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A review of chamber experiments for determining specific emission rates and investigating migration pathways of flame retardants

Rauert, Cassandra; Lazarov, B.; Harrad, Stuart; Covaci, A.; Stranger, M.

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Corresponding Author: Ms. Cassandra Rauert,

Corresponding Author's Institution: University of Birmingham

First Author: Cassandra Rauert

Order of Authors: Cassandra Rauert; Borislav Lazarov; Stuart Harrad; Adrian Covaci; Marianne Stranger

Abstract: The widespread use of flame retardants (FRs) in indoor products has lead to their ubiquitous distribution within indoor microenvironments with many studies reporting concentrations in indoor air and dust. Little information is available however on emission of these compounds to air, particularly the measurement of specific emission rates, (SERs) or the migration pathways leading to dust contamination. Such knowledge gaps hamper efforts to develop understanding of human exposure. This review summarizes published data on SERs of the following FRs released from treated products: polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), tetrabromobisphenol-A (TBBPA), novel brominated flame retardants (NBFRs) and organophosphate flame retardants (PFRs), including a brief discussion of the methods used to derive these SERs. Also reviewed are published studies that utilize emission chambers for investigations/measurements of mass transfer of FRs to dust, discussing the chamber configurations and methods used for these experiments. A brief review of studies investigating correlations between concentrations detected in indoor air/dust and possible sources in the microenvironment is included along with efforts to model contamination of indoor environments. Critical analysis of the literature reveals that the major limitations with utilizing chambers to derive SERs for FRs arise due to the physicochemical properties of FRs. In particular, increased partitioning to particulates due to their lower vapour pressures cause "sink" effects i.e. loss through absorption to chamber surfaces. Moreover, extended experiment times are often required at room temperature conditions for formation of steady state conditions inside the chamber. The limitations of chamber experiments are discussed as well as their potential for filling gaps in knowledge in this area.

UNIVERSITY OF
BIRMINGHAM

Cassandra Rauert,
Division of Environmental Health & Risk Management,
School of Geography Earth and Environmental Sciences,
University of Birmingham,
Birmingham,
B15 2TT,
UK
Tel. +44 121 414 5431
Fax +44 121 414 3078
Email c.b.rauert@bham.ac.uk

The Editor,
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July 25, 2013

SUBMISSION OF REVIEW ARTICLE "A REVIEW OF CHAMBER EXPERIMENTS FOR DETERMINING SPECIFIED EMISSION RATES AND INVESTIGATING MIGRATION PATHWAYS OF FLAME RETARDANTS"

Dear Sir

I hereby submit the above paper for consideration by *Atmospheric Environment* as a Review Article. I believe that it warrants publication in this journal as it provides important and novel insights into the use of emission chambers for researching migration of flame retardants to indoor air and dust.

The above paper is a resubmission to Atmospheric Environment and the US office of Atmospheric Environment (Raman H. Singh) has expressed their willingness to handle the paper again.

I trust that I have submitted all the necessary information at the website, but if you require any further information in order to expedite the review process, please don't hesitate to get in touch. I look forward to hearing from you.

Best Regards

Cassandra Rauert

HIGHLIGHTS

- This review provides a summary of the available evidence for the influence of putative sources on indoor contaminations with FRs
- Studies are collated that use emission chambers to elucidate EFs and mass transfer to dust of FRs
- The different chamber configurations/ methodological approaches used are summarized
- Limitations/difficulties encountered with chamber experiments are identified
- Knowledge gaps and future research directions are identified

TITLE

A review of chamber experiments for determining specific emission rates and investigating migration pathways of flame retardants

Authors

Cassandra Rauert[a], Borislav Lazarov[b], Stuart Harrad[a], Adrian Covaci[c], Marianne Stranger[b]

Affiliations

[a] School of Geography Earth and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK
[b] Environmental Risk and Health Unit, VITO, Boeretang 200, 2400 , Mol, Belgium
[c] Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium

Corresponding author

Cassandra Rauert
Division of Environmental Health & Risk Management, Public Health Building, School of Geography, Earth & Environmental Sciences, University of Birmingham,
Birmingham, B15 2TT, UK
Tel +44 (0)121 414 5431
Fax +44 (0)121 414 3078
c.b.rauert@bham.ac.uk

Abstract

The widespread use of flame retardants (FRs) in indoor products has lead to their ubiquitous distribution within indoor microenvironments with many studies reporting concentrations in indoor air and dust. Little information is available however on emission of these compounds to air, particularly the measurement of specific emission rates, (SERs) or the migration pathways leading to dust contamination. Such knowledge gaps hamper efforts to develop understanding of human exposure. This review summarizes published data on SERs of the following FRs released from treated products: polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), tetrabromobisphenol-A (TBBPA), novel brominated flame retardants (NBFRs) and organophosphate flame retardants (PFRs), including a brief discussion of the methods used to derive these SERs. Also reviewed are published studies that utilize emission chambers for investigations/measurements of mass transfer of FRs to dust, discussing the chamber configurations and methods used for these experiments. A brief review of studies investigating correlations between concentrations detected in indoor air/dust and possible sources in the microenvironment is included along with efforts to model contamination of indoor environments. Critical analysis of the literature reveals that the major limitations with utilizing chambers to derive SERs for FRs arise due to the physicochemical properties of FRs. In particular, increased partitioning to particulates due to their lower vapour pressures cause "sink" effects i.e. loss through absorption to chamber surfaces. Moreover, extended experiment times are often required at room temperature conditions for formation of steady state conditions inside the chamber. The limitations of chamber experiments are discussed as well as their potential for filling gaps in knowledge in this area.

Keywords

Emission Chamber, Specific Emission rate, Flame Retardants, Mass transfer to dust

Outline

Abbreviation List

Abbreviation	Name		Abbreviation	Name
ABS	Acrylonitrile-butadiene-styrene		PUF	Polyurethane foam
BFR	Brominated Flame Retardant		PVC	Polyvinyl chloride
BTBPE	1,2-bis(2,4,6 tribromophenoxy) ethane		RH	Relative Humidity
CLIMPAQ	Chamber for Laboratory Investigations of Materials, Pollution and Air quality		SERa	area Specific Emission Rate
DBDPE	decabromodiphenyl ethane		SERu	unit Specific Emission Rate
Deca-BDE	Deca brominated diphenyl ether		SVOC	Semi-Volatile Organic Compound
DEHP	di(2-ethylhexyl)phthalate		TBB (EH-TBB)	2-ethylhexyl-2,3,4,5-tetrabromobenzoate
DnBP	di-*n*-butylphthalate		TBBPA	Tetrabromobisphenol-A
EF	Emission Factor		TBEP (TBOEP)	tri (2-butoxyexthyl) phosphate
FLEC	Field and Laboratory Emission Cell		TBPH (BEH-TEBP)	bis (2-ethylhexyl) 2,3,4,5-tetrabromophthalate
FR	Flame Retardant		TCEP	tris (2-chloroethyl) phosphate
HBCD	Hexabromocyclododecane		TCPP (TCIPP)	tris (1-chloro-2-propyl) phosphate
HIPS	High impact polystyrene		TDCPP (TDCIPP)	tris (1,3-dichloro-2-propyl) phosphate
K_{OA}	Octanol to air partitioning coefficient		TEHP	tris(2-ethyl hexyl phosphate)
NBFR	Novel Brominated Flame Retardant		TEP	triethyl phosphate
Octa-BDE	Octa brominated diphenyl ether		TMP	trimethyl phosphate
PBDE	Polybrominated diphenyl ether		TMPP	tricresyl phosphate
PBT	Persistent, Bioaccumulative and Toxic		TnBP (TNBP)	tri(*n*-butyl) phosphate
vPvB	very Persistent, very Bioaccumulative		TPhP (TPHP)	triphenyl phosphate
Penta-BDE	Penta brominated diphenyl ether		VDU	Video Display Unit
PFR	Organophosphate Flame Retardant		VOC	Volatile Organic Compound
POP	Persistent Organic Pollutant		V_P	Vapour Pressure

1. Introduction

Flame retardants (FRs) are chemical additives found in many electrical items and materials used widely in indoor microenvironments such as homes, offices, cars and schools. They are added as part of the manufacturing process through either additive or reactive processes. FRs are either covalently bonded to the polymer during manufacture (reactive FRs), or simply added to the polymer after manufacture (additive FRs). Additive FRs are considered less intimately bound to the treated product thereby facilitating release during normal use, and indeed elevated concentrations have been found in many indoor microenvironments (Harrad et al., 2010a).

Polybrominated diphenyl ethers (PBDEs) are a group of additive brominated flame retardants (BFRs) that occur in three formulations. The Penta-BDE formulation is used to flame retard polyurethane foam (PUF) in carpets, vehicle interiors, furniture, and bedding; as well as in printed circuit boards and microprocessor packaging in computers. The Octa-BDE formulation is used to treat thermoplastics, such as high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) copolymers; while the Deca-BDE formulation is used in HIPS applied primarily in plastic housings for electrical goods (TVs and computers), as well as in textiles (Harrad et al., 2008b). The Penta-BDE and Octa-BDE formulations are listed as persistent organic pollutants (POPs) under the Stockholm Convention, decision SC-4/14 and SC-4/18, (UNEP, 2009) and the use of Deca-BDE is phased out in Europe. Recently, Deca-BDE has been listed as "a substance of very high concern because of its persistent, bioaccumulative and toxic/ very persistent and very bioaccumulative (PBT/vPvB) properties" by the EU (ECHA, 2012) and as such there is a need for alternative FRs.

Hexabromocyclododecane (HBCD) is another additive BFR. It is used widely to flame retard polystyrene foams for thermal insulation of buildings, back coating of fabrics for furniture, and HIPS used in enclosures for electronic equipment, such as TVs (Harrad et al., 2010a; Weil and Levchik, 2007). Currently HBCDs are also under consideration for listing under the Stockholm Convention (UNEP, 2012). Tetrabromobisphenol-A (TBBPA) on the other hand has been used as both a reactive FR, in epoxy and polycarbonate resins for printed circuit boards and electronic equipment, and as an additive FR in HIPS or ABS resins (Abdallah et al., 2008). When used as a reactive FR, it can still be emitted to the surrounding environment, if an excess of non-polymerized TBBPA is present in the final treated product (Abdallah et al., 2008). The global demand for TBBPA increased on average by 19% per year between 1992 and 1998, with demand continuing to grow by 8-9% per year between 1998 and 2004 (ECHA, 2006).

With the banning/phasing out of PBDEs, the use of organophosphate flame retardants (PFRs) (Van den Eede et al., 2011; Van der Veen and de Boer, 2012) and novel brominated flame retardants (NBFRs) (Covaci et al., 2011) is increasing, see Table 1. For consistency in this review, PFRs are referred to as the nomenclature used in the article reviewed with the new suggested nomenclature by (Bergman et al., 2012) stated in brackets. PFRs are used as additive FRs and plasticisers in a wide range of products and NBFRs are also primarily used as additive FRs with the exception of some TBBPA derivatives used as reactive FRs. The different uses of these FRs are summarised in Table 1.

The reported known or estimated worldwide production volumes of the above mentioned FRs are summarised in Table 2. Limited information is publicly available regarding production volumes, especially for NBFRs and PFRs, and is provided here with caution given the associated uncertainty. If a newer chemical is not yet listed with the European Chemicals Agency (ECHA) then it is assumed the chemical is produced below 1000 tonnes per year i.e. it is deemed a "low production volume chemical". The limited information on production volumes/market demand introduces significant uncertainty to attempts to identify which FRs (if any) are used in any given product, as well as efforts to estimate emissions from such products and the microenvironments within which they are located.

The toxicological effects of FRs in humans remain uncertain; however PBDEs may act as endocrine disruptors through alterations in thyroid hormone homeostasis, and have been reported as developmental neurotoxicants, with impacts on liver and kidney morphology and sexual development (Besis and Samara, 2012). Moreover, HBCDs have been linked with reproductive, developmental, neurotoxic and thyroid effects (USEPA, 2010b). The possible toxicological effects of these FRs are of concern as detectable levels of the above-mentioned FRs have been reported in indoor air and dust, important contributors to human exposure (Harrad et al., 2010a; Harrad et al., 2010b).

Despite the known presence of FRs in indoor environments and their potential adverse effects, little is known about their emission and/or migration pathways into air and dust, a gap exacerbated by a lack of consistent data on their physicochemical properties. In particular, estimations of vapour pressure (V_P) and octanol to air partitioning coefficients (K_{OA}) are unreliable, rendering calculation of realistic emission factors (EFs) and specific emission rates (SERs) highly uncertain, as shown by Prevedouros et al. (2004) who calculated EFs of PBDEs -47, -99 and -153 from previously reported V_P and K_{OA} data. The European Commission of Health Consumers (EU, 2011) uses V_P as the standard method to calculate emissions of FRs from products. As V_P and K_{OA} are highly correlated (Moeckel et al., 2010), similar emission estimates are expected using these estimated values. This is often not the case (Prevedouros et al., 2004), and Moeckel et al. (2010) suggest that using reported V_P values represents a 'worst-case' scenario due to the unreliability of available data and the influence of the matrix from which emission is being predicted. Dust to air partition coefficients, also directly related to K_{OA} and hence reliant on the accuracy of available data, can predict equilibrium concentrations in air and dust thus permitting calculation of the mass transfer of semi-volatile organic compounds (SVOCs) to particulates or dust (Schripp et al., 2010). Limited information is available on migration pathways of FRs into particulates/dust with proposed hypotheses including: deposition after volatilisation of the more volatile FRs, abrasion of fine particles from treated products through wear-and-tear thus allowing transfer of less volatile FRs, and transfer via direct contact between the treated product and dust (Figure 1). Deposition of the less volatile congeners, particularly PBDE-209, may also occur to a limited extent, resulting in the relatively low ng/g level concentrations reported in some studies (Kefeni and Okonkwo, 2012). Multiple migration pathways may also occur concurrently with lower level background contamination from atmospheric deposition overlaid with inputs from abraded particles/fibres.

Information on calculated SERs and mass transfer to dust, are used in exposure assessment models and risk assessments that evaluate the risks arising from human exposure associated with the use of products treated with FRs. The high uncertainty in reported values of physicochemical properties of FRs decreases the reliability of calculations of SERs and of FR distribution between gas/particulate phases. As a result, there is a clear need for experimental measurements of such parameters.

This paper reviews all research published in the open literature up to the end of December 2012, on the use of emission chambers for determining SERs of FRs from flame-retarded products and the subsequent mass transfer to dust. It also discusses the limitations of such chambers and their potential for filling knowledge gaps in this area. Although there are a number of published studies investigating chamber experiments of phthalates, due to space restrictions this review will only focus on FRs. Where relevant, discussions of other SVOC studies (e.g. phthalates) that provide insight into the study of FRs have been included.

The aims of this review are thus to: 1) summarise the available evidence for the influence of putative sources on indoor contaminations with FRs; 2) collate studies using emission chambers to elucidate SERs and mass transfer to dust of FRs; 3) summarise the different chamber configurations/methodological approaches used; 4) identify limitations/difficulties encountered with chamber experiments, and 5) identify knowledge gaps and future research directions.

2. Evidence for the influence of putative sources on indoor contamination with FRs

Air and dust are important vectors of human exposure to FRs (Harrad et al., 2010a; Harrad et al., 2010b), hence indoor concentrations and their relationship with putative sources are of interest, especially when in microenvironments displaying highly elevated concentrations. For example, the highest known reported levels of BDE-209 in dust are 2.2 mg/g in a UK house dust sample (Harrad et al., 2008a) and 210 mg/g in a US car dust sample (Batterman et al., 2009). The following two sections provide only a brief outline of studies exploring correlations between indoor FR contamination and putative sources. The following is intended to provide a brief overview of the topic rather than a comprehensive literature review.

Although this relationship is sometimes blurred by source misclassification (Allen et al., 2007; Gevao et al., 2006; Wu et al., 2007), generally, higher indoor concentrations of BFRs are associated with the presence of greater numbers of electronic equipment or PUF-containing furniture (offices rather than houses) (D'Hollander et al., 2010; Gevao et al., 2006; Mandalakis et al., 2008; Watkins et al., 2011). Mandalakis et al. (2008) reported air from a Greek office accommodating network servers and telecommunications infrastructure to display elevated ΣPBDE concentrations of 11,000 pg/m^3 (nearly two orders of magnitude greater than the next highest sample) strongly suggesting electrical equipment to be a significant source of PBDE contamination. Thuresson et al. (2012) analysed dust from offices, houses and apartments, day care centres, and cars in Sweden, also reporting significantly higher concentrations of PBDEs and HBCDs in dust from offices (average ΣPBDEs = 1200 and ΣHBCDs = 300 ng/g) compared to houses (average ΣPBDEs = 510 and ΣHBCDs = 100 ng/g). However, ΣPentaBDEs were even higher in day care centres, with an average concentration of 240 ng/g, suggested to be due to the number of foam mattresses present. Fulong and Espino (2013) investigated dust from 8 different university microenvironments in the Philippines with the highest BDE-209 concentrations occurring in a small computer centre containing four old and new computers (4,000 ng/g). The lowest levels were present in an office lounge containing only one TV set (1,000 ng/g). Similarly, Kefeni and Okonkwo (2012) reported the highest dust concentrations of BDE-209 (600 ng/g) in a South African office containing the highest number of old computers, sofas, foam chairs and electronics of those offices studied.

Concentrations of ΣPBDEs in dust from Hong Kong workplaces exceeded those in homes by 2 to 60 times as reported by Kang et al. (2011). In this study electronics factories displayed the highest concentrations (2,000 to 40,000 ng/g), likely due to the electrical equipment (particularly computers) assembled in the factories. Chen et al. (2008) investigated atmospheric ΣPBDE concentrations in Chinese houses, offices and other workplaces and concentrations were generally higher in workplaces than houses, but not significantly. The office with the highest concentration of ΣPBDEs (8,000 pg/m^3) contained 28 computers and 31 PUF-containing chairs, whereas the office with the lowest reported concentration (200 pg/m^3) contained only 15 computers. The computers in the second office were not in use and the ambient temperature was lower (8^{o}C), possibly resulting in lower emissions of the more volatile congeners.

PFRs and NBFRs have also been investigated in indoor dust from New Zealand homes (Ali et al., 2012) by analysing dust from floors and mattresses. BTBPE, DBDPE, bis (2-ethylhexyl) 2,3,4,5-tetrabromophthalate or TBPH (BEH-TEBP), tri-phenyl-phosphate or TPhP (TPHP), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate or TBB (EH-TBB), tri-(2-butoxyexthyl)-phosphate or TBEP (TBOEP), and tri-*n*-butyl-phosphate or T*n*BP (TNBP) there were significant positive correlations ($p < 0.05$) between the concentrations in mattress dust and the corresponding floor dust from the same microenvironment, suggesting a common source of the contamination. However, the levels of TBEP (TBOEP) were significantly higher in floor than mattress dust, likely explained by the use of TBEP (TBOEP) in floor wax and PVC floor coverings.

Van den Eede et al. (2011) compared levels of PFRs in Belgian homes and stores and found a general trend of higher concentrations in stores. In a similar vein, Brommer et al. (2012) analysed dust from German microenvironments for PFRs, PBDEs and DBDPE with concentrations in offices and cars generally higher than in homes for all analysed FRs, consistent with the above mentioned trend. Webster et al. (2010) compared levels of PFRs in US homes, offices and cars with offices containing 2 times higher concentrations than homes of bis (2-ethylhexyl) 2,3,4,5-tetrabromophthalate or TBPH (BEH-TEBP) (2,037 ng/g compared to 932 ng/g in homes) and cars containing four fold higher concentrations than homes of tris(1,3-dichloro-2-propyl) phosphate or TDCPP (TDCIPP). NBFRs were also measured with similar levels of 2-ethylhexyl 2,3,4,5-tetrabromobenzoate or TBB (EH-TBB) found in the three microenvironment categories (260 ± 30 ng/g), suggesting different sources of PFRs and NBFRs. In the UK, Harrad et al. (2008a) investigated levels of DBDPE and BTBPE in house, office and car dust with offices and cars generally containing higher concentrations than houses. One house dust sample however had high concentrations of both DBDPE and BTBPE at 3,400 and 1,900 ng/g respectively. Concentrations of NBFRs in UK day care and primary school dust have also been reported (Harrad et al., 2010b), with one sample containing unusually high levels of BTBPE at > 45 μg/g. Putative sources of this contamination were not able to be determined.

The general trend of higher concentrations in microenvironments with larger numbers of putative sources shows the importance of assessing FR emissions from these sources. For this reason, SERs from treated products constitute important information to ascertain the rate at and extent to which a given FR is emitted from such products into the surrounding microenvironment. As mentioned above, the wide range of FRs present in goods and materials used indoors can easily lead to source misclassification. Often essential information about the product such as which FR is present or its age is not available, making classification difficult. Objects suspected to contain FRs have been classified together in studies (Allen et al., 2007), when it is unknown if the product has been treated with a given FR (Gevao et al., 2006) making statistically significant correlations difficult to ascertain.

No statistically significant correlations between putative sources and PBDE concentrations in air were reported in a study of Kuwait homes (Gevao et al., 2006). The absence of a correlation was attributed to insufficient information on which products had been treated with PBDEs. A study by Hazrati and Harrad (2006) reported significantly higher PBDE concentrations in air from a UK room containing numerous PUF-containing chairs and PCs, than in rooms with fewer sources. However, consistent evidence of significant correlation between putative PBDE sources and indoor contamination was not detected in this study. Likewise, Kang et al. (2011) did not find significant correlations between PBDE concentrations in Hong Kong house dust and house characteristics; including numbers of foam furniture and electronic appliances present, age of the house, floor area, and carpet coverage. Tan et al. (2007) did not detect significant correlations between PBDE concentrations in indoor dust and microenvironment characteristics in Singapore, such as number of TVs/computers, flooring material and floor area. In the German microenvironment study of Brommer et al. (2012), tris (1-chloro-2-propyl) phosphate or TCPP (TCIPP) concentrations and numbers of foam containing items in the sampled area were not significantly correlated. PBDEs were also detected in this study, although generally at much lower levels, suggesting the possibility of source misclassification, whereby some products contained PBDEs rather than PFRs.

Allen et al. (2007) reported no statistically significant correlations between USA indoor air concentrations of PBDEs and the number of furniture or electronic items in the room or other home characteristics. Product misclassification was investigated further in another study by Allen et al. (2008) using an X-ray fluorescence (XRF) analyser. No significant associations were found between indoor dust concentrations of PBDEs and numbers of putative sources in the room. In contrast, using XRF to identify products containing bromine (household furniture and televisions) and hence possibly treated with BFRs, yielded significant associations between counts of treated products and PBDE concentrations in the corresponding dust samples. Significant variation in bromine concentration was seen between similar products (television concentrations ranged from <5 – 190,000 ppm) showing the ease with which putative sources may be misclassified, greatly affecting correlation studies.

Statistically significant positive relationships were observed by Harrad et al. (2004) between all Penta-BDE congeners measured in UK indoor air samples and the number of electrical appliances and PUF-containing chairs in sampled rooms. The highest PBDE levels occurred in rooms containing numerous computers and PUF containing chairs, whereas the lowest concentrations were seen in rooms with no such items. Likewise, the Swedish study by de Wit et al. (2012) revealed statistically significant correlations between PBDE and HBCD concentrations in air and dust and the microenvironment characteristics, including numbers of different putative sources in the sampled area e.g. numbers of mattresses, numbers of electronics etc.

3. Source attribution via studies of within-room and within-building spatial and temporal variation in contamination

Spatial and temporal variability of FR contamination of dust within microenvironments has also been investigated, providing information on the influence of putative sources on sampled areas. Within-room and within-house spatial variability in concentrations of PBDEs in UK dust was studied by Muenhor and Harrad (2012). Two of the rooms studied showed differences in PBDE dust concentrations within the room. In one case, concentrations close to putative sources (TV, laptop, chair and sofa) vastly exceeded those in dust sampled more than two metres away from the source. The study also investigated temporal variability, analysing samples every month over 8 months and noting insertion and removal of putative sources. Concentrations of ΣPBDEs increased substantially with the addition of a TV to one room, while a decrease in ΣPBDE concentrations was observed following the removal of an old bed. Another room saw a marked increase in concentrations of BDEs -153 and -154 when two laptops were introduced.

Similarly, another study by Harrad et al. (2008a) reported temporal trends of PBDEs in dust of three rooms, over a 8-10 month sampling period. Substantial increases in BDE-209 concentrations were noted in one room after the insertion of a fabric padded bed cover and polyester fabric window blinds (17,000 to 42,000 ng/g). Another room in the study saw a magnitude of order increase in BDE-209 concentrations (1,300 to 36,000 ng/g), coinciding with the addition of a new mattress and curtains to the room. It is suggested that these results show fabrics treated with BDE-209 can be a substantial source of contamination for indoor environments. Increased concentrations of HBCDs in UK dust samples taken closest to the source have also been investigated by Harrad et al. (2009). One office in this study saw concentrations of HBCDs in dust sampled closest to a PC and related electronic equipment containing 4-5 times higher concentrations than samples taken from other areas in the same room. Similarly, dust from another room revealed a marked declining concentration gradient, with ΣHBCDs decreasing from 24,000 to 5,700 ng/g over a distance of five meters from the TV.

The evidence of higher concentrations in areas closest to putative sources, combined with statistically significant relationships between putative sources and contamination levels in the sampled environment show the importance of correct classification of putative sources. Particular needs exist for better information about SERs and mass transfer from products and/or air to particulates, to help determine exposure and model contamination of indoor microenvironments. As technology becomes increasingly embedded in our lifestyles, the number of flame-retarded products used in indoor environments e.g. electronics is likely to increase, with correspondingly enhanced potential for contamination with FRs.

4. Modelling Studies

Human exposure in indoor environments is commonly assessed via measurements of concentrations of FRs in indoor air and dust combined with exposure factors such as inhalation and dust contact rates. As an alternative, mathematical modelling of the indoor environment may be used to calculate EFs and SERs and potential exposure via various indoor matrices (Schripp et al., 2010). The following chapter is not intended as a comprehensive review of modelling studies rather a brief discussion of models, their associated uncertainties and to highlight the need for empirical emission and mass transfer data of FRs.

Multimedia fugacity models have been used to estimate emissions from entire populated areas, such as a model of PBDE emissions from central Stockholm (Palm, 2001), recently adapted to include a module representing a generic indoor environment (Palm Cousins, 2012). The model utilizes data on the use, lifetime, and movement of treated products in an 8-compartment steady state, multimedia chemical fate model. The estimated air concentrations of PBDE congeners were similar to the concentrations reported in other studies. However soil concentrations differed by up to a factor of 100. This difference is likely due to uncertainties in the model and the lack of reported measured concentrations in soil from the Stockholm area.

Similarly, the multimedia mass balance model of Batterman et al. (2009) calculated emission rates of PBDEs from in-use building materials and the contents of US houses. In this study, measured concentrations of air and dust along with air exchange rates from various US houses were used to model average emissions. By using a mass balance approach based on measured concentrations these houses were used as a "natural" test chamber for calculating EFs. Using this data the area predicted emission rate for the US was calculated at 20 ng/m^2/h^1 However, the authors reported large uncertainties due to underestimates and assumptions with this model, including assuming the air is well mixed in each compartment and the concentrations are at steady state. Notwithstanding uncertainties in various modelling approaches, there are reasonable similarities between different modelled emission estimates. The calculated European emission estimates for Penta-BDE in 2000 by Denier van der Gon et al. (2007) are in good agreement with values obtained by Prevedouros et al. (2004) who calculated EFs using the vapour pressures of PBDEs.

A dynamic substance flow analysis model of Deca-BDE emissions in Europe has also recently been developed Earnshaw et al. (2013), mapping estimated emissions of BDE-209 in Europe from the 1970s to 2000s. The concentration emitted follows the trend of BDE-209 consumption, which peaked in the late 1990s, as emissions peaked in 2004 at 10 tonnes per year. Uncertainties exist in the model concerning the significance of emission pathways, particularly emissions from landfill. Theoretical EF values rather than those obtained from direct measurement are used in the model however as stated by Earnshaw et al. (2013), product specific EFs would refine the model and improve the accuracy of estimated emissions.

Zhang et al. (2009) studied a UK office environment for which PBDE concentrations were reported previously by Hazrati and Harrad (2006), supplemented by additional measurements of PBDE concentrations in the PUF containing chairs and carpet in the office. A multimedia fugacity model was developed and applied to the office using these data and EFs for scenarios based on two different computers in the office calculated to be 5.4 and 35 ng ΣPBDE/h. An estimate of emissions from treated computers in use in North America was calculated at ~8.5-55 kg per year. The values reported by Zhang et al. (2009) are in line with EFs for computers derived from chamber studies by Kemmlein et al. (2003). Although some modelling studies have reported EFs that are consistent with each other, many uncertainties remain. To address these, improved knowledge of the physicochemical properties of FRs, combined with direct determination of EFs and SERs from chamber studies is recommended.

5. Chamber studies

Direct determination of emissions of chemicals from treated products is typically carried out in environmental chambers, where relevant conditions (e.g. temperature, relative humidity (RH), air exchange rate, air velocity, ratio between the product quantity and the chamber volume (known as the loading factor)) can be controlled without influences from the outside atmosphere. Emissions of the target FRs are computed based on off-line measurements in the exhaust air flow of the room, with further account taken of FRs emitted but remaining in the chamber, either sorbed to chamber walls ("chamber effects"), to the product itself or to dust (if inserted in the room). The emitted mass is then normalised to the quantity of the test material present in the chamber, the air exchange rate and the duration of the experiment. The main purpose of measuring the emission of chemicals from treated products is to assess the potential for exposure of these chemicals and ultimately any adverse effects on human health. Moreover, emission measurements can be used to develop models to predict indoor concentrations under different environmental conditions and use scenarios, or to compare SERs for different materials and product use scenarios.

5.1. Chamber studies on emissions of FRs

There are only a few chamber studies focussing on emissions of FRs from indoor materials published in peer-reviewed journals (Bakó-Biró et al., 2004; Kemmlein et al., 2003; Ni et al., 2007; Salthammer et al., 2003). This is likely due to the difficulties of determining low concentrations and the need for longer studies in order to reach steady state conditions in the chamber. In fact, there are few cases where a limited number of days (e.g. less than 50 days) is sufficient to measure time-release behaviour of SVOCs at room temperature (Clausen and Kofoed-Sørensen, 2009) and longer experimental durations are often impractical. Kemmlein et al. (2003) reported equilibrium conditions after 60 days in a 0.02 m^2 glass test chamber for TCPP emissions from insulating boards. Investigations at elevated temperature are useful as the experimental time needed to reach steady state conditions are reduced and in some cases loss to sink effects is reduced (Clausen et al., 2012). Increasing the temperature however may decrease the relevance of chamber experiments to relating results back to ‘real world’ scenarios. Specific details of the reported chamber studies are listed in Table 3 and a summary of the reported specific emission rates of FRs is given in Table 4.

Kemmlein et al. (2003) measured emissions of a broad range of FRs (PBDEs, HBCDs, TBBPA and PFRs) from different types of building materials and consumer goods (e.g. computers, TVs, printed circuit boards). All products, with the exception of a TV housing unit and a PC housing, were obtained directly from the manufacture and tested immediately. The experiments were conducted in three types of emission test chambers: two glass cells (0.001 m^3 and 0.02 m^3) and a standard volatile organic compound (VOC) emission stainless steel test chamber (1 m^3). Emission chamber conditions were controlled at 23 ± 0.1 °C (50 ± 3% RH) for building materials and consumer goods, and at 60 ± 0.1 °C (8 ± 3% RH) to simulate operational conditions of printed circuit boards. Active air sampling was conducted using a glass tube equipped with pre-cleaned PUF plugs. Tris (2-chloro-isopropyl) phosphate or TCPP (TCIPP) was one of the most commonly emitted PFRs in PUF applications and depending on the sample, area specific emission rates (SERa) of TCPP (TCIPP) varied in the range of 21 ng/m^2h (upholstery stool) to 140 µg/m^2h (assembly foam with rough surface). Emissions of HBCD from polystyrene insulating boards were investigated with emissions not detected in air after a test period of more than 100 days. This may be due to high experimental LODs (between 0.09 and 1.8 ng/m^3), an issue also reported by Bakó-Biró et al. (2004) for SVOCs. Also, low sampling volumes (5-40 m^3) may be of relevance as SERs or SVOCs have shown to be strongly dependent on the air exchange rate in the chamber (Clausen et al., 2010). However, after rinsing the chamber walls with solvent, 21 µg/m^2 (0.02 m^3 chamber) and 0.33 µg/m^2 (0.001 m^3 chamber) were recovered for ΣHBCDs. The reported SERa of ΣHBCD from polystyrene insulating boards, calculated from these concentrations, varied between 0.1 ng/m^2h and 29 ng/m^2h.

Salthammer et al. (2003) also investigated various polyurethane products (e.g. insulating foams, flooring materials) for emissions of triethyl phosphate (TEP). A self constructed glass chamber of 1m^3 volume was used with controlled experimental conditions of 23^{o}C (45% RH). However Tenax TA sorptive material, commonly used for analysis of VOCs, was used for analyte capture rather than PUF plugs as in the Kemmlein et al. (2003) study. The calculated SERa for TEP after 24 h, was > 100 µg/m^2h for products which were less than 5 weeks old and obtained directly from the manufacturer. In all experiments the measured SERa decreased over time and after 168 h only traces were measured, showing the importance of product age when testing volatile compounds.

The Kemmlein et al. (2003) study also measured emissions of TCPP (TCIPP), triphenyl phosphate or TPP (TPHP) and PBDEs from electronic goods, including TV sets, computer configurations, PCs and TV housings. The PC and TV housings were post-consumer products hence had the opportunity for substantial release of the more volatile FRs during their life cycle before testing. The unit specific emission rates (SERu) determined were 10 - 85 ng/unit hour for organophosphates and 0.6 -14.2 ng/unit hour for PBDEs. The calculated SERu of PBDEs from printed circuit boards ranged from 0.04 to 14.2 ng/unit hour, depending on the congener. Raising test temperatures also increased emissions of some FRs by up to 500 times. Testing emissions at 23 °C from printed circuit boards saw BDE-28 and BDE-47 concentrations ranging from 0.9 to 3.4 ng/m³ over a period of 30 days. After increasing the temperature to 60 °C BDE-17, BDE-99, BDE-66, BDE-100, BDE-154, and BDE-153 were also detected and the concentrations of BDE-28 and BDE-47 increased significantly. Similarly, Clausen et al. (2012) reported a 200 fold increase in steady state emissions of the phthalate di-(2-ethylhexyl)phthalate (DEHP), another SVOC, with a temperature increase from 23 to 61 ^{o}C.

Bakó-Biró et al. (2004) measured the emissions from a personal computer system in a 1 m³ glass test chamber. Samples from the exhaust airflow of the chamber were collected on Tenax TA for VOCs and also XAD-II for SVOCs. Although the presence of BFRs was expected in the tested PC systems, no emissions were detected in the air samples. It was presumed this result was due to the poor sensitivity of the analytical method (LOD 20 µg/m³). The test temperature increased from 24 °C at the start of the experiment to 32 °C during the experiment due to heat released from the working computer system. Carlsson et al. (2000) also reported increased temperatures of up to 50 °C on the top outlet cover of video display units (VDUs) during operational conditions. In this experiment, emissions from brand new VDUs were monitored in two furnished offices (57.8 m³ and 25.9 m³). The VDUs were kept in continuous operation mode for 8 days in the 57.8 m³ office (short-term emission study) and 183 days in the 25.9 m³ office (long-term emission study) with emissions collected on PUFs. Prior to the test background concentrations of selected PFRs such as tri(*n*-butyl) phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP), tri(chloropropyl) phosphate (TCIPP), tri(2-butoxyethyl) phosphate (TBOEP) and triphenyl phosphate (TPHP), were measured in both office modules without the presence of VDUs. After one day of sampling in the presence of the VDUs, triphenyl phosphate (TPHP) was measured at concentrations of up to 82 ng/m³ (57.8 m³ office) and 94 ng/m³ (25.9 m³ office). After 8 days, the concentrations of triphenyl phosphate (TPHP) decreased to 40% of the concentrations detected on day 1 in both offices.

Moreover, by the end of the long term emission study (183 d) the concentration of triphenyl phosphate (TPHP) had decreased to 8.6 ng/m³.

Ni et al. (2007) developed a passive flux sampler for measuring emissions of PFRs. The passive flux sampler is a static mode sampler using the diffusion of chemicals inside a closed air volume from the material surface to a trap medium. Emissions are collected on an Empore C18FF disk and emissions of tris(2-chloroisopropyl)phosphate or TCPP (TCIPP) were studied from wallpapers. The samples were delivered straight from the manufacturer and experiments started immediately after delivery. The measured concentrations decreased by almost 10 fold over the test period of 280 days. Wallpaper samples with different TCPP (TCIPP) contents were examined at different temperatures (to simulate different environments) during the experiment. The calculated SERa at temperatures of 25 °C (normal room temperature), 40 °C (maximum room temperature in Japanese residence without air conditioning) and 60 °C (the interior temperature of a vehicle left exposed to summer sun) were respectively 644.8 µg/m².h, 1135.7 µg/m².h and 2841.2 µg/m².h. The authors reported a good correlation (r^2=0.935) between emissions and the TCPP (TCIPP) content of the wallpaper under test. A drawback of the passive flux sampler is the fact that it is restricted to study of only small sampling areas in comparison to other emission chambers hence results produced by the passive flux samplers are more prone to be influenced by any inhomogeneity of FR concentrations in the material tested.

5.2. Chamber studies on mass transfer to dust of SVOCs

Alongside emissions to indoor air, migration to indoor dust is another important pathway of relevance to human exposure. At the time of this review no published articles have focused on the migration pathways of FRs into dust. Two studies have used modified chambers/test cells to investigate deposition and transfer via direct contact to house dust of phthalates (another class of SVOC). Issues encountered with studying emissions of SVOCs in this way, such as long times to reach steady state conditions inside the chamber, were highlighted and can be extrapolated to underline how these experiments can be performed to investigate FRs.

Schripp et al. (2010) investigated the mass transfer of the SVOCs di(2-ethylhexyl)phthalate (DEHP) and di-*n*-butylphthalate (DnBP) to different samples of house dust, soil and sand from emission sources. Deposition of volatilised phthalates was investigated in 0.5 m^3 stainless steel chambers using different air velocities. Glass plates, coated with pure phthalate or with plasticized wall paint containing 1% w/w of phthalate, were placed inside the chamber along with 3 g of house dust, soil or sand. Significant increases of DHEP were not seen in any of the solid matrices, potentially due to incomplete equilibrium inside the chamber. Significant increases in concentrations detected in all the different dust or soil matrices were reported for DnBP with higher concentrations (>10 times higher) seen in dust and soil than in sand. This is likely due to the different organic carbon contents of the solid matrices influencing the level of deposition, and a weak correlation was reported between phthalate uptake and the organic carbon content of a matrix. Greater concentrations in dust/soil were also associated with higher air velocities inside the chamber, due to different emission behaviours in each scenario. A higher air velocity increases vaporisation of analytes and increases subsequent mass transfer to dust.

Migration (direct contact) experiments were also conducted by Schripp et al. (2010) using a 3 L glass flask with 130 mg of pre-extracted dust placed directly on top of plasticized PVC foil (containing DEHP). Another portion of dust (130 mg) was placed on a shelf above the foil to investigate deposition from volatiles. There was no significant uptake of DEHP in the dust separated from the source, but higher mass transfer was reported in the dust in direct contact.

Clausen et al. (2004) also investigated the uptake of DEHP via direct contact from PVC flooring into indoor dust. A “chamber for laboratory investigations of materials, pollution and air quality” (CLIMPAQ) emission test chamber contained five pieces of PVC with the upper side of the top pieces layered with 0.5 g of homogenized house dust. After specified time periods, the dust was sampled. Transfer of DEHP to the dust was four-fold greater compared to that emitted to the air. Air emissions were also similar in chamber scenarios containing dust compared with those without, suggesting uptake by the dust represents an additional pathway of release from the PVC.

Proposed mechanisms for mass transfer to dust include phthalate uptake via capillary forces (Schripp et al., 2010) or that the dust in direct contact acts as an adsorbent of phthalates from the source (Clausen et al., 2004). Moreover, abrasion (physical breakdown of the PVC caused by the vacuuming process) may also be responsible for the high levels observed in dust. In conclusion, Clausen et al. (2004) suggested that since particles and dust can increase total contamination of indoor environments, the migration of contaminants from sources to dust is of importance when evaluating the potential for human exposure.

6. Research gaps and future perspectives

6.1. Sink Effects

A commonly reported issue for chamber studies of SVOCs like FRs is loss to sink effects, as compounds with higher boiling points have increased adsorption to chamber walls (Uhde and Salthammer, 2006). Methods suggested to reduce this loss include lining the chamber with a Teflon coating and electroplating stainless steel wall surfaces (Destaillats et al., 2008), or using hand polished surfaces such as in the Field and Laboratory Emission Cell (FLEC), for a greater reduction of active sites (Clausen et al., 2004). Reducing contact time through increased air exchange rates and decreasing chamber surface to volume ratios, using new approaches such as passive flux samplers (Ni et al., 2007)**,** may help reduce these effects, but as yet no comparative studies have investigated this. Procedures for eliminating sink effects have not been reported, however investigations of post-experiment recovery of lost analytes have been reported. These methods include heating the chamber to elevated temperatures, collecting subsequent air emissions; and rinsing the chamber walls with solvent, to determine concentrations recovered from the chamber walls (Katsumata et al., 2008; Kemmlein et al., 2003). Heating an emission chamber to 80^{o}C has recovered detectable concentrations of BDE47, BDE99 and BDE100 (Kemmlein et al., 2003). A cooled plate (fogging device) inside the chamber has also been used as a means of assessing sink effects (Uhde et al., 2001). Kemmlein et al. (2003) placed convex glass pieces inside the emission chamber throughout experiments. The glass piece was rinsed with toluene, post experiment, with detectible concentrations of TBBPA (64-116 ng/m^{3}) recovered.

Repeated mass balance experiments may provide information on the magnitude of such losses (Destaillats et al., 2008) for different FRs, through measurements of FR mass entering a chamber and mass recovered post-experiment. A reproducible concentration loss (as evidenced e.g. by RSD values for a number of experiments falling within an acceptable range) can be incorporated into calculated emissions and subsequent SERs, and calculations of mass transferred to dust. As sorption of SVOCs to chamber walls is often not a linear process (Clausen et al., 2004), this method assumes that chamber conditions reach steady state to allow a reproducible calculated loss. However, as the emission rate is slow for SVOCs and partitioning to chamber walls is strong, a long time can be required to reach steady state (Xu et al., 2012), making this method unsuitable for many FRs.

Even with an accurate measure of sink effects, limitations exist for chamber experiments when extrapolating information to indoor models as the isolated chamber conditions differ from those in the environment being simulated. Indoor environments themselves provide other surfaces that act as FR sinks, such as thin films on glass windows (Butt et al., 2004). Typically, sink effects within an indoor environment are unknown and as test chambers do not easily mimic “real-world” fluctuating environmental conditions (Schripp et al., 2010), there is difficulty in extrapolating results from emission chamber tests to indoor microenvironments. The lack of a thorough investigation into sink effects, especially for FRs, highlights this as an increasingly important area of research to: 1) determine the extent of this absorption loss on FR analysis, and 2) correctly report EFs and SERs, as well as subsequent levels of deposition to dust from treated products.

6.2. Appropriate conditions for a standardized testing method

One standardized method (ISO, 2011) exists for investigating area specific emission rates of SVOCs (defined as any organic compound with a boiling point in the range of 240-260°C to 380-400°C) in a Micro-chamber™. Operation of the chamber at 200-220°C, post experiment, is required to recover greater than 80% of SVOCs in a standard solution. As SVOCs vary considerably in their physicochemical properties, it is unreasonable to assume this level of recovery is achievable for all SVOCs, including FRs. As stated in the ISO 16000-25:2011 standard, the extent of loss is dependent on the compound and additional tests are encouraged to ‘increase understanding of these [sink] effects’. Not all commercially available standard test chambers have the capability for higher temperatures, which is also likely to affect some FRs through thermal degradation or thermal rearrangement. The HBCD diastereomers in the technical formula rearrange from the γ-HBCD to the α-HBCD diastereomer at temperatures above 100°C (Heeb et al., 2008), hence more appropriate standard procedures are needed. Air flow rates can also differ between experiments as chambers have been operated at lower flow (3 mL/min (Bakó-Biró et al., 2004)) than average indoor scenarios (~20 mL/min (Bakó-Biró et al., 2004)) to improve LODs but in a standardized cases for testing VOC emissions, higher air flows are required (100-200 mL/min) (ECMA, 2010).

The stage in the life-cycle of the treated product is an important influence on SERs for the more volatile FRs. Ni et al. (2007) reported an almost 10 fold decrease in TCPP (TCIPP) emissions over a 280 day sampling period for wallpaper obtained directly from the manufacturer and tested immediately. Similarly, Carlsson et al. (2000) saw a 10 fold decrease in triphenyl phosphate (TPHP) emissions from a computer video display unit over a 183 day sampling period. These studies show that source age is an important consideration for comparative studies. Bakó-Biró et al. (2004) tested computer modules with 500 hours of use in a simulated room and calculated emissions of a range of SVOCs. After 2000 hours of use, the same modules were placed in emission chambers to obtain SERs for comparison with the simulated room experiment. Comparisons are difficult however due to the different age/use of the treated product between the two tests, stressing the importance of careful experimental design for chamber experiments.

The standardized methods for VOC testing recommend conducting chamber experiments at room temperature (23°C) (ECMA, 2010). Operating electronics however can reach temperatures of 50°C (Carlsson et al., 2000) and chamber experiments with functioning electronics inside have increased chamber temperatures to at least 32°C (Bakó-Biró et al., 2004). As such, calculating emissions from products at room temperature may not be relevant for determining total exposure, so this is also an important consideration when designing chamber experiments. The operational state of electronics, whilst tested in the emission chamber, is another variable. Whether the equipment is idle, in standby mode, partly operational or in full operation for the duration of the test can influence the emissions detected (Destaillats et al., 2008). The ECMA (2010) standardized method for testing VOCs from computers requires testing whilst tapping keystrokes on the computer, but this will not simulate all systems in action. Underestimations of emissions produced by fully functioning equipment and contamination by fine particle abrasion causing migration to dust may result, leading to underestimations of levels of exposure. Age and operational state of the material along with chamber temperature are important considerations for designing relevant chamber experiments, yet little is known about variations in results caused by these parameters. Research is required to provide relevant standardized methods, with appropriate experimental parameters specified, to create uniformity in the reported literature.

6.3. Particulate generation and mass transfer to dust

Another consideration for SVOC measurements, requiring further research, is particle generation from laser printers and subsequent ozone reactions inside the chamber (Lee et al., 2001). Printer generated VOCs react with ozone to form secondary organic aerosols (Wang et al., 2012) suggesting the possibility of similar reactions with SVOCs that influence measurements of emissions of FRs. As emitted SVOCs can be present in both the gas and particle phases of air due to their lower vapour pressure (Weschler and Nazaroff, 2008) preferential adsorption to generated particles will also effect emission, or gas phase, measurements. Enhanced emissions from the product due to the presence of particulates is also a necessary area for research, as mass transfer to particulates (dust) can be an additional emission pathway increasing total emissions of volatiles (Clausen et al., 2004). Particles also have an important role in transport of SVOCs to indoor environments and contribute to exposure via inhalation (Benning et al., 2013) hence these interactions are an important area for future research. At the time of this review there were no reported studies investigating the gas-particle interactions of emitted FRs. However phthalates, particularly DEHP, have been reported in these studies providing insights into future directions for FR studies. The study by Benning et al. (2013) conducted emission chamber investigations of DEHP, emitted from vinyl flooring, and the interaction with ammonium sulphate particles. The mass transfer of DEHP was increased with the presence of particles, with the partitioning to particles suggested to be affected by inorganic compared to organic particles, the particle surface area, or the degree of coverage of the particle surface area by the sorbed SVOC. As SVOCs sorb to particles, the organic matter content of the particle increases, promoting further partitioning to the particle (Weschler and Nazaroff, 2008).

Measurements of the mass transfer of SVOCs to dust have been shown to be difficult in chamber experiments, and chamber designs need to be modified with longer experimental durations required for steady state to be reached inside the chamber. Schripp et al. (2010) observed different rates of mass transfer to dust than would equate to the concentrations reported in studies of house dust. This possibly indicates limitations of their chamber set up, although comparisons are difficult due to variable compositions of dust samples. The different physical compositions of indoor dust samples (particularly organic content) may lead to different rates of mass transfer, with Schripp et al. (2010) reporting greater mass transfers to particulate matrices with higher organic contents. Chamber experiments often omit environmental influences encountered in indoor scenarios that may influence dust and contaminant concentrations, such as diurnal variations in human activities that contribute to re-suspension of indoor particles and dust. In indoor environments, the presence of airborne particles is expected to decrease the time to reach equilibrium concentrations of FRs in dust (Schripp et al., 2010). However, the complex nature of indoor dust limits precision in predicting sorption behaviour of the FR, which can increase uncertainty of modelled results. At present, there are no standardized protocols for measuring mass transfer to dust of FRs as the experiments are difficult to set up and require chamber modifications. This area of research has few reported studies, but is very important as knowledge on migration pathways of FR are needed to improve risk assessments of their applications in indoor environments.

In summary, the literature reviewed in this article demonstrates how emission chambers have been utilized to generate SERs from products treated with FRs. There are still many research areas that require investigation to improve these experiments and increase knowledge of the migration of FRs into indoor air and dust. Thorough investigations of sink effects and how the different FRs are affected by such effects are needed. For measuring

SERs, the most appropriate parameters to test electronic equipment require identification, including operational state of the equipment during the emission test and the most appropriate chamber temperature. Standardized methods are needed for chamber tests of FRs that allow determination of SERs that best represent the conditions of indoor environments. Investigations into the migration pathways of FRs to dust are an important area of research and at the time of this review, there were no published chamber experiments that address this area. Appropriate designs for modified chamber experiments are needed so all hypothesized migration pathways can be investigated. The reported difficulties with reaching steady state conditions within a realistic experimental time frame for some FRs needs to be addressed, together with considerations of whether mass transfer measurements are relevant if steady state conditions inside the chamber are not reached. Standardized methods to handle all these parameters do not yet exist, showing that more research is needed in this area. We conclude that chamber experiments are clearly a useful tool for measuring SERs of FRs and are promising for investigating migration pathways to indoor dust, although more research is required in this area, particularly in the development of standardized methods that facilitate comparisons between reported studies.

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Figure 1: Hypothesised migration pathways of FRs from treated products into indoor air and dust

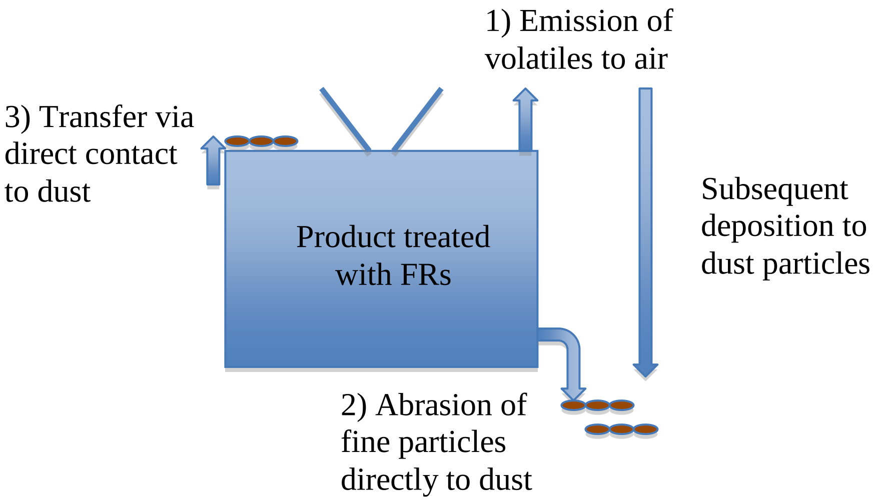

Table 1: Summary of uses of various PFRs and NBFRs

Class of FR	***Compound/functional group***	***Use***	***Reference***
PFR	chlorinated alkyl phosphates	flexible and rigid polyurethane foams	(Van den Eede et al., 2011)
	non-halogenated alkyl phosphates	unsaturated polyester resins, cellulose acetate, poly vinyl chloride (PVC), ABS and synthetic rubber	
	triphenyl phosphate - TPHP and tricresyl (or tolyl) phosphate -TMPP	PVC, cellulosic polymers, thermoplastics and synthetic rubber	
	(tri (2-butoxyexthyl) phosphate - TBOEP	and in floor wax and rubber stoppers	
NBFR	decabromodiphenyl ethane - DBDPE	replacements for PBDEs in HIPS, ABS copolymers and textiles	(Covaci et al., 2011).
	1,2-bis(2,4,6 tribromophenoxy) ethane - BTBPE	thermoplastics, thermoset resins, polycarbonate and coatings	
	bis(2-ethylhexyl) tetrabromophthalate – BEH-TEBP	PVC, neoprene, wire and cable insulation, film and sheeting, carpet backing, coated fabrics, wall coverings and adhesives	
	BEH-TEBP and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) Mixture	Firemaster 500 commercial product	

Table 2: Summary of available data on production volumes of FRs

FR	***Country***	***Year***	***Production volume (metric tons/year)***	***Reference***
PBDEs	Worldwide	2003	56,400	(USEPA, 2010a)
		1999-2002	40,000 - 67,000	
Penta-BDE		1999	8,500	(Boon et al., 2002)
Octa-BDE		1999	3,800	(Boon et al., 2002)
Deca-BDE		1999	54,800	(Boon et al., 2002; Covaci et al., 2011)
		2003	56,400	(Covaci et al., 2011)
HBCD		2001	16,700	(Canada, 2011)
		2003	22,000	(Covaci et al., 2011)
	Netherlands	1996	500 - 1,000	(ECHA, 2008)
		1999-2002	1,000 - <5,000	
		2002	5,000-7,000	
	UK	1996-2003	1,000 - 5,000	
TBBPA	Worldwide	1992	50,000	(ECHA, 2006)
		1998	145,000	
		2006	150,000	
NBFRs	Worldwide	2011	Estimated at 180,000	(Covaci et al., 2011)
PFRs	EU	2004	84,000	(Van den Eede et al., 2011)
		2006	91,000	

Table 3. Overview of chamber types, volume, operation conditions and analytical techniques used in the reviewed emission studies.

Chamber material	***Chamber volume***	***Operation conditions***	***Material tested***	***Chemical compound(s) determined***	***Reference***
Glass	20 dm^3	Temperature – 23.0 (± 0.1) °C Humidity – 50.0 (±3)% Air flow rate – 0.128 m^3/h Air exchange rate – 0.5/h	Insulating materials, foams, computers, TV	PBDEs, HBCD, TBBPA, PFRs	(Kemmlein et al., 2003)
Stainless steel	1 m^3	Temperature – 23.0 (± 0.1) °C Humidity – 50.0 (±3)% Air flow rate – 1.1 m^3/h Air exchange rate – 0.5/h			
Glass	20 dm^3	Temperature – 60.0 (± 0.1) °C Humidity – 8.0 (±3)% Air flow rate – 0.128 m^3/h	Printed circuit board		
Glass	1 m^3	Temperature – 23.0 °C Humidity – 45.0 % Air exchange rate – 1/h	PU Foams	PFRs: TEP, TCEP, TDCIPP, TCIPP	(Salthammer et al., 2003)
Glass	1 m^3	Temperature – 25.0 – 32.0 °C Humidity – 25.0 % Air exchange rate – 2/h	Computers	BFRs	(Bakó-Biró et al., 2004)
Office module	58 m^3	Temperature – 23.0 °C (50 °C) Air exchange rate – 3.5/h	Computer video display units	PFRs TNBP, TCEP, TCIPP, tris(2-ethyl hexyl phosphate) (TEHP)	(Carlsson et al., 2000)
	26 m^3	Temperature – 23.0 °C (50 °C) Air exchange rate – 3.5/h			
Glass /passive flux sampler/	8.7 cm^3	Temperature – 23.0 °C	Wallpapers	PFRs: trimethyl phosphate (TMP), TBP, TEP, TCEP, TEHP, TDCIPP, TMPP, TCIPP, TBOEP, TPHP	(Ni et al., 2007)

Table 4. Summary of reported specific emission rates of various flame retardants determined using chamber studies.

Product	***FR***	***SERa***	***Reference***
Building materials, SERa, µg/m².h			
Insulation boards	TCIPP	0.21- 0.60	(Kemmlein et al., 2003)
	HBCD	0.004 – 0.029	
PUR foams	TCIPP	50 – 140	
Upholstery foam	TCIPP	77	
Wallpaper materials	TCIPP	262.3 – 2166.8	(Ni et al., 2007)
Electronics			
TV set housing, SERa, ng/m².h	BDE-100	0.5	(Kemmlein et al., 2003)
	BDE-153	1.0	
	BDE-154	0.2	
	BDE-28	0.2	
	BDE-47	6.6	
	BDE-66	0.5	
	BDE-99	1.7	
	ΣHeptaBDE	4.5	
	ΣNonaBDE	0.8	
	ΣOctaBDE	1.5	
		SERu	
Printed circuit board, SERu, ng/unit.h	BDE-100	1.3	(Kemmlein et al., 2003)
	BDE-153	0.04	
	BDE-154	0.1	
	BDE-17	0.6	
	BDE-28	1.9	
	BDE-47	14.2	
	BDE-66	0.6	
	BDE-85	0.1	
	BDE-99	2.6	
	TPHP	496	
PC housing	TBBPA	0.4	(Kemmlein et al., 2003)
Desktop computer system	TPHP	25 – 85	
Monitors	TCEP	<5 – 34	(Wensing, 2004)
	TCIPP	<5 – 2465	
	TDCIPP	<5	
	TNBP	10 – 18	
	TPHP	23- 133	