car 09	1.2	0.40	2.4	0.77	0.29	1.0	<0.01	6
Car 10	0.96	0.61	20	172	1.1	741	<0.01	930
Car 11	<0.03	7.7	31	3.3	11	8.4	1.6	63
Car 12	0.09	0.23	8.0	1.7	5.7	0.11	0.05	16
Car 13	<0.03	2.4	370	1.3	2.1	31	0.07	400
Car 14	<0.03	1.5	69	76	1.1	3.8	<0.01	150
Car 15	<0.03	0.30	54	0.74	0.49	32	0.06	88
Car 16	<0.03	1.6	300	3.4	4.4	140	0.51	440
Car 17	<0.03	0.43	160	1.6	0.64	130	<0.01	290
Car 18	0.15	1.2	46	12	6.0	410	2.2	470
Car 19	<0.03	5.1	85	3.5	3.1	100	0.91	200
Car 20	<0.03	1.4	53	2.3	2.6	63	0.74	120
Car 21	<0.03	3.0	22	0.27	6.4	1.5	4.0	38

Appendix 10 *Descriptive Statistical Summary of PFR Concentrations (µg/g) in Car Dust Samples from Australia, Germany, and UK*

	TnBP	Australia	Germany	UK	**TCEP**	Australia	Germany	UK
Minimum		<0.03	<0.03	<0.03		<0.06	<0.06	<0.06
5th percentile		<0.03	<0.03	<0.03		0.03	<0.06	0.23
Median		0.11	<0.03	<0.03		2.0	0.40	1.23
Geometric mean		0.13	0.04	0.04		2.0	0.32	1.02
Average		0.78	0.09	0.14		9.1	0.98	1.95
95th percentile		4.7	0.43	0.96		40	5.3	7.7
Maximum		8.4	0.63	1.2		62	5.1	8.7
Standard Deviation		1.8	0.16	0.32		16	1.7	2.4
Relative Standard Deviation		230	190	220		180	170	120
	TCIPP	Australia	Germany	UK	**TPHP**	Australia	Germany	UK
Minimum		0.31	0.29	2.4		0.33	0.33	0.27
5th percentile		2.30	0.77	8.0		1.2	0.48	0.74
Median		24	2.9	53		3.7	1.8	3.3
Geometric mean		21	3.1	47		4.4	1.7	3.6
Average		51	8.5	83		9.1	2.5	15
95th percentile		170	23	290		30	7.0	76
Maximum		310	100	370		85	11	170
Standard Deviation		67	22	94		15	2.5	39
Relative Standard Deviation		130	270	110		170	100	260

	EHDPP Australia	Germany	UK	**TDCIPP** Australia	Germany	UK
Minimum	0.18	0.01	0.29	0.06	<0.03	0.11
5th percentile	0.21	0.17	0.49	0.12	<0.03	1.0
Median	0.63	1.17	2.2	2.3	4.1	31
Geometric mean	0.67	0.61	2.1	4.1	5.2	21
Average	0.98	1.1	2.9	64	85	110
95th percentile	2.6	1.9	6.5	350	530	410
Maximum	4.9	1.9	11	730	620	740
Standard Deviation	0.97	0.68	2.5	150	180	190
Relative Standard Deviation	100	63	86	240	210	170

	TMPP Australia	Germany	UK	**ΣPFR** Australia	Germany	UK
Minimum	<0.01	<0.01	<0.01	2.6	1.3	6.1
5th percentile	<0.01	<0.01	<0.01	8.9	3.8	16
Median	0.31	0.86	0.59	90	20	110
Geometric mean	0.14	0.64	0.22	69	30	110
Average	9.2	16	1.0	140	110	210
95th percentile	36	130	4.0	460	530	470
Maximum	240	150	5.6	850	640	940
Standard Deviation	40	44	1.4	180	190	230
Relative Standard Deviation	440	270	140	120	160	110

Appendix 11 *Individual concentrations of Office dust samples analysed in this study*

Germany

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Off 01	<0.03	<0.06	5.5	0.81	0.19	<0.03	0.34	6.9
Off 02	<0.03	5.6	8.8	0.43	0.26	0.49	0.28	16
Off 03	0.28	0.41	1.6	0.67	0.62	<0.03	<0.01	3.6
Off 04	0.76	2.3	1.3	4.1	3.8	<0.03	<0.01	12
Off 05	0.17	12	5.1	1.5	0.31	2.0	0.44	21
Off 06	0.36	<0.06	1.8	8.1	0.45	<0.03	0.25	11
Off 07	<0.03	<0.06	0.58	0.20	0.54	<0.03	<0.01	1.3
Off 08	<0.03	5.42	7.8	1.2	1.56	0.26	0.62	17
Off 09	0.21	3.29	13	8.8	0.19	0.88	1.2	28
Off 10	0.07	<0.06	3.1	1.3	0.45	1.9	1.4	8.2
Off 11	0.04	<0.06	0.42	0.26	0.16	<0.03	<0.01	0.89
Off 12	0.07	0.45	0.36	0.28	0.27	<0.03	<0.01	1.43
Off 13	0.04	0.35	1.3	1.2	0.36	2.2	0.49	6.0
Off 14	0.09	0.86	4.8	6.2	0.41	0.85	1.6	15
Off 15	0.06	<0.06	0.81	0.85	0.13	0.13	<0.01	2.0
Off 16	<0.03	<0.06	0.18	0.47	a)	0.05	<0.01	0.70
Off 17	0.25	0.13	0.65	1.8	a)	0.21	<0.01	3.1
Off 18	0.41	0.14	0.70	1.8	a)	0.13	0.37	3.5
Off 19	0.29	0.11	0.69	1.7	a)	0.08	<0.01	2.8
Off 20	<0.03	0.17	2.5	2.7	a)	0.14	<0.01	5.5
Off 21	0.28	0.13	0.88	4.8	a)	0.29	<0.01	6.4
Off 22	0.23	0.09	9.4	1.5	a)	0.06	<0.01	11
Off 23	0.18	0.11	9.1	3.1	a)	0.14	1.3	14
Off 24	0.21	0.15	0.39	4.4	a)	0.26	<0.01	5.4
Off 25	0.34	0.11	5.3	2.3	a)	0.15	1.8	10

a) sample analysed in Belgium, EHDPP was not targeted in Belgium therefor no concentration available

Kazakhstan

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Off 01	<0.03	2.2	1.3	29	0.41	2.3	<0.01	36
Off 02	0.37	4.1	1.9	4.5	0.31	1.3	0.75	13
Off 03	<0.03	2.8	1.6	**19**	0.57	1.3	2.1	27
Off 04	<0.03	0.95	2.5	48	0.19	<0.03	10	62
Off 05	0.13	5.8	4.0	6.1	0.55	<0.03	<0.01	16
Off 06	<0.03	1.0	4.5	0.39	0.12	0.08	5.7	12
Off 07	0.48	3.9	100	0.78	0.08	4.0	<0.01	110
Off 08	0.18	1.3	0.87	4.6	0.21	0.54	<0.01	8

UK

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Off 01	<0.03	1.7	33	6.5	1.9	0.05	<0.01	43
Off 02	0.24	0.87	55	1.4	0.57	3.0	0.18	62
Off 03	<0.03	0.80	97	2.7	7.7	0.40	<0.01	110
Off 04	0.27	0.82	57	19	35	0.46	0.56	110
Off 05	0.14	3.6	54	11	8.0	8.9	<0.01	85
Off 06	<0.03	0.87	52	21	5.5	0.22	<0.01	80
Off 07	<0.03	0.90	58	18	9.8	0.30	1.2	89
Off 08	<0.03	1.4	82	7.4	13	0.53	<0.01	100
Off 09	<0.03	0.67	19	3.5	3.0	0.21	<0.01	26
Off 10	<0.03	0.42	10	3.8	0.94	0.06	1.2	17
Off 11	<0.03	<0.06	17	2.3	5.9	0.13	<0.01	25
Off 12	<0.03	<0.06	8.8	0.66	0.87	0.04	<0.01	10
Off 13	<0.03	0.31	22	1.4	2.3	0.16	0.23	26
Off 14	0.11	0.33	14	1.1	2.4	2.1	0.04	20
Off 15	<0.03	0.18	18	2.1	4.7	0.35	<0.01	25
Off 16	0.08	2.1	19	20	20	0.14	<0.01	62
Off 17	0.02	0.23	24	1.7	4.1	1.2	<0.01	31
Off 18	0.11	1.0	67	5.2	27	1.0	0.53	100
Off 19	0.08	0.92	16	1.6	1.4	0.35	0.25	20
Off 20	<0.03	5.7	48	44	22	51	<0.01	170
Off 21	<0.03	0.77	23	3.6	4.2	1.1	0.08	32
Off 22	<0.03	5.2	25	3.2	4.1	1.1	0.20	39
Off 23	0.05	1.9	33	4.3	5.3	2.3	<0.01	46
Off 24	<0.03	2.0	47	6.9	10	0.48	<0.01	66
Off 25	0.97	1.0	52	4.7	3.1	1.5	<0.01	63
Off 26	0.13	1.3	48	6.2	7.0	2.6	<0.01	65
Off 27	0.15	<0.06	14	0.56	0.84	0.34	0.32	16
Off 28	0.04	0.79	15	3.2	1.5	0.97	<0.01	21
Off 29	0.05	0.37	10	1.3	1.2	0.26	<0.01	14
Off 30	0.07	1.4	15	2.2	4.6	0.76	<0.01	24
Off 31	0.04	1.3	48	7.8	9.8	1.0	<0.01	68
Off 32	<0.03	0.37	39	6.5	3.0	2.9	5.2	57
Off 33	0.07	1.0	61	6.5	34	0.41	<0.01	100

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Off 34	0.05	0.42	32	3.6	7.9	3.1	<0.01	47
Off 35	<0.03	0.38	34	11	8.4	1.3	3.3	59
Off 36	<0.03	0.37	25	7.2	2.6	1.1	<0.01	36
Off 37	0.05	<0.06	8.9	2.3	2.8	0.39	<0.01	14
Off 38	<0.03	<0.06	8.9	1.9	2.6	0.30	<0.01	14
Off 39	0.04	0.44	19	31	3.4	0.22	<0.01	54
Off 40	<0.03	0.24	25	1.4	2.3	3.4	<0.01	32
Off 41	<0.03	0.30	230	3.1	3.5	0.53	<0.01	230
Off 42	<0.03	1.5	17	7.7	12	1.7	1.3	41
Off 43	0.05	0.63	46	2.8	5.8	1.1	0.33	57
Off 44	<0.03	3.1	14	2.6	2.5	2.5	0.05	24
Off 45	0.25	2.0	41	36	68	12	<0.01	160
Off 46	<0.03	0.48	47	50	8.6	2.1	<0.01	110
Off 47	0.03	3.8	19	31	81	<0.03	<0.01	140
Off 48	<0.03	1.2	17	2.3	5.2	0.28	0.42	27
Off 49	0.27	0.85	43	11	21	0.23	0.50	77
Off 50	0.04	0.70	22	1.3	0.15	<0.03	<0.01	25
Off 51	<0.03	1.0	140	5.5	8.0	0.83	<0.01	160
Off 52	<0.03	3.1	17	1.5	3.7	<0.03	<0.01	25
Off 53	<0.03	0.5	3.6	3.1	9.4	0.03	0.42	17
Off 54	0.51	0.5	40	0.68	0.59	0.37	1.7	44
Off 55	<0.03	2.2	35	5.4	4.5	0.32	<0.01	47
Off 56	<0.03	2.6	29	2.0	6.2	0.59	<0.01	40
Off 57	0.06	2.0	56	6.0	5.6	0.27	0.40	70
Off 58	<0.03	22	220	9.9	15	5.7	0.09	280
Off 59	<0.03	28	130	11	21	0.14	<0.01	190
Off 60	1.30	23	110	7.7	14	0.82	0.10	160
Off 61	0.13	160	51	10	24	0.36	1.4	247

Appendix 12 *Descriptive Statistical Summary of PFR Concentrations (µg/g) in Office Dust Samples from Germany, Kazakhstan and UK*

	TnBP	Germany	Kazakhstan	UK	**TCEP**	Germany	Kazakhstan	UK
Minimum		<0.03	<0.03	<0.03		<0.06	0.95	<0.06
5th percentile		<0.03	<0.03	<0.03		<0.06	0.97	<0.06
Median		0.17	0.07	<0.03		0.13	2.5	0.87
Geometric mean		0.10	0.07	0.04		0.21	2.3	0.88
Average		0.18	0.15	0.10		1.3	2.7	5.0
95th percentile		0.40	0.44	0.27		5.6	5.2	22
Maximum		0.76	0.48	1.3		12	5.8	160
Standard Deviation		0.18	0.18	0.21		2.7	1.7	21
Relative Standard Deviation		99	120	220		210	62	420
	TCIPP	Germany	Kazakhstan	UK	**TPHP**	Germany	Kazakhstan	UK
Minimum		0.18	0.87	3.6		0.20	0.39	0.56
5th percentile		0.37	1.0	8.9		0.26	0.53	1.1
Median		1.6	2.2	33		1.5	5.3	4.3
Geometric mean		1.8	3.3	31		1.5	5.6	4.6
Average		3.4	15	44		2.4	14	8.2
95th percentile		9.4	68	130		7.7	42	31
Maximum		13	100	230		8.8	48	50
Standard Deviation		3.6	35	44		2.4	17	10
Relative Standard Deviation		110	240	100		99	120	130

	EHDPP	Germany	Kazakhstan	UK	**TDCIPP**	Germany	Kazakhstan	UK
Minimum		0.13	0.08	0.15		<0.03	<0.03	<0.03
5th percentile		0.15	0.09	0.84		<0.03	<0.03	0.03
Median		0.36	0.26	5.3		0.14	0.91	0.48
Geometric mean		0.40	0.25	5.2		0.12	0.33	0.54
Average		0.65	0.31	10		0.41	1.20	2.1
95th percentile		2.2	0.56	34		2.0	3.4	5.7
Maximum		3.8	0.57	81		2.2	4.0	51
Standard Deviation		0.94	0.19	14		0.66	1.4	6.7
Relative Standard Deviation		150	62	140		160	120	320
	TMPP	Germany	Kazakhstan	UK	**ΣPFR**	Germany	Kazakhstan	UK
Minimum		<0.01	0.01	<0.01		0.75	8	10
5th percentile		<0.01	0.01	<0.01		1.0	9	14
Median		<0.01	0.38	<0.01		6.4	22	47
Geometric mean		0.06	0.18	0.03		5.8	25	50
average		0.41	2.32	0.33		8.5	36	70
95th percentile		1.6	8.48	1.4		20	94	190
Maximum		1.9	9.99	5.3		28	111	280
Standard Deviation		0.59	3.66	0.85		6.9	35	61
Relative Standard Deviation		140	160	250		81	99	87

Appendix 13 *Individual concentrations of Couch dust samples analysed in this study*

Australia

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Cou 01	0.11	4.8	1.6	1.0	0.54	2.4	0.04	11
Cou 02	0.98	<0.06	1.3	0.68	0.11	0.25	<0.01	3.3
Cou 03	<0.03	<0.06	2.1	0.47	0.11	0.58	<0.01	3.3
Cou 04	<0.03	0.44	2.0	1.5	0.18	0.28	0.04	4.4
Cou 05	<0.03	<0.06	3.9	0.98	0.14	0.42	<0.01	5.5
Cou 06	<0.03	1.4	20	2.8	0.19	2.1	0.10	26
Cou 07	0.10	0.89	2.5	1.5	0.32	<0.03	<0.01	5.3
Cou 08	<0.03	0.76	1.6	2.5	0.40	<0.03	0.40	5.7
Cou 09	0.14	0.58	86	4.7	0.11	0.05	<0.01	91
Cou 10	0.43	0.29	0.87	0.55	0.65	3.9	0.28	7.0
Cou 11	3.0	0.54	4.5	0.79	0.24	2.2	<0.01	11
Cou 12	<0.03	6.7	83	16	1.0	1.3	4.0	110
Cou 13	<0.03	5.2	110	29	1.2	0.78	6.6	150
Cou 14	0.06	1.3	4.8	0.95	0.22	0.56	<0.01	7.9
Cou 15	0.16	0.57	2.3	3.3	1.5	<0.03	<0.01	7.8
Cou 16	<0.03	0.60	2.6	21	11	0.50	0.10	36
Cou 17	<0.03	6.2	11	1.6	0.36	2.3	<0.01	22
Cou 18	2.8	0.70	3.6	0.37	0.09	0.31	<0.01	7.9
Cou 19	<0.03	1.0	4.7	2.1	0.77	1.3	0.15	10
Cou 20	0.09	0.72	210	1.8	1.2	7.5	0.08	220
Cou 21	<0.03	<0.06	2.9	2.7	0.43	0.41	<0.01	6.4
Cou 22	<0.03	2.7	2.3	3.3	0.78	2.4	0.12	12
Cou 23	<0.03	0.40	2.0	0.42	0.30	0.41	<0.01	3.5
Cou 24	0.25	0.72	1.7	0.64	0.39	0.39	<0.01	4.1
Cou 25	<0.03	1.3	550	10	0.08	0.15	<0.01	570
Cou 26	0.06	0.46	2.1	0.97	0.52	<0.03	<0.01	4.1
Cou 27	1.0	0.29	0.82	1.7	0.23	0.85	<0.01	4.9
Cou 28	0.13	1.5	3.1	1.7	0.32	1.0	0.29	8.0
Cou 29	<0.03	1.2	6.6	8.3	0.15	0.19	<0.01	16
Cou 30	<0.03	0.40	1.3	0.66	0.14	0.05	<0.01	2.5
Cou 31	0.18	0.15	2.1	1.2	0.24	0.26	<0.01	4.1
Cou 32	0.12	0.64	0.89	2.0	0.25	2.4	<0.01	6.3
Cou 33	<0.03	2.9	12	0.93	1.0	3.2	0.85	21
Cou 34	0.13	2.5	22	4.0	1.0	3.6	0.40	33
Cou 35	0.06	27	1.7	2.1	0.18	0.64	0.01	31
Cou 36	1.4	3.9	4.9	22	5.1	2.2	<0.01	39
Cou 37	<0.03	0.38	0.97	1.2	1.0	0.29	0.10	4.0
Cou 38	<0.03	0.97	3.0	8.5	0.49	2.4	<0.01	15
Cou 39	0.10	1.2	3.5	28	0.58	1.7	<0.01	36
Cou 40	<0.03	0.35	1.2	2.8	0.78	0.10	0.61	5.8
Cou 41	<0.03	3.7	4.6	6.3	0.65	4.9	<0.01	20

UK

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Cou 01	0.60	<0.06	1.8	0.18	0.28	2.4	<0.01	5.2
Cou 02	<0.03	<0.06	240	2.7	0.49	0.16	1.6	250
Cou 03	0.19	<0.06	320	6.2	0.80	2.1	<0.01	330
Cou 04	1.3	0.84	1600	3.0	1.8	1.6	0.81	1600
Cou 05	0.95	2.8	58	8.4	2.2	1.5	2.8	76
Cou 06	0.15	<0.06	860	3.2	1.9	2.7	0.43	870
Cou 07	4.8	<0.06	1400	1.7	2.4	2.2	0.89	1400
Cou 08	0.50	1.7	360	2.0	2.5	2.0	1.0	370
Cou 09	0.13	0.03	1400	1.5	0.98	1.7	0.06	1400
Cou 10	0.04	3.4	1900	0.97	0.44	703	0.09	2600

Appendix 14 *Descriptive Statistical Summary of Concentrations (µg/g) of PFRs in Couch Dust Samples from Australia (Aus) and the UK*

	TnBP		**TCEP**		**TCIPP**	
	UK	Aus	UK	Aus	UK	Aus
Minimum	<0.03	<0.03	<0.06	<0.06	1.8	0.82
5th percentile	<0.03	<0.03	<0.06	<0.06	27	0.89
Median	0.34	<0.03	<0.06	0.72	610	2.9
Geometric mean	0.29	0.06	0.14	0.76	330	4.6
Average	0.87	0.28	0.89	2.1	810	29
95th percentile	3.2	1.4	3.1	6.2	1700	110
Maximum	4.8	3.0	3.4	27	1900	550
Standard Deviation	1.4	0.67	1.3	4.3	700	92
Relative Standard Deviation	170	240	150	210	86	320

	TPHP		**EHDPP**		**TDCIPP**	
	UK	Aus	UK	Aus	UK	Aus
Minimum	0.18	0.37	0.28	0.08	0.16	<0.03
5th percentile	0.53	0.47	0.35	0.11	0.78	<0.03
Median	2.4	1.8	1.4	0.39	2.0	0.58
Geometric mean	2.0	2.3	1.1	0.41	2.8	0.53
Average	3.0	5.0	1.4	0.86	72	1.3
95th percentile	7.4	22	2.4	1.5	390	3.9
Maximum	8.4	29	2.5	11	700	7.5
Standard Deviation	2.5	7.4	0.86	1.80	220	1.6
Relative Standard Deviation	83	150	63	210	310	120

	TMPP		**ΣPFR**	
	UK	Aus	UK	Aus
Minimum	<0.01	<0.01	5.2	1.3
5th percentile	<0.01	<0.01	37	1.5
Median	0.62	<0.01	620	6.4
Geometric mean	0.22	0.02	390	8.6
Average	0.77	0.35	890	39
95th percentile	2.2	0.85	2100	140
Maximum	2.8	6.6	2600	640
Standard Deviation	0.88	1.2	840	95
Relative Standard Deviation	120	340	94	240

Appendix 15 *Individual concentrations of mattress dust samples analysed in this study*

	TnBP	**TCEP**	**TCIPP**	**TPHP**	**EHDPP**	**TDCIPP**	**TMPP**	**ΣPFR**
Mat 01	0.16	0.53	2.0	3.1	0.91	<0.03	2.4	9.1
Mat 02	<0.03	0.30	0.36	0.25	<0.01	<0.03	<0.01	0.91
Mat 03	0.11	<0.06	0.47	0.61	0.05	<0.03	0.11	1.4
Mat 04	<0.03	<0.06	2.7	3.7	0.10	0.05	<0.01	6.6
Mat 05	<0.03	<0.06	1.3	2.7	0.10	0.08	<0.01	4.2
Mat 06	0.10	1.0	1.4	0.19	0.07	0.12	<0.01	2.8
Mat 07	<0.03	<0.06	0.99	0.52	0.30	0.05	<0.01	1.9
Mat 08	0.05	0.37	2.0	1.5	0.08	0.44	0.44	4.9
Mat 09	0.10	<0.06	0.82	0.26	0.19	<0.03	0.11	1.5
Mat 10	<0.03	<0.06	0.09	0.16	<0.01	<0.03	<0.01	0.26
Mat 11	<0.03	0.42	0.22	0.65	<0.01	0.09	<0.01	1.4
Mat 12	0.49	0.33	0.71	2.5	0.07	0.81	<0.01	4.9
Mat 13	<0.03	0.21	0.44	2.3	0.37	0.44	<0.01	3.7
Mat 14	<0.03	<0.06	3.4	0.77	0.12	0.04	<0.01	4.3
Mat 15	<0.03	<0.06	1.1	0.30	0.14	0.22	<0.01	1.7
Mat 16	<0.03	0.72	1.6	1.9	0.44	0.07	0.07	4.7
Mat 17	<0.03	0.98	12	1.7	0.50	0.04	<0.01	15
Mat 18	<0.03	<0.06	31	0.39	0.55	0.12	1.4	34
Mat 19	0.13	0.57	1.6	0.51	0.10	0.04	0.04	3.0
Mat 20	<0.03	0.03	1.7	0.36	0.06	<0.03	0.03	2.2
Mat 21	0.05	0.76	2.5	3.1	0.45	0.13	0.13	7.1
Mat 22	0.65	0.61	0.04	1.5	<0.01	<0.03	<0.01	2.8
Mat 23	<0.03	<0.06	0.50	1.1	0.06	0.68	0.68	3.0
Mat 24	0.06	0.86	1.0	4.5	0.08	0.13	<0.01	6.7
Mat 25	0.06	0.26	0.68	1.9	0.16	0.03	0.03	3.1
Mat 26	0.97	<0.06	9.2	0.76	0.31	2.9	<0.01	14
Mat 27	<0.03	<0.06	2.4	1.1	0.09	0.20	<0.01	3.7
Mat 28	<0.03	1.5	1.7	1.1	0.75	0.15	0.15	5.3
Mat 29	<0.03	0.50	2.8	1.6	0.08	0.12	0.12	5.2
Mat 30	0.05	0.50	2.1	1.8	0.29	4.1	4.1	13
Mat 31	<0.03	<0.06	1.1	0.04	<0.01	<0.03	<0.01	1.2
Mat 32	0.15	<0.06	0.27	0.33	0.24	0.04	0.24	1.3
Mat 33	0.09	0.47	0.60	1.6	0.15	0.13	0.13	3.2

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Mat 34	0.06	<0.06	0.53	1.9	0.23	0.48	<0.01	3.2
Mat 35	0.05	0.33	0.72	1.1	0.35	0.24	0.24	3.0
Mat 36	0.23	<0.06	0.26	0.17	0.35	<0.03	0.03	1.0
Mat 37	2.0	<0.06	0.79	3.3	0.10	0.03	<0.01	6.2
Mat 38	<0.03	0.72	3.1	0.68	0.08	0.18	<0.01	4.8
Mat 39	<0.03	0.03	5.4	0.59	0.25	1.2	0.22	7.8
Mat 40	<0.03	0.55	8.3	21	0.12	0.17	<0.01	30
Mat 41	<0.03	0.03	0.24	0.17	0.11	<0.03	<0.01	0.5
Mat 42	0.12	0.03	0.48	0.38	0.36	0.07	<0.01	1.4
Mat 43	<0.03	0.52	0.52	0.91	0.48	0.09	<0.01	2.5
Mat 44	<0.03	0.03	0.82	0.94	0.12	0.18	<0.01	2.1
Mat 45	<0.03	1.6	4.5	0.25	0.28	<0.03	<0.01	6.6
Mat 46	<0.03	3.6	7.7	0.78	0.43	<0.03	0.50	13
Mat 47	0.04	0.03	0.47	0.45	0.15	2.2	<0.01	3.4
Mat 48	0.07	0.73	3.7	10.2	0.46	0.69	0.69	17
Mat 49	0.05	0.82	1.8	0.49	0.13	0.31	0.31	3.9
Mat 50	<0.03	0.92	0.58	4.4	0.64	<0.03	<0.01	6.5
Mat 51	<0.03	<0.06	0.13	10.8	0.52	0.03	0.03	11
Mat 52	0.04	0.28	2.5	1.1	0.29	1.3	1.3	6.8
Mat 53	<0.03	0.36	17	2.2	0.34	0.58	0.03	21
Mat 54	0.05	6.5	1.9	2.4	0.33	0.77	0.03	12
Mat 55	0.06	0.41	1.8	0.77	0.12	0.04	0.04	3.3
Mat 56	<0.03	0.33	3.1	1.4	0.13	0.02	<0.01	5.0
Mat 57	<0.03	0.32	0.69	0.83	0.18	0.14	<0.01	2.2

Appendix 16 *Individual concentrations of bedroom dust samples analysed in this study*

	TnBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Bed 01	<0.03	0.55	4.3	3.0	0.75	1.42	1.4	11
Bed 02	0.11	<0.06	0.54	1.9	0.17	0.07	<0.01	2.8
Bed 03	0.19	<0.06	0.46	1.6	0.12	0.45	<0.01	2.8
Bed 04	<0.03	1.0	2.4	0.59	0.27	0.49	0.19	5.0
Bed 05	<0.03	3.1	5.1	1.5	0.24	0.31	0.14	10
Bed 06	<0.03	0.32	0.54	2.6	0.20	3.76	0.23	7.6
Bed 07	0.05	<0.06	1.1	1.0	0.18	0.08	<0.01	2.4
Bed 08	0.08	<0.06	0.54	6.6	0.19	0.05	<0.01	7.5
Bed 09	0.06	0.41	7.4	0.20	0.43	0.04	<0.01	8.5
Bed 10	<0.03	4.3	3.0	0.54	0.57	0.67	<0.01	9.1
Bed 11	<0.03	4.1	1.6	6.3	0.95	<0.03	<0.01	13